Corrosion behaviour of lean duplex stainless steel in advanced oxidation process (AOP) based wastewater treatment plants

Maarten Nagels [1], Brent Verhoeven [1], Nicolas Larché [2], Raf Dewil [1], Barbara Rossi [3,4 *]

[1] KU Leuven, Department of Chemical Engineering, Process and Environmental Technology Lab (PETLab), Jan De Nayerlaan 5, B-2860, Sint-Katelijne-Waver, Belgium

[2]French Corrosion Institute, RISE, Rue Rivoalon 220, F-29200, Brest, France.

[3]University of Oxford, Department of Engineering Science, Parks Road, Oxford, United Kingdom.

[4] KU Leuven, Department of Civil Engineering, Materials and Structures, Jan De Nayerlaan 5, B-2860, Sint-Katelijne-Waver, Belgium

* corresponding author: barbara.rossi@new.ox.ac.uk (B. Rossi)

Abstract

The corrosion of lean duplex stainless steel alloys is examined when applied as a construction material in advanced oxidation processes. Both electrochemical and immersion experiments have been carried out when subjecting wastewater to ozone or Fenton oxidation. The electrochemical experiments suggest that the presence of dissolved ozone at the levels tested does not result in an increased pitting susceptibility for none of the alloys included in the research. However, the application of Fenton reagents induces pitting corrosion to the studied lean duplex alloys. The immersion experiments highlight that crevice corrosion occurs during wastewater treatment with both ozone and Fenton reagents.

Keywords: Advanced Oxidation Process; Electrochemistry; Fenton; Lean Duplex stainless steel; Ozone

1. Introduction

Advanced Oxidation Processes (AOPs) are a class of wastewater treatment techniques that are based on the production of hydroxyl radicals (OH*). The application potential of AOPs lies mainly in the treatment of wastewater containing recalcitrant organic compounds. The removal of these compounds by conventional techniques, which are mainly based on aerobic or anaerobic biological degradation of organic matter, is generally not achievable due to their low biodegradability [1,2]. Various types of AOPs have been developed, including treatments based on ozone and hydrogen peroxide, which differ in the production pathway of the OH* [3,4].

Ozone can react with organic compounds in two different ways: indirectly or directly. Indirect oxidation involves radicals whereas direct oxidation represents the reaction of the organics with molecular ozone. Indirect oxidation is enhanced at pH levels above 10 while direct oxidation mainly occurs in acid environments (< pH 4). Both mechanisms occur at pH levels between 4 and 10. Ozone is a strong oxidizing agent, with a standard potential of 2.07 V referred to standard hydrogen electrode (SHE), although OH* is even more powerful with a standard potential of 2.80 V versus SHE [5]. Different ozone based AOPs exist, such as O_3/H_2O_2 and O_3/UV. Also, hydrogen peroxide (H_2O_2) based AOPs are being applied, for example H_2O_2/UV and (photo)-Fenton. They all realize the production of OH*. Using H_2O_2/UV, OH* is produced via the direct photolysis of H_2O_2 generates OH* [4]. In the Fenton process, ferrous iron (Fe^{2+}) is used in an acid environment to catalyse the decomposition of H_2O_2, resulting in the generation of ferric iron (Fe^{3+}) and OH* [6]. Each OH* production pathway has its specific applicability. In most existing AOP installations on an industrial scale, ozone based techniques are applied. Hydrogen peroxide based AOPs such as Fenton are currently not yet well implemented but because of the large focus on pilot-scale testing nowadays, an upcoming adaptation by industry is expected [7].

Because of the highly oxidative aqueous environments that are created in AOP installations and the corrosive nature of the strong oxidizing agent OH*, localized corrosion of the metal alloys used as construction materials is a point of attention. Especially Fenton-based systems have been shown to be particularly susceptible [8]. A correct materials selection for the reactor, piping, pumps and other equipment that are exposed to the oxidative environment is hence essential. Nevertheless, this is mostly based on experience rather than on scientific evidence related to corrosion resistance.

Austenitic stainless steel grades (e.g., EN 1.4307 and EN 1.4404) are usually used in water treatment plants but are not an optimal choice for AOP applications. More corrosion resistant alloys, such as duplex stainless steel (austenitic-ferritic), are required in this case. The most frequently used duplex grade is EN 1.4462, which has better corrosion properties than EN 1.4404 in chloride-rich media [9]. Alloy EN 1.4462 contains at least 22% Cr, 5% Ni, 3% Mo and 0.16% N [10]. The low nickel content and the better corrosion properties of duplex stainless steel result in a more cost-effective material compared to austenitic stainless steel [11]. Alternative materials with a lower concentration of alloying elements are lean duplex stainless steels. Lean duplex alloys such as EN 1.4162 and EN 1.4362 have a low Mo content while maintaining a corrosion resistance that is at least equivalent to austenitic stainless steel. Nevertheless, less alloyed and cheaper alloy stainless steels (such as the lean duplex grades) are usually avoided to guarantee a long lifespan of the AOP installation due to their presumed equivalent corrosion resistance. However, the current scientific literature and documented field experience on this matter is scarce.

Sato et al. [12] investigated the effect of dissolved ozone on the corrosion of austenitic stainless steels (EN 1.4301) by immersion and electrochemical tests in de-ionized water. The immersion experiments were carried out with water circulating at a slow (5-10 cm/s) and fast flow rate (1.7 m/s). The authors observed that the corrosion rate increased with increasing ozone concentration at both flow rates. Metals dissolve according to Eq. 1, and ozone is reduced to oxygen (Eq. 2), which is further reduced to hydroxyl ions (Eq. 3).

$$Me \rightarrow Me^{n+} + n\,e^- \qquad \text{Eq. 1}$$

$$O_3 + H_2O + 2\,e^- \rightarrow O_2 + 2\,OH^- \qquad \text{Eq. 2}$$

$$O_2 + H_2O + 4\,e^- \rightarrow 4\,OH^- \qquad \text{Eq. 3}$$

These equations show that ozone acts as an acceptor of the electrons produced by the dissolution of the metal and, therefore, could increase the reaction rate of Eq. 1. On the other hand, research has shown that the passivation properties of stainless steel can be enhanced by ozone, resulting in a better localized corrosion resistance. This was also exposed in Sato et al.'s research [12].
Brown and Duquette [5] investigated the effect of dissolved ozone (0.2 to 0.4 ppm) on austenitic stainless steel grades (EN 1.4301, EN 1.4307, EN 1.4401 and EN 1.4404) in artificial seawater at neutral pH. Cyclic polarization analysis revealed that, at elevated ozone concentrations, the

passive film stabilized against pit initiation. No hysteresis loop was observed, which indicates the resistance to localized corrosion by the ozone-passivated surface. Immersion tests, on the other hand, showed that crevice corrosion is more severe in ozonated compared to aerated artificial seawater. In general, ozonation resulted in crevice corrosion rates that were an order of magnitude higher compared to aeration.

Further research on the effect of dissolved ozone on the corrosion behaviour of stainless steel was performed by Pehkonen [13]. In this research, austenitic grades (EN 1.4307, EN 1.4404) were studied in acid environments (pH 3) in the presence of dissolved ozone at 50 °C. Pehkonen [13] described that the corrosion of stainless steels in ozonated solution is not only an electrochemical but also a physical phenomenon during which the following steps occur: (i) increase in the thickness of the oxide layer; (ii) local corrosion initiation; (iii) increased corrosion damages resulting in weakened adhesion of the oxide layer; (iv) peeling of the oxide form the surface; (v) further oxidation of the exposed steel with corrosion damage. Pehkonen [13] observed that dissolved ozone (> 0.5 ppm) greatly increases the thickness of the passive oxide layer with 60-260 nm while dissolved oxygen has little or no effect on the oxide layer. Hence, dissolved ozone could decrease the risk of localised corrosion because of the increased passivity. However, wide shallow corrosion damages were formed during the immersion and polarisation tests but were passivated.

Liao et al. [14] reviewed the existing literature on the effect of ozone on localized corrosion of stainless steel alloys in sea- and freshwater. They stated that ozone gas leads to an acceleration of crevice corrosion, while decreasing the risk of pitting corrosion. Pitting corrosion is inhibited by ozone because of its capability to re-passivate initiated pits and to prevent microbiologically induced corrosion (MIC). Furthermore, Brown et al. [15] showed that an increase in flow rate (known to have a significant impact on the localized corrosion susceptibility of stainless steel alloys in ozonated water which contains chlorides) results in a stabilization of the passive film on stainless steel and thus increasing the breakdown potential.

Nonetheless, the mentioned literature only investigated conventional austenitic stainless steel grades. So far, corrosion measurements were not yet carried out on other grades such as (lean) duplex. Also, the presence of organic pollutants that are being oxidized by either ozone or OH° can influence the corrosion.

Besides the effect of ozonation on the corrosion resistance of stainless steels, the Fenton process (Fe^{2+}/H_2O_2) is also of great importance because of the presence of H_2O_2 may not be disregarded. Li et al. [16] showed that H_2O_2 affects the passivation characteristics of the metal surface

depending on the pH of the solution. At neutral pH, H_2O_2 inhibited corrosion while it increases at acid pH [16]. Besides, the ferrous iron (Fe^{2+}) present at the metal surface can react with the dosed H_2O_2 in order to generate Fe^{3+} and OH°.

Highly corrosion resistant materials are generally recommended in AOP installations, particularly in the presence of chloride contamination (e.g., super duplex or 6Mo stainless steels, Nickel-based alloy, etc.). However, these alloys can be very expensive while the applicability of less expensive (leaner) duplex stainless steel grades could be considered under certain conditions. The scope of this research is to assess the corrosion of lean duplex stainless steel and define their limits of use in different AOP treatment plants. Immersion tests and electrochemical experiments were carried out on a selection of lean duplex stainless steel grades in synthetic and industrial wastewater in the presence and absence of AOPs (ozone and Fenton). Pitting corrosion was studied using electrochemical methods while the susceptibility to crevice corrosion was studied by immersion experiments.

2. Materials and methods

2.1 Materials

Various lean duplex stainless steel grades were tested and compared to duplex stainless steel EN 1.4462 and austenitic stainless steel (EN 1.4307 and EN 1.440). The samples were manufactured from coils of flat products with a plate thickness of 3 mm.

The chemical composition and corresponding pitting resistance number (PREN) of the studied stainless steel alloys used for the electrochemical and immersion experiments carried out in this research are provided in Table 1. The resistance to pitting corrosion of stainless steel is estimated by the PREN which is based on its chemical composition: PREN = %Cr + 3.3%Mo + 16%N.

Table 1. Chemical composition of the studied stainless steel alloys.

Common designation	EN	C (%)	Cr (%)	Ni (%)	Mo (%)	N (%)	Mn (%)	PREN
304L	1.4307	0.02	18.0	8.0	0.2	0.1	1.2	20
316L	1.4404	0.017	17.0	10.0	2.0	0.0	1.8	24
2101	1.4162	0.03	21.5	1.5	0.3	0.2	5.0	26
2202	1.4062	<0.03	22.9	2.6	0.2	0.2	1.3	27
2304	1.4362	<0.03	22.8	3.8	0.5	0.1	1.8	26
2404	1.4662	0.02	24.0	3.6	1.6	0.3	3.0	33

2205	1.4462	<0.03	22.8	5.5	3.0	0.2	1.8	35

2.2 Electrochemical measurements

The electrochemical experiments (dynamic polarisation) were conducted according to ASTM G61 [17]. A glass electrochemical reactor of 1.0 L was used to perform the experiments. A potentiostat (Gamry) was used to apply an electric potential on a working electrode compared to an Ag/AgCl (3.5 M) reference electrode while the current density was measured via the counter electrode (graphite rod). All potentials within this research were converted from Ag/AgCl (3.5 M) to the standard hydrogen electrode (SHE), which is the most common reference potential in electrochemistry. The difference in potential from Ag/AgCl (3.5 M) to SHE is +205 mV. The working electrode was made from the studied alloy. The metal sample was embedded in an epoxy resin to expose the metal surface to the solution, thus eliminating preferential corrosion on the edges of the metal sample. The surface of the material was wet grinded with a 1200-grit SiC paper, rinsed with distilled water, cleaned with ethanol and dried. The test solution consisted of collected wastewater from an industrial wastewater treatment plant of a tank cleaning company located in Antwerp (Belgium). The wastewater was aerated, ozonated or treated with Fenton reagents during the electrochemical experiment. Each test was carried out in triplicate. The ionic composition of the different collected batches of industrial wastewater is given in Table 2.

178 **Table 2.** Ionic composition (ppm) of the tested wastewater, used for the electrochemical tests.

Batch	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
1	805.84	/	0.85	0.55	101.74	1414.39	18.53	86.51	32.62	9.98
2	889.25	/	/	1.08	106.91	741.34	20.44	103.35	68.38	10.09
3	932.30	/	0.62	/	191.99	644.80	0.54	181.00	106.42	12.43
4	1126.99	/	0.29	0.08	100.56	730.29	21.44	115.51	118.96	13.23
5	1021.48	/	0.08	0.10	77.10	663.17	14.22	98.83	105.59	11.63
Average	955.17	/	0.45	0.45	115.66	838.80	15.03	117.04	86.40	11.47

179

180 Two different electrochemical tests were performed in a sequence. First, the open-circuit
181 potential (OCP) between the working and the reference electrode was measured for 60 min
182 (E_{corr}). Then, a cyclic potentiodynamic polarization measurement (CYCL) was performed to
183 study the pitting susceptibility of the alloy in the specific environment. The starting potential
184 was taken as E_{corr} - 100 mV, which was increased with a scan rate of 600 mV/h. The increase
185 in potential stopped when the end potential was reached, which was the production of oxygen
186 (E_{ox}) + 100 mV (912 mV/SHE), or when the maximum current density was reached
187 (0.005 A/cm^2). The latter indicates a strong increase in current density meaning that localized
188 corrosion has happened (pitting). The last step of the polarization measurement was the reverse
189 scan, which started when the end potential or end current density was reached. During the
190 reverse scan, the potential decreased until the corrosion potential (E_{corr}) was reached. If
191 localized corrosion is present, the reverse scan results in a positive hysteresis loop. Formed pits
192 on the sample's surface were studied by optical microscopy (KH-8700, Hirox).

During the electrochemical tests, aeration and ozonation were both carried out in a neutral environment (pH = 7). An air pump with a gas flow rate of 100.0 L/h was used to inject the air. Ozone was produced with an ozone generator (COM-SD-30, Anseros) with an ozone capacity of 30.0 mg O_3/h. In case of Fenton treatment, the hydrogen peroxide and the ferrous iron catalyst were added at the start of the OCP measurement. For tests in acidic conditions, the pH was adapted from pH 7 to 3 using a 10 vol% sulfuric acid solution, which is necessary to avoid precipitation of the iron catalyst. The amount of hydrogen peroxide was based on the chemical oxygen demand (COD) of the wastewater: 2 mg H_2O_2/mg COD, while the iron catalyst was calculated using the following ratio: 0.1 g Fe/g H_2O_2 [6]. Hydrogen peroxide solution 30 wt/vol% (VWR Chemicals) and an acidified 100 g/L $FeSO_4.7H_2O$ solution (Carl Roth) were used as Fenton reagents. To avoid decomposition during storage, stabilized hydrogen peroxide was used for the corrosion experiments which was additionally stored in a refrigerator. After addition of the Fenton reagents to the wastewater and the pH correction (pH 3), hydrogen peroxide decomposed into hydroxyl radicals.

2.3 Immersion experiments and sample preparation

In addition to the electrochemical experiments, immersion tests were performed to study the crevice susceptibility of the studied grades in lab and full-scale AOP installations. Crevice formers were used according to ISO18070:2015 to obtain a well-defined crevice geometry with a constant pressure of 3 N/mm^2 [18]. The selected alloys were cut into coupons with defined dimension (150 mm x 100 mm) and the cut edges were polished (up to P600). Finally, the crevice formers were fixed on the coupons with a fixed torque of 3 Nm, as specified in ISO18070:2015 The metal specimens were fixed on a module made of PVC tubes, PVC plates and Polyamide (PA) threaded rods with PA spacers to avoid contact between the different specimens. After the immersion experiment, the corrosion attacks (if any) were measured by focalization technique using an optical microscope (Leica DM2500) equipped with micrometric gauge from Mitotuyo.

2.3.1. Lab-scale immersion

The lab-scale AOP immersion experiments were performed with synthetic wastewater. This water was created by adding NaCl, NH_4Cl and Na_2SO_4 to tap water in order to mimic the ionic composition of industrial wastewater (Table 2). The ionic composition of the test solution was checked on a weekly basis using a Metrohm 883 Basic IC Plus ion chromatograph. The

Metrohm 833 Basic ion chromatography system can measure both anion and cation concentrations. For the anion system, a Metrosep A Supp 5 column and eluent containing 0.32 mM Na_2CO_3 and 0.1 mM $NaHCO_3$ was used. The flow rate of the eluent was 0.7 mL/min. The anion system also contained a surpressor system. The cation system was equipped with a Metrosep C 6 column and used a solution of 1.7 mM HNO_3 and 1.7 mM dipicolinic acid as eluent at a flow rate of 0.9 mL/min.

A polypropylene (PP) box was used as recipient for 50.0 L synthetic wastewater in which the module with the mounted metal specimens was placed. For the lab-scale ozone immersion experiment, an ozone generator (COM-SD-30, Anseros) with an ozone capacity of 30.0 mg O_3/h and a gas flow rate of 100.0 L/h ensured that the test solution was continuously saturated with ozone gas. The injection of ozone gas was performed with a ceramic diffuser. The total duration of the lab-scale ozone immersion experiment was 4 months. For the lab-scale Fenton immersion experiment, the wastewater was treated with Fenton reagents instead of ozone injection. The calculation of the amount of hydrogen peroxide and iron catalyst was based on the same ratios than during the electrochemical measurement: 2 mg H_2O_2/mg COD & 0.1 g Fe^{2+}/g H_2O_2 [6]. Thus, 37 mL of H_2O_2 and 55 mL of iron catalyst were added to treat the 50 L synthetic wastewater while the pH was automatically controlled at 3. As previously mentioned, a hydrogen peroxide solution 30 w/v% and an acidified 100 g/L $FeSO_4.7H_2O$ solution were used as Fenton reagents. To mimic the treatment scheme of a full-scale installation, the addition of the Fenton reagents was automatically repeated every 8 h. Dosage pumps (Etatron D.S.) were used to add the correct volume of H_2O_2 and iron catalyst to the test solution while a pH regulator with dosage pump (Etatron D.S.) controlled the pH by adding diluted NaOH or H_2SO_4 solution. The oxidation reduction potential (ORP) was measured during the entire immersion experiment. Due to the difficulty to maintain controlled condition in this complex environment, the total duration of the lab-scale Fenton immersion experiment was limited to 1 month.

2.3.2. Full-scale immersion

During the full-scale immersion tests, the module with mounted metal coupons was placed in industrial wastewater. The pilot-scale installation consisted of a sequencing batch reactor (SBR) with a maximum volume of 1.0 m^3 that was used as biological wastewater treatment. The obtained effluent from this reactor underwent a further ozone or Fenton treatment as an additional step. The full installation was constructed in a 20 ft shipping container and was

placed on-site at the premises of a tank truck cleaning company (Antwerp, Belgium). This company mainly cleans tanks that have contained nutrient or chemical loadings. A schematic overview of the pilot-scale installation used in the tests is included in Fig. 1. The pilot-scale installation was fed with wastewater originating from the full-scale physicochemical treatment unit of the company. This is the same wastewater that is fed to the company's full-scale biological wastewater treatment. The wastewater was introduced in a buffer tank with a volume of 400 L, from which the SBR was fed.

For the full-scale ozonation immersion experiment, the effluent of the SBR was subjected to an ozonation treatment duration of 9 h per day. The ozone system consisted of an oxygen concentrator (SEP-300, Anseros) to produce a 90% oxygen stream from ambient air, which was subsequently fed to an ozone generator (COM-AD-01-IP, Anseros) to produce ozone by high voltage gas discharge tubes. The maximum ozone production of the generator was 2.75 gO_3/h at a gas flow rate of 100 L/h at 20 °C. This flow rate was kept constant during the whole pilot plant operation. The ozone stream was injected in the wastewater using a venturi-system. A static mixer was installed to increase the gas-liquid transfer. The total duration of the full-scale ozone immersion test was 6 months.

The same Fenton setup and treatment configuration from the lab-scale immersion experiment was used during the full-scale immersion test. However, the Fenton reagents were added to daily fresh effluent from the SBR instead of stagnant synthetic wastewater. The Fenton setup was incorporated in the wastewater treatment unit as depicted in Fig. 1. The full-scale Fenton immersion test was the same as on lab-scale, i.e., 1 month.

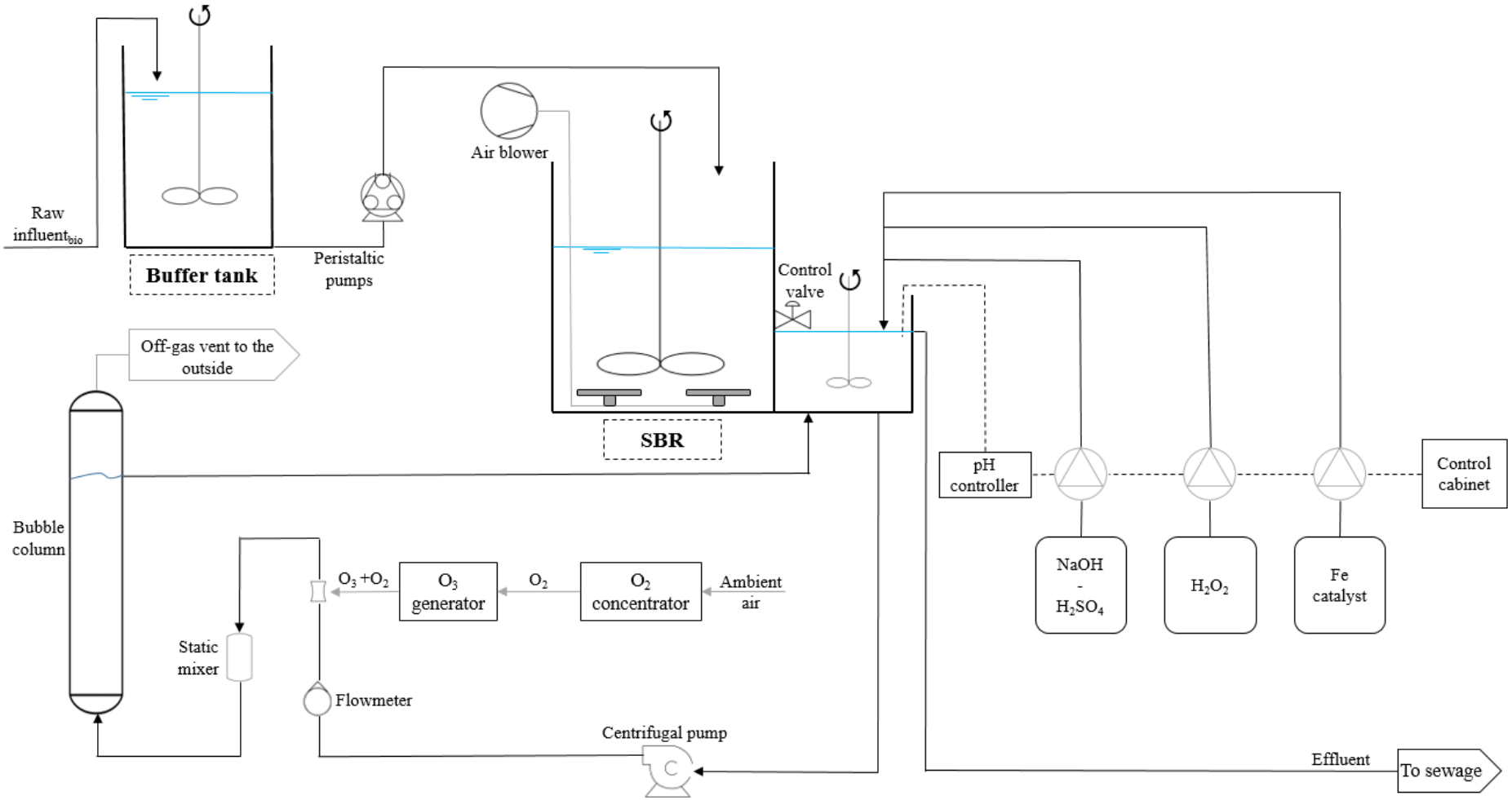


Fig. 1. Schematic overview of the pilot-scale biological wastewater treatment with the ozonation and Fenton unit.

3. Results and discussion

3.1. Electrochemical experiments

Each stainless steel grade was tested in 3 different conditions (air, ozone and Fenton) using the industrial wastewater and each test was repeated 3 times. The aerated wastewater was used to act as a reference to compare to the AOP treated wastewater. The pitting susceptibility was studied using CYCL measurements in wastewater treated with air (Fig. 2), ozone (Fig. 3) and Fenton reagents (Fig. 5). Only one polarization curve is shown per grade and environment instead of 3 to maintain clarity in the results overview. A complete summary is provided in Table 3.

For the aerated wastewater, none of the alloys showed any increase in current density during the total duration of the CYCL. This suggests that there is no or low risk of pitting corrosion in the tested aerated wastewater. For all tested alloys, the corrosion potential tends to be in the same range between -350 mV and -280 mV/SHE.

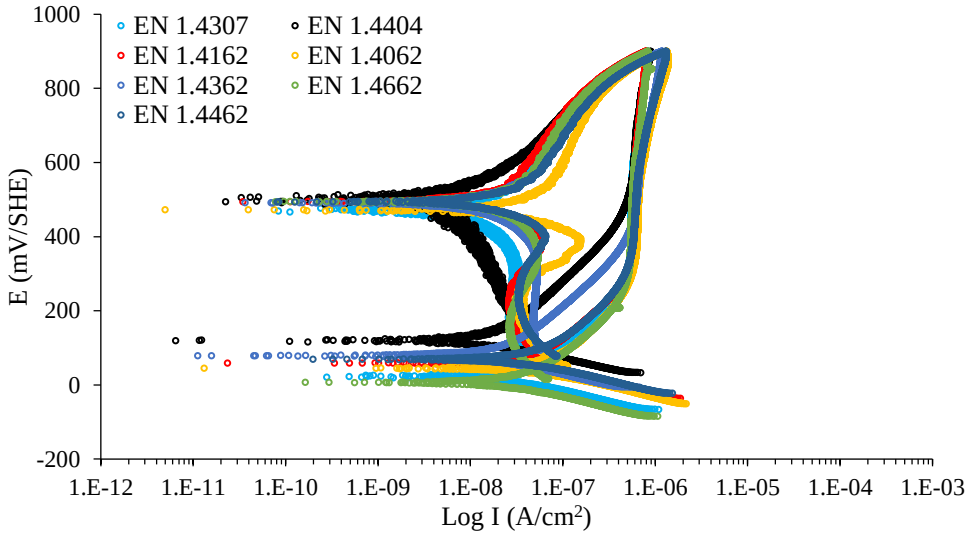


Fig. 2. Polarization curve of the tested alloys in aerated wastewater.

The effect of ozonated wastewater on the susceptibility of pitting corrosion is shown in Fig. 3. From this data, it is apparent that an increase in current density was found for grades EN 1.4307 and EN 1.4162. However, this was only observed for one out of three repetitions and both breakdown potentials (E_{bd}) were higher than the oxygen formation potential at pH 7 (812 mV/SHE), i.e., 880 and 862 mV/SHE, for EN 1.4307 and EN 1.4162, respectively. Hence, the risk of pitting corrosion can still be considered as low in the tested media.

Apart from the E_{bd}, metastable pitting could be observed for grade EN 1.4162 at 630 mV/SHE. This means that a pit was initiated but followed by repassivation, preventing the propagation of

the corrosion. As expected, for the ozonation treatment, the corrosion potential of the tested coupons was higher compared to their corrosion potential in aerated wastewater (it varies between -288 and -206 mV/SHE), representing an average increase of circa 100 mV. This shift in corrosion potential in the noble direction is the result of the high reduction potential of the O_3/O_2 redox couple (2.80 V/SHE). However, these corrosion potentials differ from some published studies [13,19], which found corrosion potentials in the range of 800-900 mV/SHE for stainless steel in ozonated seawater. It is possible that the use of ambient air instead of pure oxygen in combination with a low capacity ozone generator (30 mg O_3/h) resulted in lower ozone concentrations in the aqueous phase. Hence, the increase in corrosion potential was less significant compared to previous reported literature.

Except for grades EN 1.4307 and EN 1.4162, no significant differences can be observed between the different alloys in ozonated wastewater, under the tested condition.

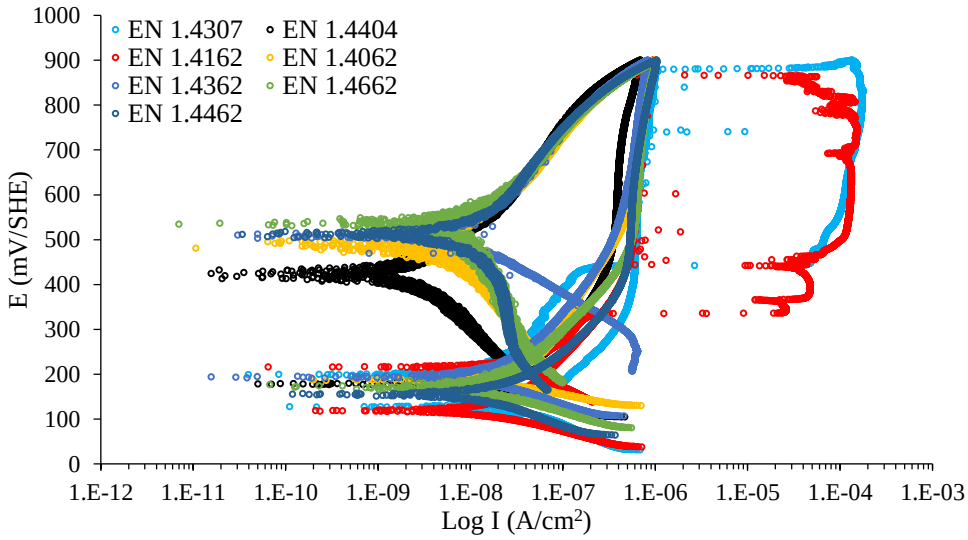


Fig. 3. Polarization curve of the tested alloys in ozonated wastewater.

The polarisation curves of grades EN 1.4307 and EN 1.4162 suggest that pits have been formed on the metal surface. This was confirmed by the microscopic analysis as shown in Fig. 4, where it can be observed that one pit was formed in ozonated wastewater for grade EN 1.4307 and EN 1.4162 with a pit depth of 145 and 240 µm, respectively. However, the breakdown potentials were higher than the oxygen formation at pH 7 (812 mV/SHE) potential and are therefore situated in the transpassive region. Such high potentials could be reached at higher ozone concentration, as seen by Pehkonen [13] and Wyllie and Duquette [19]. Hence, alloy EN 1.4307 and EN 1.4162 may show pitting corrosion at higher ozone levels.

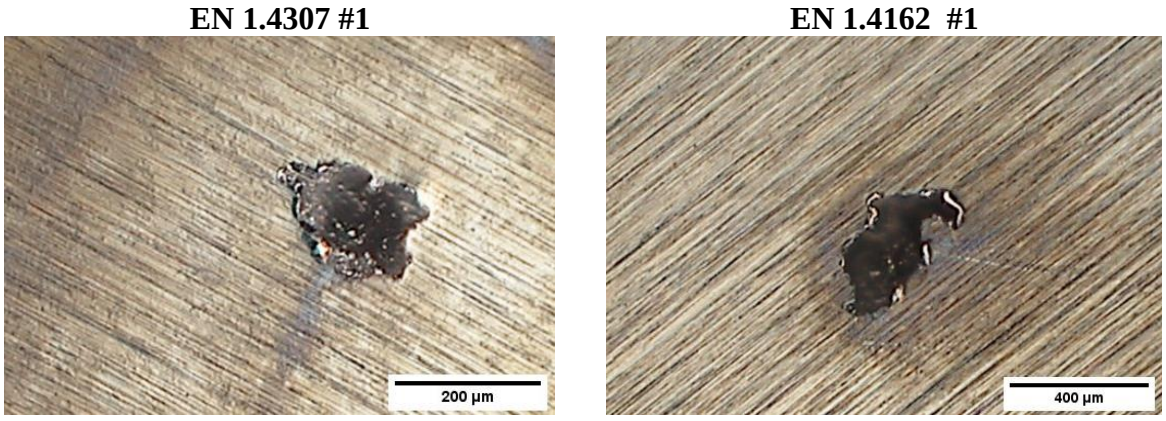


Fig. 4. Microscopic images of observed pits on EN 1.4307 and EN 1.4162 in ozonated wastewater.

Finally, the polarisation curves of the studied alloys in wastewater treated with Fenton reagents are provided in Fig. 5. Similar corrosion potentials were observed for each tested alloy, i.e., between 602 and 622 mV/SHE. Hence, the Fenton reagents lead to a highly oxidative environment with an increase in corrosion potential of circa 750 mV compared to aerated wastewater. This increase is due to the acid environment and the presence of hydrogen peroxide. During the polarisation measurement, only grade EN 1.4162 showed an increase in current density resulting in the breakdown of the passive protective layer. In summary, grade EN 1.4162 suffered from pitting corrosion twice out of three conducted polarisation measurements with an average E_{bd} of 800 ± 73 mV/SHE, which is below the oxygen formation potential at pH 3 (1048 mv/SHE).

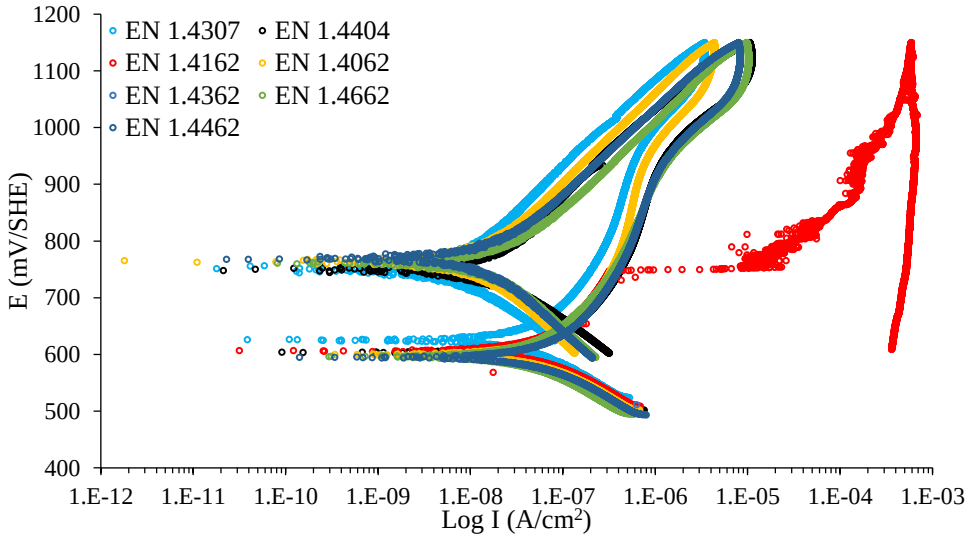


Fig. 5. Polarization curve of the tested alloys in wastewater treated with Fenton reagents.

The microscopic images of the surface of EN 1.4162 after the electrochemical tests are shown in Fig. 7. Four pits were observed on the surface of the first sample with an average pit depth

of 183 ± 47 µm, while the second sample had 3 pits with a similar average pit depth of 193 ± 50 µm.

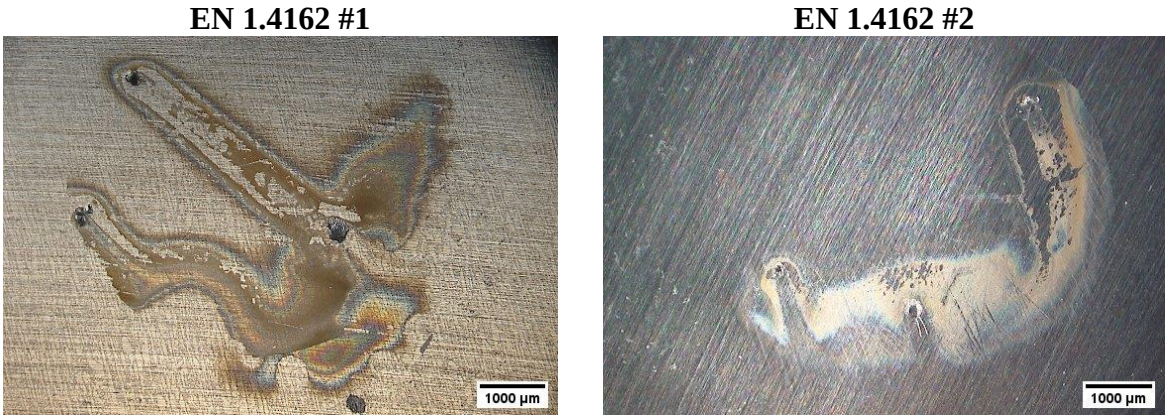


Fig. 6. Microscopic images of observed pits on two different EN 1.4162 samples in wastewater treated with Fenton reagents.

The results of the performed polarisation experiments are summarized in Table 3. Based on those, it can be concluded that for none of the alloys there is a corrosion risk when used in aerated wastewater at the tested chloride concentration. At the tested levels, grade EN 1.4307 and EN 1.4162 did show some pits at the end of the polarization measurement in ozonated wastewater and the use of Fenton reagents led to the failure of grade EN 1.4162.

Table 3. Summary results localized corrosion from polarization measurements.

Alloy	Aeration Ambient T (26.1 °C) Chloride ~ 1000 ppm pH ~ 7		Ozonation Ambient T (26.1 °C) Chloride ~ 1000 ppm pH ~ 7 Ozonation ~ 30 mg/h		Fenton reagents Ambient T (26.1 °C) Chloride ~ 1000 ppm pH ~ 3 Fenton ~ 2 mg H_2O_2/COD	
	Pitting?	E_{bd} (mV/SHE)	Pitting?	E_{bd} (mV/SHE)	Pitting?	E_{bd} (mV/SHE)
EN 1.4307	No pit	/	Pit (1/3)	880	No pit	/
EN 1.4162	No pit	/	No pit	/	No pit	/
EN 1.4362	No pit	/	Pit (1/3)	870	Pit (2/3)	800 ± 73
EN 1.4462	No pit	/	No pit	/	No pit	/
EN 1.4404	No pit	/	No pit	/	No pit	/
EN 1.4062	No pit	/	No pit	/	No pit	/
EN 1.4662	No pit	/	No pit	/	No pit	/

3.2. Immersion experiments

3.2.1. Lab-scale ozone immersion

The ionic composition of the synthetic wastewater remained stable during the total duration of the immersion experiment with an average chloride concentration of 1000 ± 41 ppm, except for

the nitrate ion concentration, which rapidly increased from 0.91 to 357 ppm NO_3^-. This can be explained by the formation of nitric oxide when ambient air is used instead of pure oxygen to produce ozone gas, as seen in Eq. 4.

$$N + O_2 \rightarrow NO + O \quad \text{(Eq. 4)}$$

Highly corrosive nitric acid can further be formed from nitric oxide in a humid environment [4]. In other words, it is likely that nitric acid was being produced by the ozone generator during the immersion experiment. This is also visible in the pH profile depicted in Fig. 7. At day 50, a pH drop from pH 6.84 to 3.69 took place due to the continuous production of nitric acid. Hence, the pH was weekly checked and adjusted by manually adding a diluted NaOH solution to maintain the neutral environment. Unfortunately, it seemed difficult to maintain a stable neutral environment due to constant formation of nitric acid. The shift of pH should, therefore, be taken into account when assessing the results from this immersion experiment.

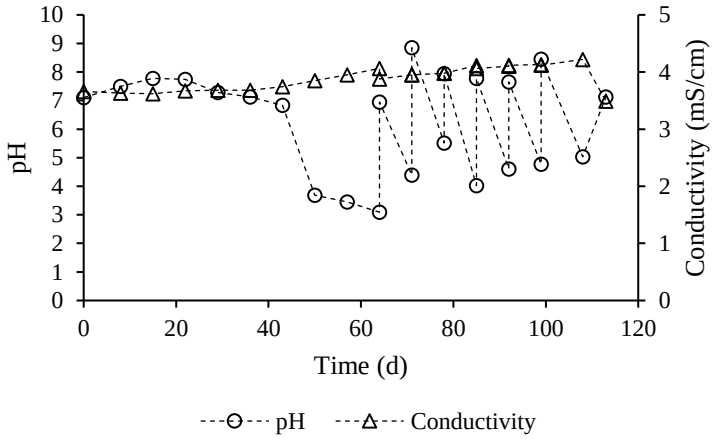
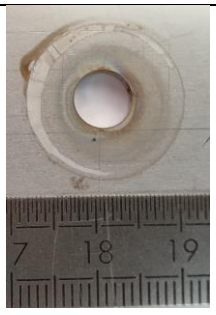


Fig. 7. Conductivity and pH profile during lab-scale ozone immersion experiment.

After 4 months, the immersion experiment was terminated, and the metal specimens were removed and analysed. Images of the most affected metal surfaces of the tested alloys are provided in Fig. 8 and a summary of the crevice corrosion susceptibility is shown in Table 4.

Alloy	**EN 1.4307**	**EN 1.4404**	**EN 1.4162**
Photo most affected coupon			
Max crevice depth (µm)	38 µm	29 µm	41 µm
EN 1.4062	**EN 1.4362**	**EN 1.4662**	**EN 1.4462**

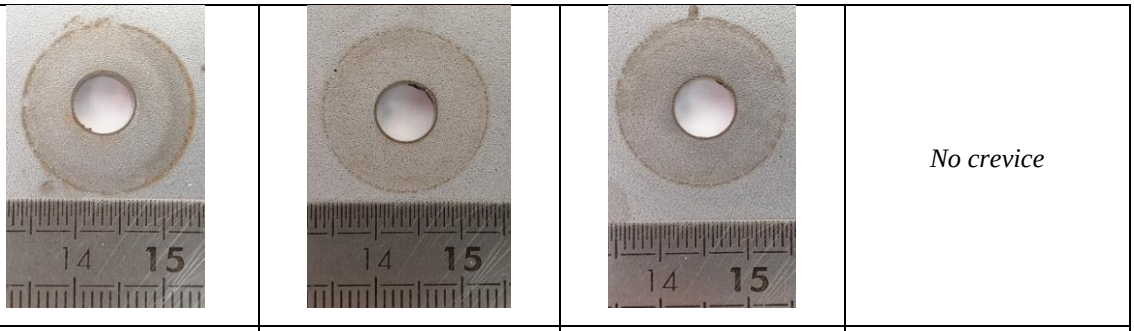


Fig. 8. Summary of the most affected alloys after 4 months of exposure to ozonated synthetic wastewater.

Only grade EN 1.4462 did not suffer from crevice corrosion. In addition, grade EN 1.4662 was able to withstand the ozonated environment with only minor visible superficial corrosion attacks. The other alloys suffered from crevice corrosion (at least 3 times out of the 6 coupons) with a maximum crevice depth of 41 µm for grade EN 1.4162. This finding further supports the idea that grades with a low PREN are more susceptible to localized corrosion.

3.2.2. Lab-scale Fenton immersion

The continuous addition of the iron catalyst affected the oxidation-reduction potential (ORP), conductivity and ionic composition of the synthetic wastewater during the lab-scale Fenton immersion test. Firstly, the used catalyst ($FeSO_4.7H_2O$) resulted in an increase in sulphate anion concentration from 235 to 1390 ppm SO_4^{2-}. Secondly, the conductivity increased linearly from 3.53 to 5.36 mS/cm due to the continuous addition of conductive Fe^{2+} ions [20]. Finally, the ORP showed a decreasing trend with an average value of 482 ± 34 mV (Fig. 9). The increase in iron catalyst concentration could cause a faster degradation of the added hydrogen peroxide, which therefore resulted in lower ORP values.

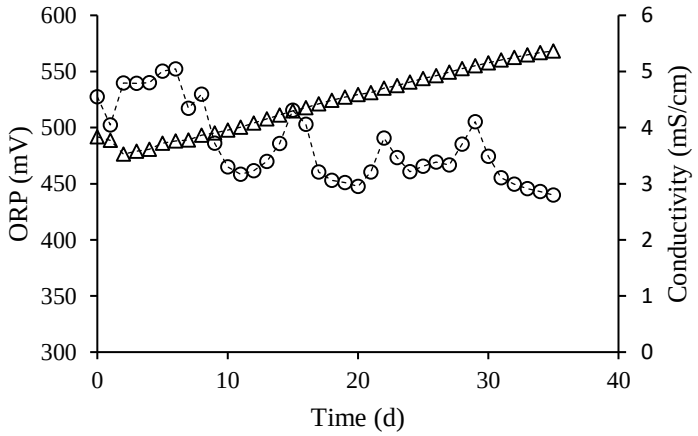


Fig. 9. Conductivity and ORP profile during lab-scale Fenton immersion experiment.

Furthermore, the use of NaOH to adjust the pH resulted in an increase of sodium cation concentration from 597 to 1143 ppm. Because of dilution, the addition of the different reagents

caused a reduction of the chloride concentration from 926 to 570 ppm. Overall, the ionic composition was not stable due to continuous operation of the Fenton setup, which may have had an impact on the crevice corrosion evaluation. After 1 month of exposure, the metal samples were retrieved from the Fenton unit and examined with a microscope. The most affected samples are shown in Fig. 10.

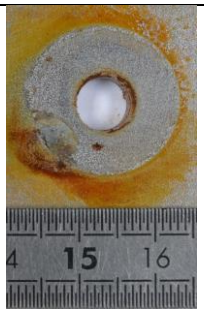
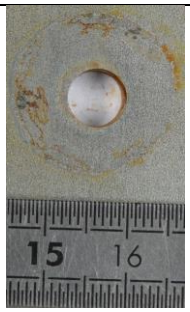
Alloy	**EN 1.4307**	**EN 1.4404**	**EN 1.4162**
Photo most affected coupon			
Max crevice depth (µm)	745 µm	629 µm	675 µm
EN 1.4062	**EN 1.4362**	**EN 1.4662**	**EN 1.4462**
		*No crevice*	*No crevice*
75 µm	62 µm	0 µm	0 µm

Fig. 10. Summary of the most affected alloys after 1 month of exposure to synthetic wastewater treated with Fenton reagents.

As seen in Fig. 10, the metal samples severely suffered from crevice corrosion except for grades EN 1.4662 and EN 1.4462. Crevice corrosion was observed on all the tested specimens of grades EN 1.4307 and EN 1.4162 with a maximum crevice depth of 745 and 675 µm, respectively. Both grades EN 1.4062 and EN 1.4362 corroded twice out of the four specimens with a maximum crevice depth of 62 and 75 µm, respectively. In other words, the increase of alloying elements in the lean duplex stainless steel results in lower crevice depths. These results show that the acid environment (pH 3) in combination with the oxidative environment (484 mV) leads to corrosive conditions for the less alloyed stainless steel alloys. Only the highly alloyed duplex stainless steels such as EN 1.4662 and EN 1.4462 withstand the Fenton environment. The observed occurrence of crevice corrosion is satisfyingly consistent with the order of the PRE numbers.

3.2.3. Full-scale ozone immersion

The total duration of the full-scale ozone immersion experiment was 6 months. During this period, the metal samples were exposed to a continuous flow of ozonated industrial wastewater. The injection of ozone gas resulted in an increase in the ORP of the treated wastewater. The typical ORP profile of the ozonated wastewater is shown in Fig. 11, indicating the ozone treatment scheme.

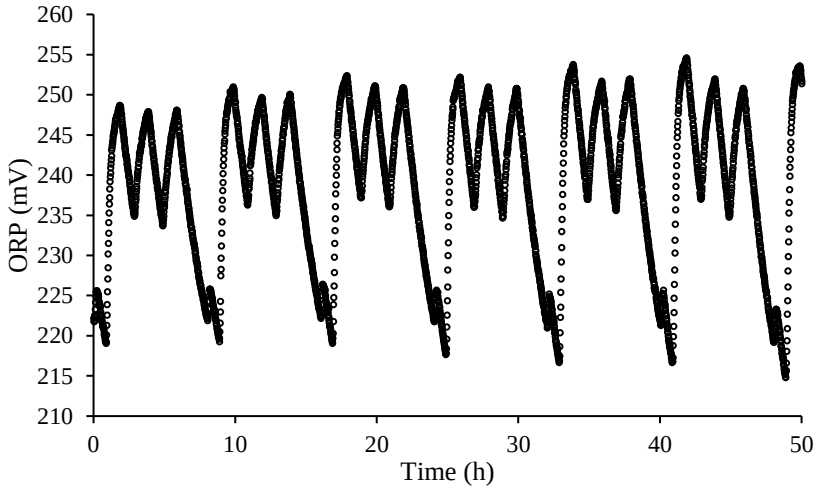
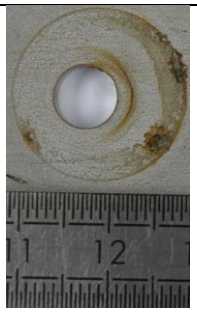


Fig. 11. ORP profile during full-scale ozone immersion experiment.

During the settling phase of the activated sludge, the ozone generator was switched off, resulting in a decrease of the ORP to approximately 215 mV. During the ozonation phase, a maximum of 250 mV was observed. Overall, the ionic composition was fairly stable during the total duration of the immersion experiment with an average chloride concentration of 1000 ± 91 ppm.

Alloy	**EN 1.4307**	**EN 1.4404**	**EN 1.4162**
Photo most affected coupon			
Max crevice depth (µm)	29 µm	26 µm	26 µm
EN 1.4062	**EN 1.4362**	**EN 1.4662**	**EN 1.4462**

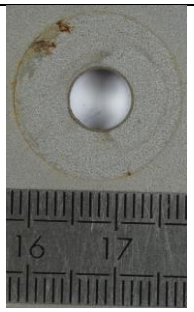
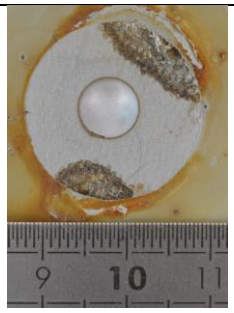
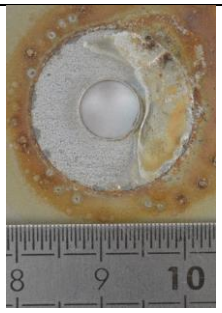
		*No crevice*	*No crevice*
25 µm	10 µm	0 µm	0 µm

Fig. 12. Summary of the most affected alloys after 6 months of exposure to ozonated industrial wastewater.

The immersion experiment in ozonated industrial wastewater (Fig. 12) shows similar results as in synthetic wastewater. Grades EN 1.4662 and EN 1.4462 did not show any sign of localized corrosion. Superficial corrosion was observed for grades EN 1.4362 while all the other alloys suffered from crevice corrosion with a maximum crevice depth of 29 µm (EN 1.4307). Apart from the fact that grade EN 1.4662 was able to withstand the ozonation in industrial wastewater while showing superficial corrosion in synthetic wastewater, the results on lab and full-scale are similar.

3.2.4. Full-scale Fenton immersion

The duration of the experiment was also 1 month (same as Fenton lab-scale). The ORP remained stable during the total duration of the immersion experiment with an average ORP value of 434 ± 30 mV, which is similar to the lab-scale Fenton immersion test. Besides, the ionic composition did not change during the immersion experiment with an average chloride concentration of 638 ± 42 ppm. It is however lower than during the previous full-scale immersion test although the same wastewater treatment plant was used. It is possible that a change in operation of the wastewater treatment plant (e.g., different dosage of coagulant chemicals in the fysico chemistry) or different composition of raw influent could have influenced the ionic composition of the effluent.

Alloy	**EN 1.4307**	**EN 1.4404**	**EN 1.4162**
Photo most affected coupon			
Max crevice depth (µm)	896 µm	649 µm	569 µm
EN 1.4062	**EN 1.4362**	**EN 1.4662**	**EN 1.4462**

	*No crevice*	*No crevice*	*No crevice*
149 µm	0 µm	0 µm	0 µm

Fig. 13. Summary of the most affected alloys after 1 month of exposure to industrial wastewater treated with Fenton reagents.

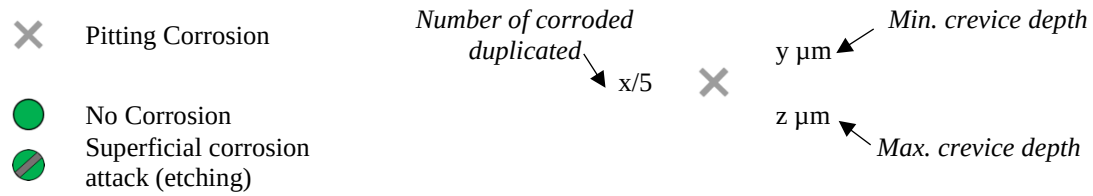
Fig. 13 summarizes the results of the full-scale immersion experiment. Grades EN 1.4362, EN 1.4662 and EN 1.4462 were able to withstand the exposure to industrial wastewater treated with Fenton reagents at pH 3 for 1 month while the other alloys suffered from crevice corrosion. At least 4 out of the 6 coupons suffered from crevice corrosion with a maximum crevice depth of 896 µm for grade EN 1.4307.

3.2.5. Summary immersion tests

A full overview of the obtained results with ISO 18070:2015 crevice assembly of the studied stainless steels in the different test conditions is given in Table 4. This table shows the amount of corroded coupons out of the 5 replicates together with the lowest and highest observed crevice depth.

Table 4. Summary of the results from the lab and full-scale immersion experiments (crevice corrosion).

	Lab-scale immersion		**Full-scale immersion**	
Alloy	**Ozonation** Duration: 4 months Average T: 18.1 °C Chloride: 1000 ppm pH: 6.3 Ozonation ~ 30 mg/h ORP: / mV	**Fenton reagents** Duration: 1 month Average T: 24.3 °C Chloride: 738 ppm pH: 3 Fenton ~ 2 mg H_2O_2/COD ORP: 484 mV	**Ozonation** Duration: 6 months Average T: 27.2 °C Chloride: 1000 ppm pH: 7 Ozonation ~ 30 mg/h ORP: 240 mV	**Fenton reagents** Duration: 1 month Average T: 14.8 °C Chloride: 638 ppm pH: 3 Fenton ~ 2 mg H_2O_2/COD ORP: 434 mV
EN 1.4307	0 4/6 ✕ 38	41 4/4 ✕ 745	0 3/6 ✕ 29	0 5/6 ✕ 896
EN 1.4404	0 4/6 ✕ 29	0 3/4 ✕ 629	0 2/6 ✕ 26	0 4/6 ✕ 649
EN 1.4162	0 4/6 ✕ 41	35 4/4 ✕ 675	0 2/6 ✕ 26	0 5/6 ✕ 569
EN 1.4062	0 4/6 ✕ 30	0 2/4 ✕ 75	0 2/6 ✕ 25	0 4/6 ✕ 149
EN 1.4362	0 3/6 ✕ 25	0 2/4 ✕ 62	0 2/6 ◍ 10	0 0/6 ● 0
EN 1.4662	0 2/6 ◍ 10	0 0/4 ● 0	0 0/6 ● 0	0 0/6 ● 0
EN 1.4462	0 0/5 ● 0	0 0/4 ● 0	0 0/6 ● 0	0 0/6 ● 0



From these results, it is clear that the austenitic and most lean duplex stainless steel coupons suffered from crevice corrosion in the tested AOP environments. Only duplex grade EN 1.4462 remained unaffected.

4. Conclusions

The main goal of the current study was to determine the localized corrosion properties in terms of pitting and crevice susceptibility of lean duplex alloys compared to the conventional austenitic stainless steels in advanced oxidation process (AOP), ozone and Fenton, treated wastewater environments. Electrochemical experiments were conducted to study the resistance to pitting corrosion, while crevice corrosion was evaluated using immersion experiments. The electrochemical experiments showed that ozonation did not have a significant impact on the pitting corrosion susceptibility of the studied alloys under the tested conditions in electrolyte containing 955 ppm of chloride. Only grade EN 1.4307 and EN 1.4162 did show an increase in current density during the tests, but at critical potentials above approx. 850 mV/SHE. In service conditions, such potential can only be reached at high ozone concentrations. The lab-scale ozone immersion experiment showed that the austenitic and lean duplex stainless steel grades suffered from crevice corrosion, while the duplex grade EN 1.4462 was unaffected. As expected, the studied alloys in ozonated wastewater are more susceptible to crevice corrosion compared to pitting. The results of the full-scale and lab-scale ozone immersion experiment are similar. From the polarisation measurements for the Fenton treatment, the critical breakdown potential of lean duplex grade EN 1.4162 was 800 mV/SHE, suggestion that this grade may be susceptible to pitting corrosion in the studied Fenton environment if its corrosion potential is not controlled (i.e., high oxidant reagent concentrations). The immersion experiments in Fenton environment showed that crevice corrosion is a severe problem for almost all the studied alloys, except for lean duplex grade EN 1.4662 and duplex grade EN 1.4462 Similar maximum crevice depths were observed at the end of both lab- and full-scale immersion experiment for grades EN 1.4307, EN 1.4404 and EN 1.4162 which were in the 600-900 µm range because the test conditions (Fenton dosage, ORP and ionic composition) of both setups were similar. This study demonstrated that the use of AOPs in chloride-containing media can increase the risk of localized corrosion of lean duplex stainless steel grades, as it is the case for commonly used austenitic grades. However, the corrosion experiments were performed at rather high chloride content (about 1000 ppm) and one ozone or Fenton level. A parametric study at lower concentrations would be required to define the critical parameters for resistance of lean duplex stainless steels.

Acknowledgements

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References

[1] Oller, I., Malato, S., & Sánchez-Pérez, J. (2011). Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. Science of the total environment, 409(20), 4141-4166.

[2] Dewil, R., Mantzavinos, D., Poulios, I., & Rodrigo, M. A. (2017). New perspectives for advanced oxidation processes. *Journal of environmental management*, *195*, 93-99.

[3] Glaze, W. H., Kang, J. W., & Chapin, D. H. (1987). The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation.

[4] Gottschalk, C., Libra, J. A., & Saupe, A. (2009). Ozonation of water and waste water: A practical guide to understanding ozone and its applications. John Wiley & Sons.

[5] Brown, B. E., & Duquette, D. J. (1993). The Effects of Dissolved Ozone on the Corrosion Behavior of 304 Stainless Steel, Monel 400 and Naval Brass in Artificial Sea Water. RENSSELAER POLYTECHNIC INST TROY NY DEPT OF MATERIALS ENGINEERING.

[6] Pera-Titus, M., García-Molina, V., Baños, M. A., Giménez, J., & Esplugas, S. (2004). Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B: Environmental*, *47*(4), 219-256.

[7] Rodríguez, R., Espada, J. J., Pariente, M. I., Melero, J. A., Martínez, F., & Molina, R. (2016). Comparative life cycle assessment (LCA) study of heterogeneous and homogenous Fenton processes for the treatment of pharmaceutical wastewater. *Journal of Cleaner Production*, *124*, 21-29.

[8] Zapp, P. E. (2004). Electrochemical Tests of Carbon Steel in Simulated Waste Containing Fenton's Reagent (No. WSRC-TR-2003-00445, R1). Savannah River Site (US).

[9] Heubner, U. (2010). Performance of Stainless Steels in Waste Water Installations. *Euro Inox*.

[10] Outokumpu. Corrosion Handbook. (2015). 11th ed.

[11] Charles, J., & Chemelle, P. (2012). The history of duplex developments, nowadays DSS properties and duplex market future trends. World Iron & Steel, 1, 46-57.

[12] Sato, Y., Suzuki, M., & Matsudaira, M. (1982). Dissolved ozone effect on corrosion of metals in water. CORROSION ENGINEERING, 31(5), 319-324.

[13] Pehkonen, A. (2001). The effect of dissolved ozone on the corrosion behaviour of some stainless steels. Helsinki University of Technology.

[14] Liao, J., Kishimoto, K., Yao, M., Mori, Y., & Ikai, M. (2012). Effect of ozone on corrosion behavior of mild steel in seawater. *Corrosion science*, *55*, 205-212.

[15] Brown, B. E., Lu, H. H., & Duquette, D. J. (1992). Effect of flow rates on localized corrosion behavior of 304 stainless steel in ozonated 0.5 N NaCl. *Corrosion*, *48*(12), 970-975.

[16] Li, F. B., Bremner, D. H., & Burgess, A. E. (1999). Dissolution and passivation of iron in acetonitrile and acetonitrile–water mixtures. Corrosion science, 41(12), 2317-2335.

[17] ASTM G61-86 (Reapproved 1998). (1998). Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys.

[18] ISO 18070:2015. (2015). Corrosion of metals and alloys — Crevice corrosion formers with disc springs for flat specimens or tubes made from stainless steel.

[19] Wyllie, W. E., & Duquette, D. J. (1997). The Effect of Dissolved Ozone on the Corrosion Behavior of Stainless Steels in Artificial Seawater. In *Corrosion97*. OnePetro.

[20] Regberg, A., Singha, K., Tien, M., Picardal, F., Zheng, Q., Schieber, J., ... & Brantley, S. L. (2011). Electrical conductivity as an indicator of iron reduction rates in abiotic and biotic systems. *Water resources research*, *47*(4).