

# INFLUENCE OF ACIDITY AND NaOCl CONCENTRATION ON THE CORROSION RESISTANCE OF STAINLESS STEELS IN CHLORINATED WATER

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## ***ABSTRACT***

Cement, galvanized steel, coated carbon steel and cast iron are commonly used for large pipes in potable distribution networks. Even if these materials have been in operation for decades, they are used to suffer from external corrosion by soils or internal corrosion by water. To solve these problems, coatings, electrochemical protection or/and monitoring of the water chemistry have often to be applied. Due to their superior corrosion resistance, stainless steels may be used without any of these protection systems, which lead to easier installation, safer operation and better water quality. In order to study the influence of chlorination biocide treatment on the corrosion resistance of austenitic and austeno - ferritic (duplex) stainless steels, electrochemical investigations have been performed in chlorinated water. The influence of pH and NaOCl concentrations are particularly investigated with a close control of the water chemistry. The results demonstrate that duplex stainless steels may be good candidate to manufacture drinking water pipes or potable storage tanks.

**Keywords:** corrosion resistance, chlorinated water, duplex and austenitic stainless steels, potable water

## **1. INTRODUCTION**

### **1.1. Stainless steels for water pipes**

Regarding the others metallic materials used for decades in water applications, like iron or cast iron, selecting stainless steels may offer several advantages.

First of all, because of their extremely low corrosion rates in a wide range of waters, stainless steels seem more secure regarding to human health. Indeed, leaching rate of stainless steels are in agreement with different drinking standards as it was showed for 316L / EN 1.4404 grade in a solution simulating drinking water [1]. Furthermore, the NSF / ANSI Standard has verified that stainless steels are highly resistant to leaching of contaminates into potable water. Hence, duplex stainless steel grades, as UNS S32205 / EN 1.4462 or UNS S32304 / EN 1.4362, have been recently incorporated into NSF/ANSI Standard 61 in addition to types 304, 304L, 316 and 316L [2].

So stainless steels have been used for more than ten years now for manufacturing, storage and transport of beer, juice soda and wine. Due to this good resistance corrosion, monitoring of water chemistry to mitigate corrosion attack is not necessary.

Another point to be considered in the material selection is the mechanical characteristics. Indeed, using high strength grades allows the reduction of the wall thickness of pipes, especially in the case of high design water pressure (10 bars and more). Among the stainless steels family, the duplex materials exhibit much higher mechanical properties than

austenitic ones as shown in Table 1. So, compared to other materials used for pipes in potable distribution network, duplex grade allows reducing the wall thickness of pipes and consequently to reduce investment costs.

Moreover, as stainless steels pipes are not coated (internal and external) [3], modifications of water piping systems may be easily and quickly achieved.

Grade (EN/UNS)	0.2 YS		UTS		E
	MPa	KSI	MPa	KSI	%
<b>Iron base</b>					
Cast iron	180	26	320	46	<5
Ductile cast iron	270	39	420	61	12
A516 Gr 60	220	32	410	60	24
A516 Gr 70	260	38	480	70	20
<b>Austenitic stainless steels</b>					
304L (1.4307)	200	29	500	72	45
316L (1.4404)	225	33	520	75	45
316LN (1.4429)	250	36	590	86	40
<b>Duplex stainless steels</b>					
UR35N (1.4362 / S32304)	400	58	600	87	25
UR45N, UR45NMo (1.4462 / S31803 / S32205)	480	69	680	98	25

**Table 1: Minimum values for tensile properties (YS: Yield Stress, UTS: Ultimate Tensile Strength and E: Elongation) of iron base and stainless steels used in potable distribution network**

The two main alloying elements of stainless steels are chromium and nickel. From a general point of view, chromium improves the pitting corrosion resistance whereas nickel additions are made for controlling microstructure. Further alloying elements may be added like molybdenum for decreasing pit propagation or nitrogen for improving mechanical properties and resistance to pit initiation. As a result, depending on stainless steels composition and chloride content of water, these materials may be resistant to aqueous corrosion in a wide range of pH at ambient temperature. Stainless steels ability for resisting to pitting corrosion may be evaluated by calculation of the Pitting Resistance Equivalent Number (PREN). Equation (1) gives the most employed formula for PREN calculation.

$$PREN = Cr_{(\%)} + 3,3Mo_{(\%)} + 16 N_{(\%)} \quad (1)$$

One must stress that such an equation does not take into account the cleanliness of the materials (non metallic inclusions such as MnS and CaS are particularly detrimental), which is a prerequisite for stainless steels to withstand pit initiation. All stainless steels tested here have a very low sulfur content (<0,003%) accounting for the absence of sulphur containing inclusions.

## **1.2. Chlorination biocide treatment**

Chlorine remains the most common biocide treatment and disinfectant used in water treatment in most countries [4]. The use of this product is essential for ensuring that water is bacteriologically safe to drink unless other reliable means of disinfection (e.g. boiling) may be used. Hypochlorous acid (HClO) and hypochlorite ion (ClO<sup>-</sup>) are the most effective forms of chlorine for achieving disinfection. From a corrosion resistance point of view, the main characteristics to consider for sodium hypochlorite solutions are, on one hand, the oxidation

power of hypochlorite ion itself and on the other hand the aggressiveness of certain decomposition by-products like chlorides (see reactions (2) and (3)).



The aim of this study was to evaluate the influence of this biocide treatment on the corrosion resistance of various stainless steels.

## **2. EXPERIMENTAL DETAILS**

### **2.1. Electrolytes**

Chloride ( $\text{Cl}^-$ ) containing electrolytes with various free chlorine concentrations (sodium hypochlorite,  $\text{NaOCl}$ ), at different pH values, were prepared from deionised water ( $R = 18,2\text{M}\Omega$ ) and used for electrochemical tests.

The pH value is adjusted by adding  $\text{HCl}$  2N.

Chloride concentration was adjusted at 250 ppm by  $\text{NaCl}$  addition and was measured with an ion chromatograph (DIONEX, DX100). This concentration was chosen because 250 ppm of chloride is the maximum concentration of standards drinking water [5-7].

Free chlorine concentration is defined as the sum of hypochlorous acid ( $\text{HClO}$ ) and hypochlorite ion ( $\text{ClO}^-$ ) concentrations. The concentrations were measured with a colorimeter using the diethyl-p-phenylene diamine (DPD) method (HI 93710, HANNA Instruments). Two free chlorine concentrations were particularly investigated: 0,2 ppm that corresponds to the residual concentration [8] and 50 ppm that is typically used for several hours as a standard method for water pipes disinfection treatments.

### **2.2. Materials**

Stainless steels used in this work are hot rolled materials produced by Industeel, Arcelor Group. The chemical analysis and PREN values of these alloys calculated by equation (1) are reported in Table 2 (heat composition). Sample dimensions were  $30 \times 30 \times 5$  mm. All samples were mechanically polished with silicon carbide ( $\text{SiC}$ ) papers up to 600 grit and followed by an ethanol cleaning.

Grade (EN/UNS)		C	Cr	Ni	Mo	N	Mn	Si	S (ppm)	PREN
Austenitic	304L (1.4307)	0.020	18.41	10.16	0.16	0.074	1.20	0.366	13	20.1
	316L (1.4404)	0.018	16.81	11.28	2.08	0.059	1.69	0.684	10	24.6
	316LN (1.4429)	0.020	17.17	11.89	2.53	0.161	1.58	0.486	8	28.1
Duplex	UR35N (1.4362/S32304)	0.024	22.68	4.10	0.25	0.094	1.20	0.392	6	25.0
	UR45N (1.4462/S31803)	0.025	22.48	5.42	2.84	0.152	1.95	0.281	6	34.3
	UR45NMo (1.4462/S32205)	0.015	22.91	5.49	3.02	0.173	1.89	0.349	8	35.6

**Table 2: Elemental composition of the alloy (%<sub>wt</sub>) and Pitting Resistance Equivalent Number (PREN) calculated by equation (1)**

Electrochemical tests were begun 24 hours after sample preparation in order to have a passive film naturally formed as a result of electrochemical reactions with the atmosphere.

### **2.3. Electrochemical tests**

Electrochemical tests were carried out at room temperature, in a three-electrode electrochemical cell which has a capacity of 600ml, connected to an EG&G Princeton 273A potentiostat and driven by a computer. A platinum sheet and a saturated Hg/ Hg<sub>2</sub>SO<sub>4</sub> (E = - 0,374 V/SCE) reference electrode were respectively used as counter and reference electrodes. The stainless steel samples were fully immersed and the electrical contact is made by mean of a wire of high-alloyed stainless steels (super duplex grade UR52N<sup>+</sup>/EN 1.4507/UNS S32520), which is electrically welded on the sample; a PTFE retractable glove protected this wire.

The following sequence was used:

1. measurement of rest potential ( $E_r$ ) during 6 h,
2. recording of potentiodynamic curve from -50 mV/ $E_r$  in the anodic direction until the current density reach 500  $\mu\text{A}/\text{cm}^2$ , with a scan rate of 900 mV/hour and using iR compensation,
3. measurement of pitting potential ( $E_{\text{pit}}$ ) at a current density of 100  $\mu\text{A}/\text{cm}^2$  or by tangential method.

After the completion of the electrochemical tests, stainless steel samples were observed by means of an optical microscope.

The first step of the electrochemical test represents the in service behaviour of the tested materials. On the contrary, the second step (plot of a potentiodynamic curve) is not representative of the in service behaviour. Indeed, the increase of the sample potential allows increasing the media aggressiveness until to favour a localised breakdown in the passive layer. The pitting potential value, for which pits are in fact observed, represents the ability of stainless to resist to pitting corrosion. The higher the pitting potential is, the lower the risk of pitting corrosion is.

## **3. EXPERIMENTAL RESULTS AND DISCUSSION**

### **3.1. Effects of different parameters on localised corrosion resistance**

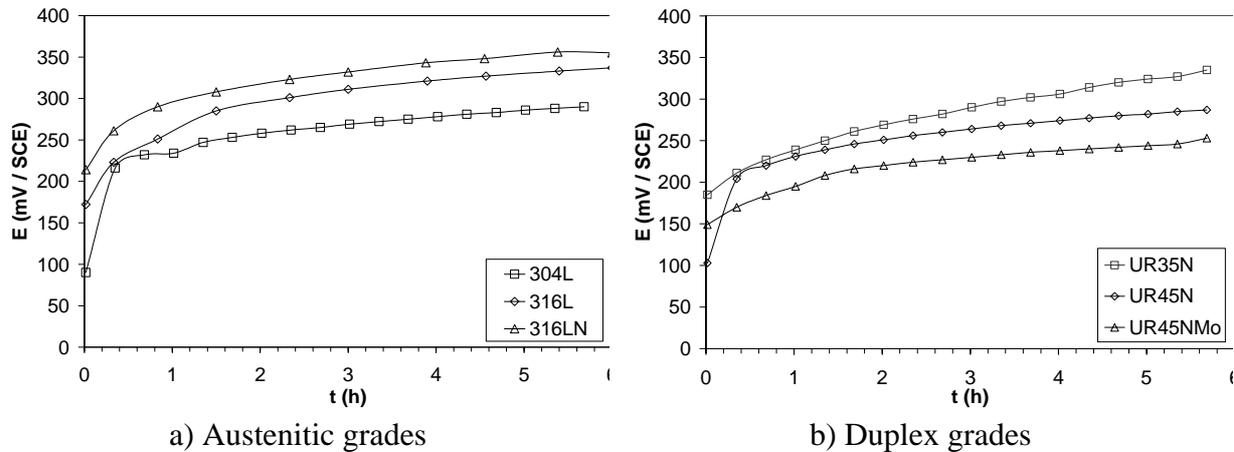
#### **3.1.1. Influence of time on $E_r$ value**

During interruption on water pipeline, the rule of "300" is usually applied. This value corresponds to the multiplication of time (in minutes) of treatment by free chlorine concentration (in ppm). For disinfection treatment, free chlorine concentration used is 50 ppm. So, in order to apply the rule, the time of treatment have to be 6 hours.

In order to study the influence of time on rest potential, measurements were performed during 6 hours in a solution containing 250 ppm of chloride, and 50 ppm of free chlorine, at pH=5,5. Figure 1 show that  $E_r$  is not stabilise after 1h30, time corresponding to the duration in the first measurements [9,10]. The reaction of free chlorine on passive film is not finished and by increasing time until 6 hours, rest potentials values increase (Table 3).

Except for 304L, all grades present a similar difference between  $E_r$  measured after 6 and 1,5h (about 55 mV) and final values after 6h are very close (about 325 mV). For 304L,  $E_r$  measured after 6 hours is only 290 mV and the increase from 1,5 to 6h is weaker too (about 30 mV).

The time of stabilisation is fixed in order to apply the rule. Furthermore, by increasing time, the stability of the passive film is also increased. So, the polarisation curve was begun after a measurement of rest potential during 6 hours.



**Figure 1: Rest potentials follow-up versus time for austenitic and duplex grades, in solution containing 250 ppm of chloride and 50 ppm of free chlorine, at pH=5,5**

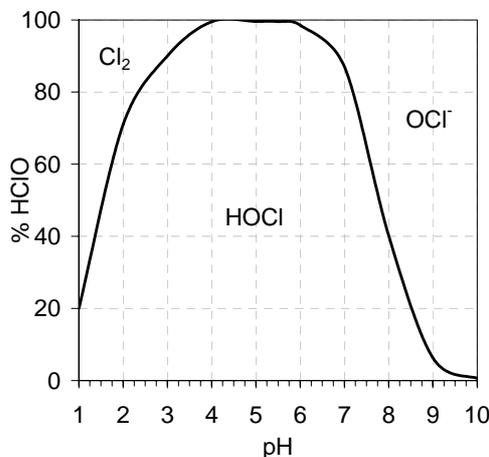
$E_r$ (mV/SCE)	304L	316L	316LN	UR35N	UR45N	UR45N Mo	Pt
<b>1h30</b>	261	280	274	260	274	-	967
<b>6h</b>	290	337	331	321	317	326	952

**Table 3: Rest potentials measured in solution containing 250 ppm of chloride and 50 ppm of free chlorine, at pH=5,5, after 1h30 and 6h**

**3.1.2. Influence of pH**

Bleach (NaOCl) solution is used to disinfect water. In water, free chlorine is present as hypochlorous acid (HClO), hypochlorite ions (ClO<sup>-</sup>) and chloride ions (Cl<sup>-</sup>) and the concentration of these species depend on pH and temperature (Figure 2). At room temperature, the percentage of free chlorine present on hypochlorous acid form (HClO) depending on the pH value is given by the equation (4). Some typical values are also presented in Table 4.

$$HClO (\%) = 100 \times (1 + K_i \cdot 10^{pH})^{-1} \text{ with } K_i = 2,898 \times 10^{-8} \text{ mol/L at } 25^\circ C \quad (4)$$

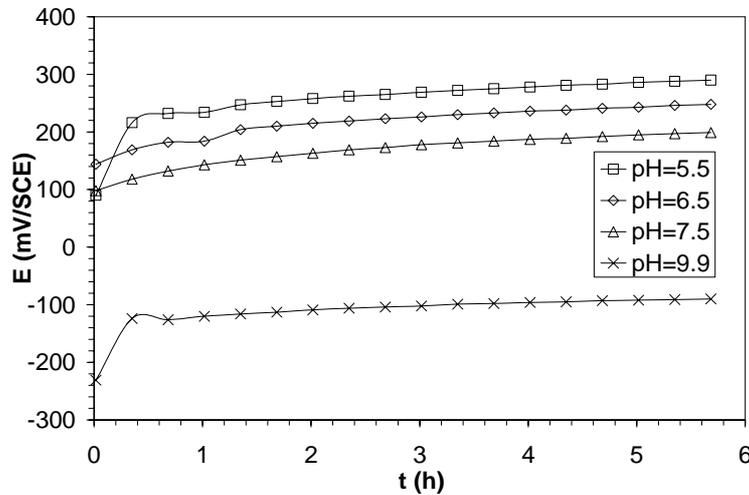


pH	5.5	6.5	7.5	9.9
% HClO	99,1	91,6	52,2	0,4
% ClO <sup>-</sup>	0,9	8,4	47,8	99,6

**Table 4: Composition of bleach solution at different pH values and 25°C**

**Figure 2: Composition of bleach solution versus pH value at 25°C**

For pH value referenced in Table 4, rest potentials have been measured during 6 hours (Figure 3) in solution containing 250 ppm of chloride and 50 ppm of free chlorine. The natural pH value of this solution is 9,9. The curves have an identical form: potential increases during the first hours and then reaches a stable value depending on the pH value.



**Figure 3: Rest potentials follow-up versus time at different pH values, in solution containing 250 ppm of chloride and 50 ppm of free chlorine for 304L**

The pH value has a strong influence on the rest potential. Indeed, the composition depends on the pH value and HClO is 25 times more oxidant than ClO<sup>-</sup> [8]. By increasing pH value, HClO concentration and so oxidising power of the solution, decrease then, rest potential decreases too (Table 4). The increase of rest potential from 9,9 to 5,5 is the most important for the lowest alloyed grade (for 304L,  $\Delta E=380$  mV/SCE and for UR45NMo,  $\Delta E=247$  mV/SCE).

For 304L, pitting potential ( $E_{pit}$ ) increases as pH decreases because of the reinforcement of the passive layer due to the oxidising power of HClO (Table 5). For UR45NMo, no pitting was observed on the surface whatever the pH value and so no pitting potential can be determined; the measured potential is the water oxidation potential.

<b>304L</b>	<b>pH</b>	<b>5.5</b>	<b>6.5</b>	<b>7.5</b>	<b>9.9</b>
	<b><math>E_r</math> (mV/SCE)</b>	290	248	199	-90
	<b><math>E_{pit}</math> (mV/SCE)</b>	1212	1174	1164	1104
	<b><math>\Delta E=E_{pit}-E_r</math> (mV/SCE)</b>	922	926	965	1194
<b>UR45NMo</b>	<b>pH</b>	<b>5.5</b>	<b>6.5</b>	<b>7.5</b>	<b>9.9</b>
	<b><math>E_r</math> (mV/SCE)</b>	284	253	218	37
	<b><math>E_{pit}</math> (mV/SCE)</b>	1340*	1340*	1321*	1274*
	<b><math>\Delta E=E_{pit}-E_r</math> (mV/SCE)</b>	1056	1087	1103	1237

**Table 5: Rest and pitting potentials values for 304L and UR45NMo, at different pH values, in solution containing 250 ppm of chloride and 50 ppm of free chlorine ( $E_{pit}$  is determined by tangential method, \*: no pitting)**

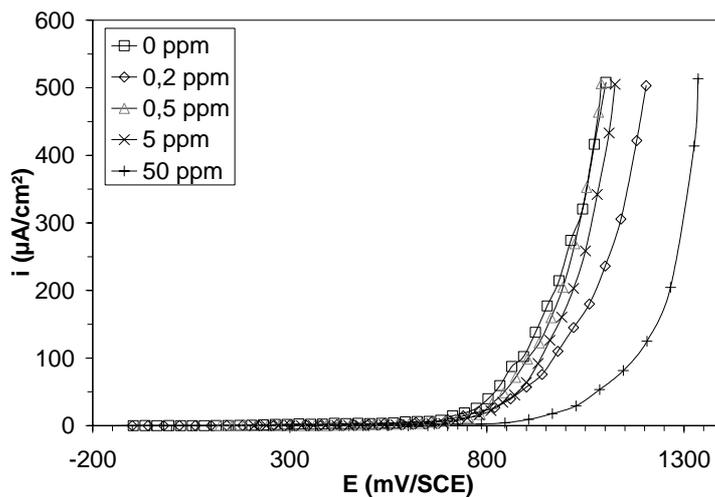
The difference between rest potential and pitting potential ( $\Delta E$ ) indicates the width of the passive domain. The same behaviour is observed for the grades 304L and UR45NMo: the width of the passive domain increases by increasing pH value. Nevertheless we can note that this effect is less pronounced for the duplex grade than for the austenitic grade and higher values of  $\Delta E$  for the duplex grade whatever the pH.

To determine the pitting corrosion resistance of the different grades, tests will be performed at pH 5,5 because:

- the concentration of HClO is the maximum at this pH value and this specie has the highest biocide power,
- this pH value corresponds to the natural pH of water,
- the width of passive domain is the lowest and so, this condition is potentially the most aggressive.

### 3.1.3. Influence of free chlorine concentration

The influence of free chlorine concentration (from 0 to 50 ppm) was carried out on the less pitting corrosion resistant stainless steel: 304L. The pH was fixed at 5,5, so the concentration of free chlorine corresponds to the concentration of HClO (Table 4).



**Figure 4: Potentiodynamic curves of 304L in solution containing 250 ppm of chloride and various concentrations of free chlorine, at pH=5,5**

Rest potentials increase with the free chlorine concentration because oxidant power of the solution increases too (Figure 4, Table 6). For pitting potentials, two increases are observed: the first one from 0 to 0,2 ppm (50 mV/SCE) and the second one, which is the most important, from 5 to 50 ppm (250mV/SCE). That seems to indicate that even low free chlorine concentrations allow a reinforcement of the passive film. Then this reinforcement effect is maximal at the highest concentration.

From 0 to 5 ppm, as  $E_{pit}$  is constant and  $E_r$  increases, the width of the passive domain decreases. At 50 ppm, the safety margin, in term of passive domain width, is about the same than those observed at 0 and 0,2 ppm.

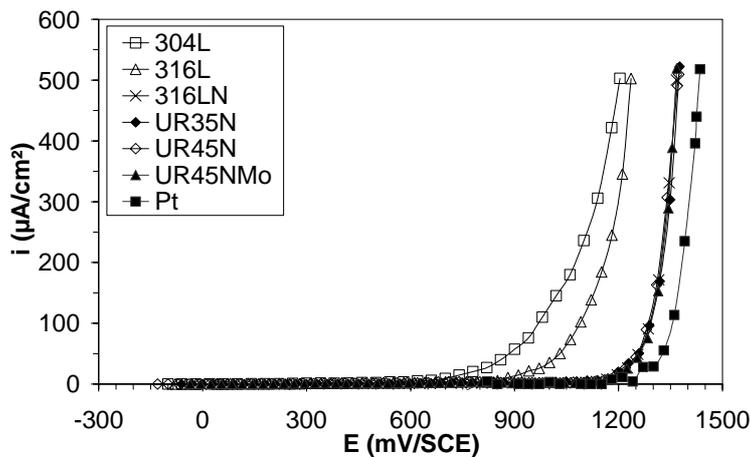
[Free chlorine] (ppm)	0	0.2	0.5	5	50
$E_r$ (mV/SCE)	-78	11	141	217	290

$E_{pit}$ (mV/SCE)	894	941	934	944	1206
$\Delta E = E_{pit} - E_r$ (mV/SCE)	972	930	793	727	916

**Table 6: Rest and pitting potentials values at different free chlorine concentrations for 304L ( $E_{cor}$  during 6 h, 250 ppm of chloride, pH=5,5,  $E_{pit}$  is determined at  $100 \mu A/cm^2$ )**

### 3.2. Residual concentration

Pitting potentials measured for stainless steels in 0,2 ppm chlorinated water show differences (Figure 5, Table 7). Only two grades show pitting: 304L and 316L. For other grades, the measured potentials correspond to the water oxidation and are in accordance with potential measured on platinum.



**Figure 5: Potentiodynamic curves of different stainless steels after 6 hours at  $E_r$ , in solution containing 250 ppm of chloride and 0,2 ppm of free chlorine (pH=5,5)**

Grades	304L	316L	316LN	UR35N	UR45N	UR45N Mo	Pt
$E_r$ (mV/SCE)	11	-61	17	-42	-80	-21	438
$E_{pit}$ (mV/SCE)	980	1091	1294*	1294*	1294*	1304*	1354*
$\Delta E = E_{pit} - E_r$ (mV/SCE)	969	1152	1277	1336	1374	1325	916

**Table 7: Rest and pitting potentials values for different grades in solution containing 250 ppm of chloride and 0,2 ppm of free chlorine, at pH=5,5,  $E_{pit}$  is determined at  $100 \mu A/cm^2$ , \*: no pitting**

For austenitic, pitting potential of Mo containing grade (316L) is higher than those of the Mo free grade (304L). By comparison of 316L and 316LN, nitrogen addition has a positive effect; it might stabilize the passive film. In these experimental conditions, austenitic-ferritic (duplex) grades UR35N, UR45N and UR45NMo are found to be as resistant as 316LN, no pitting is observed. For UR35N which does not contain Mo addition, its very high Cr level (about 23%) is doubtless responsible for this good pitting corrosion resistance. Considering  $\Delta E$ , one can observe an increase of the safety margin with PREN value.

### 3.3. Disinfection treatment

In 50 ppm chlorinated water, rest potential values of all stainless steels are roughly the same and higher than those measured at 0,2 ppm chlorinated water (Table 7 and Table 8).

For all stainless steels, pitting potentials are higher than those measured in less chlorinated water (Figure 5, Figure 6). Indeed, the solution is more oxidant at 50 ppm than at 0,2 ppm and allows a better reinforcement of the passive film. Only 304L shows pitting corrosion ; the measured potential for other grades corresponds to the water oxidation.

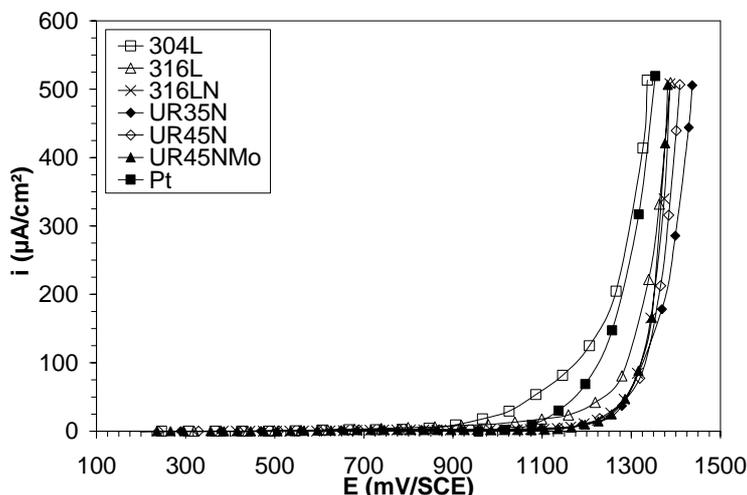


Figure 6: Potentiodynamic curves of different stainless steels after 6 hours at  $E_r$ , in solution containing 250 ppm of chloride, 50 ppm of free chlorine (pH=5,5)

Grades	304L	316L	316LN	UR35N	UR45N	UR45N Mo	Pt
$E_r$ (mV/SCE)	290	337	331	321	317	326	952
$E_{pit}$ (mV/SCE)	1206	1300*	1325*	1330*	1330*	1325*	1349*
$\Delta E = E_{pit} - E_r$ (mV/SCE)	916	963	994	1009	1013	999	397

Table 8: Rest and pitting potentials values for different grades in solution containing 250 ppm of chloride and 50 ppm of free chlorine, at pH=5,5,  $E_{pit}$  is determined at 100  $\mu A/cm^2$ , \*: no pitting

As rest potentials are equivalent and no pits have been observed, no difference is observed on the width of passive domain for 316L, 316LN and duplex grades.

#### 4. CONCLUSIONS

When free chlorine is added to water, rest potential of stainless steels increases due to the oxidation power of hypochlorite species. Furthermore, these species allow a reinforcement of the passive film and so, an increase of pitting potentials, which disappear for few stainless steels. So, the pitting potential value depends on chemical composition and particularly, on chromium, molybdenum and nitrogen contents. PREN is also a good indicator of the pitting corrosion resistance in chlorinated water.

Moreover, the use of stainless steels in drinking water network may allow to make chlorination treatment with low pH value (5,5) which may be an economic advantage. Indeed, as far as the free chlorine is concerned, hypochlorous acid HClO is a more powerful bactericide than the hypochlorite ion  $ClO^-$  [11] and its maximum concentration is obtained at

low pH. In addition, the beneficial effect of HClO on pitting corrosion resistance of stainless steel is the most important at this pH value too.

Consequently, these results demonstrate that stainless steels and more particularly duplex grades may be good candidate for water piping network and storage tanks, even when the water is chlorinated. This treatment ensures a very good safety margin for the use of stainless steels in potable distribution network. Indeed, no pitting is observed for duplex and as their mechanical properties are higher than those of austenitic stainless steels, so thinner pipes or tank wall can be used. Moreover, the release of chromium, nickel, molybdenum and iron is negligible in various water solutions and these stainless steel grades comply with European and American regulations on the quality of water intended for human consumption [2,12].

Further experiments will be carried out in order to investigate the crevice corrosion behaviour of these stainless steels in networks where the local conditions, including fittings or deposits might favour this type of corrosion.

## ***REFERENCES***

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- [1] Assessment of the stainless steels compatibility in food and health applications regarding to their passivation ability, ECSC Contract Eur n°19986, ISBN 92-894-1578-9, 2001.
- [2] [http://www.nsf.org/business/water\\_distribution/](http://www.nsf.org/business/water_distribution/)
- [3] ASTEE, “ De l’hygiène à l’environnement: cent ans d’actions”, TSM spécial issue, ISSN 0299-7258, 2005.
- [4] A. C. TWORT, D.D. RATNAYKA and M. J. BRANDT, Water Supply 5th Edition, p202, Chapter 6 : Chemistry, microbiology and biology of water, Editon Arnold, London, 2000.
- [5] Guidelines for Drinking Water Quality, World Health Organisation, 1993.
- [6] European Commission Directive on the quality of water intended for human consumption (98/83/EC), 1998.
- [7] United States Environmental Protection Agency (USEPA) requirements based on the National Primary Drinking Water Regulations as amended under the Safe Drinking Water Act of 1996.
- [8] F. MORAN, Traitement des eaux, p39, Chapter 3: Traitements physico-chimique des eaux, Editions Parisiennes, 2002.
- [9] J. PEULTIER, J-P. AUDOUARD, I. CHESSA and V. BAUDU, “Corrosion resistance of stainless steels in fresh and chlorinated water”, CEOCOR conference, Biarritz, October 2-5, 2001.
- [10] J-P. AUDOUARD, C. DERNONCOURT and J. PEULTIER, “Using duplex stainless steels to improve the reliability of water pipes”, Stainless steels world America conference, Houston, February 12-14, 2002.
- [11] C. TWORT, D.D. RATNAYKA and M. J. BRANDT, Water Supply 5th Edition, p430, Chapter 9 : Disinfection of water, Edition Arnold, London, 2000
- [12] P.-J. CUNAT, “Selection and use of stainless steels in water systems”, presented in “Stainless steel in drinking water applications” workshop, Brussels, November 19, 2003.