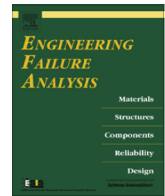




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## Corrosion in water supply pipe stainless steel 304 and a supply line of helium in stainless steel 316

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### ABSTRACT

A corrosion spreading throughout the 304 stainless steel tubing of a water system to supply various buildings was observed, and also leaks were detected in welding zones. The same place is also crossed by a gas distribution network, with a helium pipe 316 of stainless steel that required periodic repairs more or less every two years, due to the presence of leaks. The tests showed that both types of stainless steel have suffered localized corrosion induced by hypochlorite ion, in a mechanism of dry/wet, and that the welding procedure performed on the 304 stainless steel is unacceptable. Some immediate procedures were undertaken to keep systems running, but recommendations were given for a final resolution of the problems.

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## 1. Introduction

Stainless steels (SS) contain in their composition essentially iron, carbon and at least 11% of chromium, the element responsible for the corrosion resistance and that also improves the material performance to scaling, strength and wear. The high corrosion resistance of these alloys is attributed to the presence of a thin invisible film and passive [1] characterized by stability, durability, adhesion and self-repairs. Austenitic stainless steels are a special family of alloys, with exceptional corrosion resistance and outstanding mechanical properties, which make them suitable for being used as a construction material in aggressive environments, such as heat exchangers, drilling rigs for oil extraction, dairy industry, beverage industry, and wastewater treatment.

The alloy 304 SS is austenitic steel with a minimum of 18% chromium, 8% nickel and up to 0.08% carbon. It is non-magnetic steel, not susceptible of hardening by heat treatment, but alternatively can be cold deformed with the increasing tensile strength. The alloy 316 SS is also austenitic steel, with molybdenum up to 3% and higher nickel content (10–14%) of type 304 SS, which gives the possibility to be cold-hardened with a lower deformation rate. In the annealed state, exhibits excellent ductility and can be easily stretched and folded. The more deformed parts should be annealed to remove strains.

Despite the extraordinary corrosion resistance in various media, these austenitic stainless steels in chloride environments [2] may undergo pitting corrosion. The aggressiveness and ability of  $\text{Cl}^-$  ions to initiate this type of corrosion are well known [3–5]. There are several theories trying to explain the pitting initiation, such as local acidification [6,7], depassivation–repassivation behavior [8,9], point defects models [10,11], and anion penetration/migration [12,13], but for all them it is necessary to assume the adsorption of chloride anion on the metal surface.

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What essentially distinguishes the type 316 SS from the type 304 SS is the addition of molybdenum up to about 3%. The molybdenum increases the corrosion resistance of this alloy in various environments (brines, bleaching, biofluids, etc.), and, in particular, reduces or inhibits the pitting corrosion induced by the chlorides. The pitting resistant equivalent (PRE) is commonly used as an indicator of stainless steels resistance to pitting. PRE is calculated from the following expression, where one can see the importance of molybdenum, given the usual content of nitrogen in the stainless steels 300 series ( $\leq 0.10\%$ ):

$$\text{PRE} = \%Cr + 3.3 \times \%Mo + 16 \times \%N \quad (1)$$

The rate of pitting corrosion can be quite serious once initiated; there is a strong tendency to continue growing, even though most adjacent steel remains intact. Temperature is also a key factor in the early pitting [14,15] and, based on the potentiostatic determinations at +300 mV vs. SCE at pH = 6.0 and 0.1%  $\text{Cl}^-$ , the critical pitting temperature (CPT) for the 304 and 316 SS is around 30 °C and 55 °C, respectively.

The hypochlorite ion ( $\text{ClO}^-$ ) is aggressive towards stainless steels, acting similarly to moist chlorine gas, and the chloride ion ( $\text{Cl}^-$ ) is the initiator of pitting corrosion. The pitting or crevice corrosion can occur in various types of stainless steels in 15% hypochlorite solutions at room temperature. There is also an additional risk of stress corrosion at elevated temperatures. Some cases of localized corrosion on 304 SS have been reported in domestic environments associated with leachate. If this occurs, an immediate dilution by washing prevents corrosion; otherwise, a pitting corrosion can occur overnight.

Under the combined effect of stress and corrosion, stainless steels will be subject to a more rapid and severe corrosion, and also stress corrosion cracking (SCC). Consequently, the austenitic stainless steels are limited in their application to aqueous media to about 50 °C with small quantities of chlorides (parts per million). It is risky to establish the use limits, since conditions wet/dry concentrate chlorides may increase the probability of SCC.

This paper analyzes the problems of corrosion observed in metallic materials in a sector that supplies water to several buildings, and where also passes the piping system of gas distribution to one building.

## 2. Experimental details

The chemical composition of the stainless steels is presented in Table 1.

The scanning electron microscopy (SEM) images and the analysis by energy dispersive spectroscopy X-ray (EDS) were made with a FEI Quanta 400FEG equipment, fitted with a probe for micro analysis EDAX Genesis X4 M. The pressure inside the chamber was about  $6 \times 10^{-2}$  Pa. The distance between the objective lens and the sample, ranged between 6 mm and 15 mm. The SEM filament was operated at variable current and at 15 kV voltage using magnifications 100 $\times$ , 250 $\times$  and 1000 $\times$ . The SEM/EDS analysis has been performed in CEMUP (Materials Centre of the Oporto University).

The electrochemical experiments were performed in a one-compartment cell with three electrodes connected to Autolab model PGSTAT20 potentiostat/galvanostat with pilot integration controlled by GPES 4.4 software. Platinum has been used as an auxiliary electrode and Ag/AgCl (1 M in KCl) as a reference electrode. The section annulus samples of 316 SS were mounted in an Epofix resin, mechanically polished with abrasive papers SiC of decreasing sizes (250, 500, 1000, 2500 mesh) and finally with paste of diamond of 6  $\mu\text{m}$ . Before the trials, the samples were cleaned in acetone and ethanol baths provided with ultra-sounds; the open circuit potential stabilized in a period of 15 min, and finally it was polarized by applying a scan rate of 10 mV  $\text{s}^{-1}$ .

Radiographs were performed *in situ* using the equipment XRS-3 with a pulsed X-ray source and the Vidisco imaging system.

The total chlorine (aqueous molecular chlorine, hypochlorous acid and hypochlorite ion) of the water in the tank resulting from the hypochlorite hydrolysis was determinate by DPD method, and shows a value of 1.08 mg as  $\text{Cl}_2/\text{L}$ . The water condensate on a tube near the place of the tank where the recirculated water enters presents values of the order of 0.08–0.10 mg as  $\text{Cl}_2/\text{L}$ .

The temperature and humidity in the room fluctuates between 15 °C and 30 °C and 45% and 75%, respectively, depending on the season.

The methodology used to determine the eventual leak in piping was the following: (1) a general cut in gas supplies to all servers; (2) let pass about 15 min to stabilize the pressure across the network; and (3) finally, the pressure values were registered at various points. A variation of 0.25 bars is very noticeable and was taken as an indication of a leak.

## 3. Characterization of the water supply system

Fig. 1 shows the system of water supply to a set of several buildings. The public water supplies a reservoir with a capacity of 300  $\text{m}^3$ , which finality is to regulate the average daily consumption of 80  $\text{m}^3$ . The water of the tank comprising four

**Table 1**  
Chemical composition of stainless steels.

Steel type	C	P	Mn	Si	S	Ni	Cr	Mo
304	0.08	0.04	1.65	0.02	0.03	9.45	18.25	–
316	0.08	0.04	1.95	0.50	0.03	10.30	17.65	1.68

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