

CORROSION OF STAINLESS STEEL WATER STORAGE TANKS EXPOSED IN COASTAL ATMOSPHERIC CONDITIONS

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ABSTRACT

The results of corrosion survey for stainless steel tanks used in water storage at various areas are presented. More severe corrosion is observed for the area with higher airborne salinity. Damages are revealed at both outer and inner surfaces for tanks made of Type 304 and 201 steels exposed in coastal conditions. Corrosion products examined by visual inspection and SEM-EDX technique showed relatively distinctive characteristics for the outer and inner tank surfaces which are attributed to different corrosion mechanisms initiated by corrosive chloride accumulated on steel surfaces. Airborne salinity is considered the main source causing corrosion of Type 304 and 201 stainless steel tanks.

Keywords: water tank, stainless steel, airborne salinity, corrosion.

1. INTRODUCTION

Stainless steel is a widely used material for water storage due to its high corrosion resistance in natural environments. Depending on application conditions, various types of stainless steel have been recommended for water tanks. Currently, tanks made of Type 304 steel are the most popular, gradually replacing traditional means of water storage. Type 304 and 201 steel coils are commonly used to manufacture separate or coupled tank constructions. In fact, corrosion remains a main concern and its causes are not fully clarified.

Fundamentally, corrosion resistance of stainless steels in nature is due to the formation of passive films on the surface. The passive films are influenced by environmental factors, such as temperature, relative humidity (RH) and chemicals occurring in the atmosphere, including airborne salts and other pollutants. Jung R.H. et al. defined the nature of passive film to the corrosion process and confirmed that the cation ratio of chromium ($[Cr]/\{[Cr] + [Fe]\}$) in passive films formed under 30–70 % RH was similar to the alloy composition of Grade 304 steel. As proven, airborne salts play an important role in corrosion initiation by breaking passive film at certain RH and chloride concentration values [1]. According to Tsutsumi and coworkers,

the RH is determined to be 35–75 % for progressive corrosion of Type 304 steel in marine atmosphere and at RH above 75 % no corrosion is detected, even if a large amount of airborne salts is deposited, except for the initial stage of exposure [2]. In laboratory test, the critical concentration of chloride in water droplet for initiation of corrosion is evaluated at about 5-6 M [3]. Furthermore, Jung R.H. et al. reported that [1], the presence of chloride in the thin water layer facilitated selective dissolution of iron as $\text{Fe}(\text{Cl})_{\text{aq}}$, resulting in chromium enrichment in the passive film, which favors the increase of chromium ratio in the film up to 40 %. Meanwhile, chloride concentration is increased due to the water layer drying up, and a critical value is reached to generate pitting corrosion [1]. This issue is also reported in other works [4-8]. It is noted in [8], that the RH for pitting during drying (RH_{pit}) and repassivation during wetting (RH_{rep}) are correspondingly equal to 56 % and 65 %; the average chloride concentration for pitting initiation is recorded at 7.3 M.

The above described corrosion mechanism of stainless steel may typically occur in coastal humid tropical atmosphere like Vietnam conditions, where the combination of high salinity and changing temperature regime can lead to a critical chloride value on exposed surface of steel. For a better understanding of the corrosion behavior of stainless steel water tanks in practical application, a field survey has been conducted for several areas of Vietnam; the selected survey results and laboratory corrosion investigation of coupled Type 304/201 steel tanks are reported in this paper.

2. MATERIALS AND METHODS

2.1. Methods of field survey and corrosion evaluation

2.1.1. Survey locations and sampling method

The field survey for water storage tanks exposed under natural conditions was conducted in two areas of northern Vietnam, characterized by distinctive features in the context of atmospheric corrosion: the coastal urban district of Hai Phong (within 1 km from coastline) and the mountain Son La city located 430 km westward. The climatic and environmental characteristics of the survey areas were summarized in Table 1. The values of climatic parameters were obtained from local weather stations. Time-of-wetness (TOW) was calculated based on annual temperature and RH data, using an empirical equation described in [9]. Airborne salinity and sulfur dioxide concentrations were taken from Lien L.T.H. work [9]. The reported salinity values were converted from results determined by “dry gauze” method into respective “wet candle” method with twofold multiplier.

Table 1. Climatic and environmental characteristics of the survey areas.

Survey area	Climatic and environmental parameters								
	Temperature (°C)	RH (%)	TOW (h)	Precipitation (mm)	Evaporation (mm/d)	Wind speed (m/s)	Prevail. wind direction	Salinity (mg/m ² .d)	Sulfur dioxide (µg/m ³)
Hai Phong	24.0	85.5	6,406	2,307	709	0.1-8.9	E	17.5	8.0
Son La	21.1	81.0	5,171	1,473	800	0.8-2.0	S, N	1.86	0.69

Corrosion appearance was checked by visual observation with common optical devices for the outer and inner surfaces of combined Type 304/201 steel tanks. Two groups of outdoor exposed tanks at various buildings were selected for evaluation. The tanks were grouped by building ownership: private residential and public civil. At least ten tanks with minimum two years of usage were checked in each group. Tank surface was cleaned from dust, degreased before detailed checking; detected corrosion damages were recorded by photography and selective tank areas were cut off for further examination in laboratory.

2.1.2. Analysis of steels and corrosion products

The chemical compositions of selected steel cut-off taken from corrosion-damaged tanks were analyzed by Spectro Metal Analyzer (Ametek, USA) at Lab. of Materials Technology (MTLAB, HCMUT) to verify the assigned steel types used for tank construction.

The elemental compositions of corrosion products were revealed in-situ by SEM-EDX methods. JSM 6510LV (Jeol, Japan) and X-act EDX (Oxford Instrument, UK) of Institute for Tropical Technology (VAST) were used for SEM-EDX analysis. Single EDX spectra were selected for determining the corrosion product composition at the outer or inner tank surfaces. The elemental contents were taken from analyzed results of "Spectrum 2" and "Spectrum 12" spots at SEM images for the outer and inner Type 201 steel tank surfaces respectively.

The corrosion products were also analyzed using wavelength-dispersive spectroscopy (WDS) with pentaerythritol (PET), lithium fluoride (LiF) and thallium acid phthalate (TAP) diffracting crystals to detect their chemical composition and inclusion of environmental pollutants such as chlorides into rusting spots. SXFive electron probe micro-analyzer (EPMA) serial 962 of Cameca Co. (France) at Institute of Geological Sciences (IGS, VAST) was operated in this experiment with following working parameters: 20 kV voltage and 24 nA beam current, 1,000 points with 1,000 ms/point.

2.2. Electrochemical measurements

As-received Type 201 and 304 stainless steel coils with passive films were taken for conducting open-circuit potential (OCP) and cyclic potentiodynamic polarization measurement.

The tested samples were prepared from the coils with dimensions 75×50×0.5 mm and degreased with ultrasonic stirring at 60 °C for 5 min. After degreasing, the samples were soaked in acetone and given to dry, then set to conduct electrochemical measurement in 3.56 % (by weight) sodium chloride (EMSURE@ACS, p.a. Sigma-Aldrich) aerated solution, following procedures described in ASTM G 61-86 (2014) on Solartron SI 1280B Galvanostat/potentiostat (UK) at Lab. of Materials Technology (MTLAB, HCMUT). The open-circuit potentials (OCP) were recorded in the conventional three-electrode cell using sat. calomel electrode as reference. Records were carried out for a one-hour duration with OCP values fixed at the final 10 min. of the course. To reveal local corrosion and its potential (as E_{pit}), the cyclic potentiodynamical polarization was performed by scanning from E_{cor} at a scan rate 0.6 V/h forward to maximum current of 0.5 mA or maximum potential of 1.6 V, following by backward scanning to the initial E_{cor} . The commonly accepted selection of sodium chloride concentration (3.56 wt.%) was used and records of electrochemical parameters such as OCP, E_{cor} , etc. were defined according to ASTM G 61-86 (points 6.2 and 6.8).

3. RESULTS AND DISCUSSION

3.1. Corrosion of stainless steel tanks in outdoor application

The results of corrosion survey for water storage tanks exposed in outdoor application were summarized in Table 2, where ratios of corrosion-damaged tanks to all tanks examined were recorded for duration of usage.

Table 2. Ratio of corrosion-damaged tanks to all tanks examined for duration of usage.

Duration (year) \ Survey area	< 2	2 - 5	5 - 10	10 - 15	> 15
Hai Phong	0/5	0/3	2/2	2/2	1/2
Son La	0/5	0/5	0/5	1/3	0/0

Table 2 shows a clear difference in survey results: corrosion was noticeably revealed for tanks examined in Hai Phong coastal conditions after 5 years of usage, compared to corrosion case occurred to a single tank in Son La. However, the last case was revealed for a tank installed in water treatment workshop, where various chemicals were used for a prolonged period. Other corrosion-damaged results recorded in the coastal area were entirely related to the water storage tanks used in private residential houses, where attack of natural environmental parameters may be considered as the main destructive factors.

More detailed tank examination was summarized in Table 3 demonstrating corrosion behavior of the outer steel surface under constant aggressive atmospheric impact and of the inner side in contact with water as well as changing air/water service regime. As above mentioned, in Son La area, corrosion on outer surface was observed for a single tank only; meanwhile, severe corrosion damages were revealed for both the outer and inner surfaces of the tanks used in Hai Phong. Corrosion developed to a larger extent on the outer surface, where metal was possibly affected by airborne salinity and other pollutants under changing temperature-humid conditions. With higher TOW values, water films easily formed on the metal surface and were gradually enriched with deposited chlorides in the coastal area of Hai Phong. Under seasonal or daily temperature-humidity regimes, the critical concentration of chloride was reached to initiate local corrosion [3]. In contrast, corrosion was rarely detected in Son La, where aggressive atmospheric chemicals were detected in very low concentration (Table 1).

Table 3. Results of corrosion survey for water storage tanks.

Location		Son La		Hai Phong	
Surface		Outer	Inner	Outer	Inner
Corrosion on surface	Type 201 steel	Slight damage	No damage	Severe damage	Severe damage
	Type 304 steel	No damage	No damage	Slight damage	Slight damage

In fact, the vertical water tanks were for a long time designed with the upper part (usually above water level) made from Type 201 steel. The corrosion damages of both steels are demonstrated in field images of Figure 1 and Figure 2. It is clear that more extensive corrosion was registered for Type 201 compared to Type 304 steels when exposed in the atmospheric

conditions of Hai Phong. Specifically, different rust appearance in the outer and inner surface was exhibited: deep pits with red color corrosion products were formed in the first case and shallow spots with preferentially grey color in the latter case (Fig. 2).

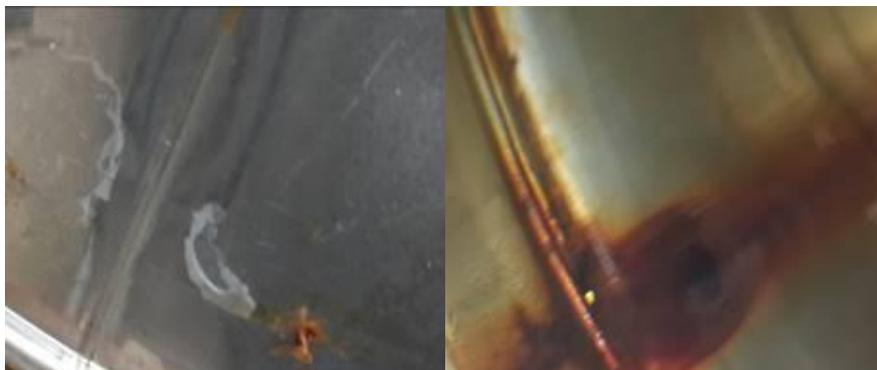


Figure 1. Field images of the outer (left) and inner (right) surface of Type 304 steel tank in Hai Phong.



Figure 2. Field images of the outer (left) and inner (right) surface of Type 201 steel tank in Hai Phong.

3.2. Characterization of corrosion products

Steel samples taken from corrosion-damaged tanks were analyzed and their chemical compositions shown in Table 4 proved that tanks were indeed constructed of Type 201 and 304 stainless steel, compared to specifications widely reported in literature.

Table 4. Chemical composition (wt.%) of corrosion-damaged steel tank.

Element Tank part	C	Si	Mn	P	Cu	Ni	Cr	Fe	Assigned Type
Upper part	0.04	0.46	7.4	0.04	1.5	4.09	15.12	bal.	201
Main part	0.05	0.41	1.03	0.03	-	8.03	18.8	bal.	304

The corrosion products on the outer and inner surfaces of the tanks were characterized by SEM-EDX and selective data are presented in Fig. 3, Fig. 4 and Tab. 5. The EDX spectra clearly show the presence of atomic chlorine in corrosion product on the outer surface of the tanks; meanwhile, no atomic chlorine is detected in corrosion product taken from the inner surface.

The chemical composition of corrosion products taken from tanks exposed in Hai Phong shows some specific features: chlorine is detected in minute quantity of 0.24 % on the outer surface (Fig. 3, Tab. 5) and no chlorine is detected on the inner surface (Fig. 4, Tab. 4) of Type 201 tank.

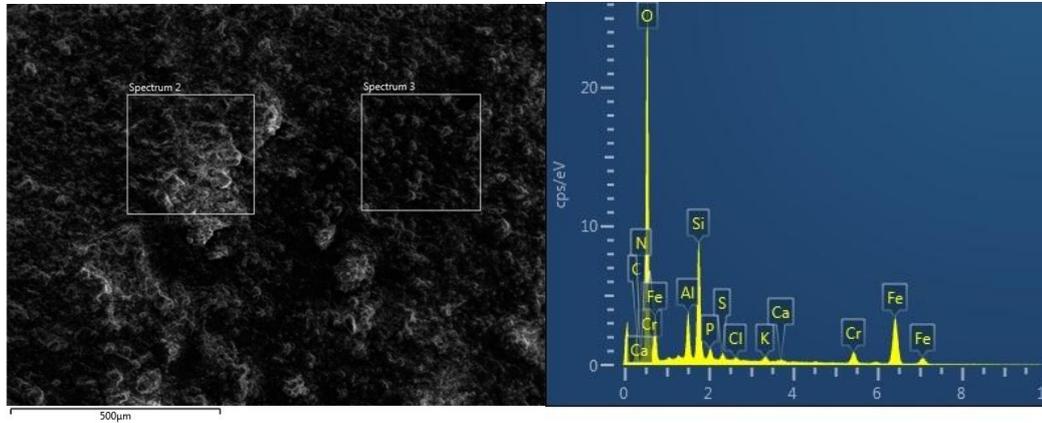


Figure 3. SEM and EDX spectra (Spectrum 2) for corrosion product on the outer surface of Type 201 steel tank exposed in Hai Phong.

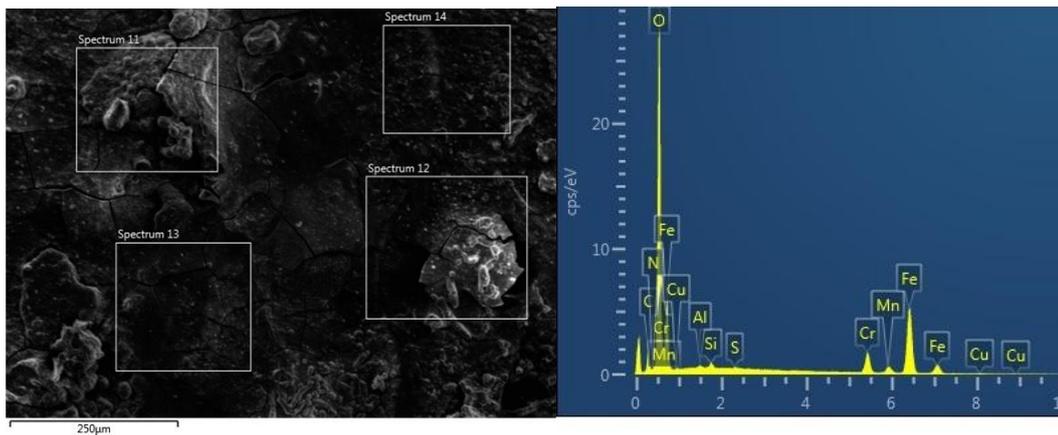


Figure 4. SEM and EDX spectra (Spectrum 12) for corrosion product on the inner surface of Type 201 steel tank exposed in Hai Phong.

Table 5. Chemical composition of corrosion products (wt.%) on the outer and inner tank surfaces determined by EDX method.

Content (%) Tank surface	O	Al	Si	Cr	Fe	P	Cu	S	C	Cl	N
Outer	45.79	2.91	7.26	3.18	22.42	0.84	-	0.50	12.48	0.24	3.63
Inner	42.70	0.18	0.39	6.60	39.21	-	0.66	0.10	6.09	0	2.13

Other results analyzed for corrosion products by EPMA method are presented in Fig. 5 and Tab. 6, where data were recalculated to nominal values (to total 100 wt.%) without oxygen inclusive. The analytical results were extracted from the respective WDS spectra for the detected elements in relevant diffracting canal.

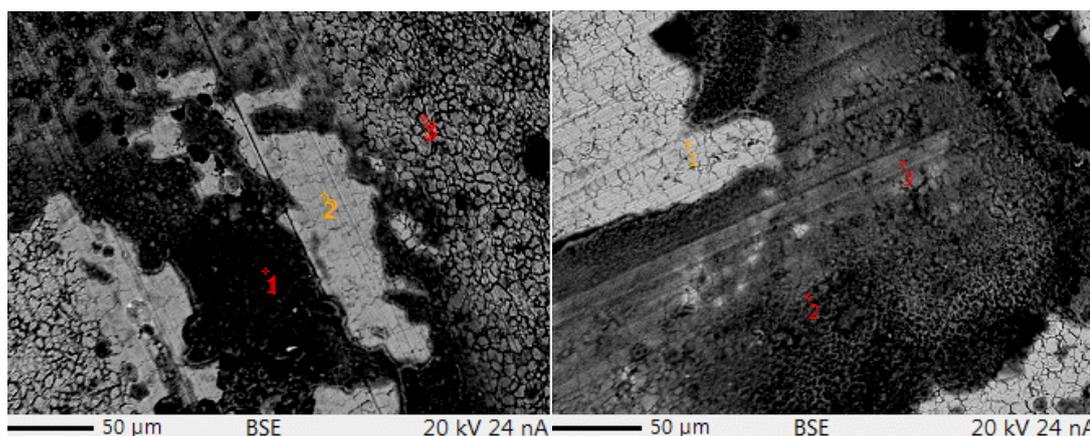


Figure 5. SEM image of analyzed areas for outer (left) and inner (right) steel surfaces.

Similar to the results of EDX method, chlorine content was not detected for corrosion product taken from the inner tank surface, while a relatively small amount was revealed on the outer tank side (Tab. 6). It is necessary to emphasize that corrosion products were taken for analysis from the upper part and covered inside the tank; and chloride, if any occurred, could not easily be washed out by potable or rain water during application.

Table 6. Chemical composition of corrosion products on outer and inner tank surfaces determined by EPMA method.

Tank surface	Position on Fig. 5	Element composition (wt.%)								
		Al	Si	Cr	Fe	P	Ni	S	Mn	Cl
Outer	2	3.4	6.3	21.2	61.7	0.7	-	0.1	4.7	0.9
	3	0.7	0.6	20.3	64.1	0.1	-	-	13.6	0.6
Inner	2	0.3	0.3	72.3	23.4	-	2.7	-	3.1	-
	3	1.0	4.3	9.4	73.2	-	-	-	12.1	-

Summarizing the results of analysis for corrosion products on Type 201 steel received by EDX and EPMA methods, the role of chlorine compound in atmospheric corrosion process on outer tank surface can be suggested. Severe corrosion damage on the outer tank surfaces is also demonstrated in Fig. 1 – Fig. 2 and this rust appearance in marine conditions is usually attributed to airborne salinity [2]. Meanwhile, generally occurred corrosion damage on the inner tank surface at the coastal Hai Phong area is hardly interpreted based purely on chloride attack due to constantly high RH (> 75 %) [3] inside the tank and undetectable chlorine content in corrosion product. This phenomenon requires more detailed examination.

3.3. Electrochemical behavior of stainless steels in chloride solution

To understand corrosion behavior of stainless steel and its passive film in chloride solution, an electrochemical examination was conducted. The OCP of both Type 304 and 201 steel

samples with passivation film were recorded for an hour duration are presented in Figure 6, when their potentiodynamic polarization curves in 3.56 % NaCl solution are featured by Figure 6.

As clearly shown in Figure 6, the OCP potentials of Type 304 sample are more positively shifted than Type 201 steel, which showed more stable passive film in chloride solution. This output is commonly explained by higher chromium content in Type 304 alloy composition. Meanwhile, the lower protective ability of Type 201 passive film is attributed to decreased nickel content and increased manganese inclusion, which deteriorate the surface oxide film in the test medium. However, due to the repassive nature of the films, the OCP are quickly restored after falling. With copper alloying component, the repassivation ability of Type 201 sample is higher expressed than Type 304 steel, but is not sustained and came to a sharp fall after 2500 s of immersion in chloride solution. Indeed, the film's repassivation process is disturbed by the presence of chlorides which promotes the initiation of localized corrosion (e.g. pitting), thereby decreasing the durability of the self-protection provided to stainless steel [10]. Nevertheless, the passive films are still formed at this point and afterwards with more positive potentials comparing to E_{cor} of iron.

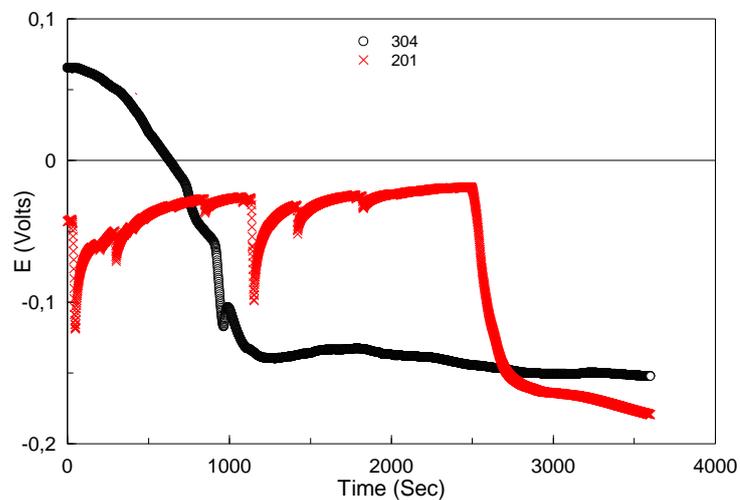


Figure 6. The OCP potentials of Type 304 and Type 201 steels in 3.56 % NaCl solution.

Based on Figure 7, the course of forward scan indicated the higher susceptibility to pitting corrosion of Type 201 grade comparing to Type 304 grade steel. Furthermore, corrosion rate is anticipated to develop more intensively for Type 201 when its passive film is damaged. This is also demonstrated by the course of backward scan to more negative potentials where the pits on Type 201 sample hardly repassivate (extremely slow decrease of current to reach passivation). Therefore, a distinctive behavior was revealed for two steel types due to clear differences in E_{pit} despite the insignificant shift in OCP.

All the above described results clearly show the strong influence of chloride on the corrosion process of Type 304 and 201 steels and explain chlorine presence in corrosion product on the outer side of the tanks. As discussed by Frankel G. [11], the three main mechanisms for passivity breakdown by chloride ions – passive film penetration, film breaking, and adsorption – can happen to bare stainless steel surface. However, in the case of metal with passive film, chloride ions initially located on the film/solution interface can either reach the metal/film interface through surface imperfections by penetration mechanism or can preferentially adsorb

on the film surface to reduce oxygen vacancies at the film/solution interface by adsorption mechanism. In the latter case, the oxygen vacancy reduction favors the increase of cation diffusion rate from the metal/film interface to the film/solution interface, which creates more metal vacancies at the metal/film interface to form a void and cause breakdown as pit initiation [12, 13]. That means, chloride's role is decisive in passive film breakdown whether these ions penetrate or not through film and its presence is not always detected in the corrosion product.

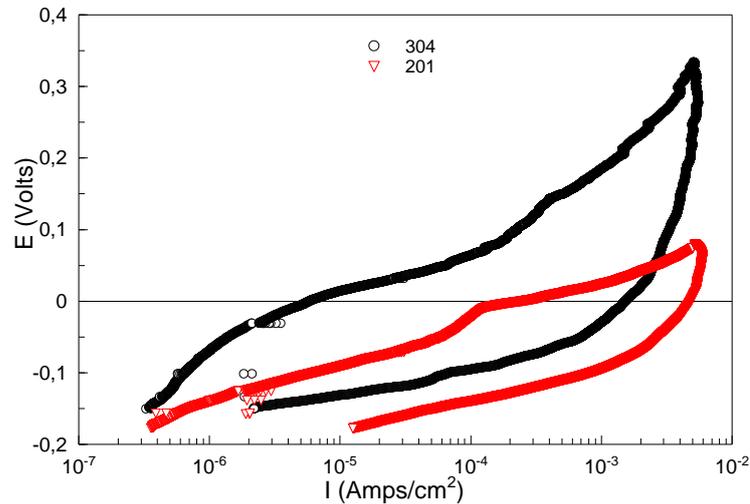


Figure 7. Potentiodynamic curves of Type 304 and Type 201steels in 3.56 % NaCl solution.

Occasionally corrosion is detected on the inner surface of tank, where chloride ions occur in low concentrations due to closed space and water service regime. As it was found, corrosion damage happened to the tanks in long term usage (more than 10 years) and with grey appearance, visually different in color compared to common rust on steel in natural conditions. It can be assumed that corrosion was initiated by excessive residual chlorine concentration during water supply in the past. According to Tuthill A.H. and coworkers [14], chlorine corrosion may happen to Type 304 steel when its residual concentration reaches approx. 2 mg/L. This concentration is unacceptable and hardly detected under current strict Water quality rules; however, it might not have always been the case for tanks in long term service. Nevertheless, this assumption requires more detailed investigation relating tank's service history and corrosion product analysis.

4. CONCLUSIONS

Field survey of Type 304/201 grade steel water storage tanks exposed in rural and coastal conditions shows strong influence of environmental parameters on corrosion. Severe damage was observed for the tanks in coastal conditions with high TOW and airborne salinity. Type 304 steel grade was more corrosion-resistant than Type 201 steel grade and the outer surface suffered more damage than the inner surface of the tanks. Chlorides are considered the main chemical factor in destroying stainless steel passivity under coastal conditions. As a result, Type 304 and especially Type 201 stainless steel grades are not recommended for use as water storage tanks in coastal conditions.

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