2-YEAR EXPOSURE OF STAINLESS STEELS AND OTHER COMMONLY USED MATERIALS IN A PILOT SIMULATING A NATURAL DRINKING WATER NETWORK: A BIOFILM DEVELOPMENT STUDY.

P. BOILLOT[1], **S. JACQUES**[1], **J. PEULTIER**[1],

A. ALLION[2]**, S. LASSIAZ**[2]**, L. PEGUET**[2],

M-C. BONNET[3]**.**

[1] ArcelorMittal, Global R&D Le Creusot, Industeel, 56 rue Clémenceau, BP19, F-71201 LE CREUSOT Cedex - pauline.boillot@arcelormittal.com

[2] ArcelorMittal Stainless Europe, F-62330 ISBERGUES

[3] EPI, ZI du Parc, F-42490 FRAISSES

Abstract

Numerous materials are commonly used in drinking water distribution networks. They are selected on the basis of their availability, technical requirements such as ease of installation and maintenance, as well as investment costs. It is well known that some materials are especially prone to fouling and biofilm development while others that are less sensitive to fouling, suffer from corrosion leading to a significant metallic cation release. Due to their surface physicochemical properties and their excellent corrosion resistance, stainless steels are promising candidates for drinking water transport providing the best hygiene conditions and service durability.

This study was conducted for more than two years in a natural drinking water loop simulating in-service conditions encountered in a distribution network (temperature, pressure, flow velocity and water chemistry).

The tested stainless steels include one ferritic (KARA 444/EN 1.4521), three austenitic (304L/EN 1.4307, 316L/EN 1.4404 and 316LN/EN 1.4429) and two duplex (UR 2304 /EN 1.4362 and UR 2205/EN 1.4462) grades. The behaviour of these alloys, in terms of scaling, biofouling and corrosion has been compared to the commonly used materials: copper, galvanized steel, polyethylene and cement.

Results indicate that even after such a long exposure, biofilms do not reach a steady state. In fact during the last months mineralization is highlighted for all materials. Moreover for stainless steels a stratification phenomenon is observed. These modifications could be the source of the uneven evolution of Open Circuit Potential (OCP). Evidence of neither free chlorine content variation nor localized corrosion on stainless steels is found. Corrosion attacks are only observed on galvanised carbon steel. While for stainless steels, negligible release rates, much below international health requirements are measured.

Key-Words: corrosion resistance - stainless steel - polyethylene - galvanized carbon steel - cement - copper - natural drinking water - biofilm - scaling - fouling - open circuit potential

1 Introduction

Numerous materials are commonly used in drinking water distribution networks. They are selected on the basis of their availability, maintenance and investment costs, technical requirements such as ease of installation, as well as impact on water quality.

As a consequence, the ability of material to promote biofilm development is a major criterion of selection. Indeed, this biological matrix is considered as a potential pathogenic microorganism reservoir to be released in a water network [1]. The main part of the microbial population is adherent to surfaces that allow them a higher resistance to disinfection treatment and access to nutrients previously adsorbed on surfaces or circulating in the media [2-4]. A biofilm is a complex, heterogeneous and progressive interface between material and media. Its formation consists first in an adsorption step of organic macromolecules, microorganisms and inorganic particles. An extracellular polymer production step (mainly polysaccharides and proteins) follows inducing its consolidation. Aggregation and erosion of a biofilm can then occur successively [5-6]. Temperature, material, hydrodynamic conditions, fluid composition and initial microflora can influence biofilm development [7-10]. The chemical composition of a material affects microorganism colonisation and morphology in particular. In addition, depending on fluid hydrodynamic conditions and/or the intrinsic ability of the microorganism, sloughing can be responsible for water network contamination [11].

By locally modifying the environment in terms of pH, redox potential or by secreting corrosive species, biofilms can induce changes on a material's surface, sometimes causing degradation. Open Circuit Potential (OCP) measurements are generally used to give information about effect of microorganisms on a metal in a natural media. A systematic OCP increase on stainless steel in the presence of a biofilm is experienced in seawater [12;13] as well as in natural fresh water [14-16]. This phenomenon, called ennoblement, is likely explained by an increase of the cathodic current density [17-19]. O_2 reduction reaction kinetics could be modified or a totally new oxidant could be produced within the biofilm. Manganese oxides generated by biodeposition and hydrogen peroxide are proposed as the new oxidative species. Manganese oxide deposits are produced by oxidizing mangano bacteria [14;16]. Hydrogen peroxide and acid production can be catalysed by enzymes like oxidases [20;21]. A synthesis of enzymatic mechanisms to explain stainless steel microbial corrosion in natural water is proposed by Landoulsi and al. [22].

This study was conducted on a natural drinking water loop simulating conditions encountered in distribution networks (temperature, pressure, flow velocity and water chemistry including disinfection treatment) for more than two years. The tested stainless steels include one ferritic (KARA 444/EN 1.4521), three austenitic (304L/EN 1.4307, 316L/EN 1.4404 and 316LN/EN 1.4429) and two duplex (UR 2304 /EN 1.4362 and UR 2205/EN 1.4462) grades. The behaviour of these alloys, in terms of scaling, biofouling and corrosion has been compared to the commonly used materials: copper, galvanized steel, polyethylene (PE) and cement. Influence of the materials on biofilm during this 2-year exposure has been published in the European Journal of Water Quality [23]. Materials have a great influence on the biofilm's development rate, fouling as well as the biofilm's structure and composition (i.e. biocontamination and mineralisation). The intermediate behaviour of stainless steels in comparison with other materials was highlighted, while no significant difference was observed between the several tested grades even between duplex and austenitics. This paper deals with the influence of biofilm and water properties on the behaviour of a stainless steel surface.

2 Experimental set-up

2.1 Materials

Chemical compositions of the stainless steels used in this work as well as their Pitting Resistance Equivalent Number (PREN) are reported in Table 1. Samples are machined from hot rolled products.

Table 1 Stainless steel chemical composition (‰$_w$) and PREN* values (* %Cr+3.3%Mo+16%N).

	Grade (EN)	C	Cr	Ni	Mo	N	Mn	Si	PREN
α	**KARA 444** (1.4521) (X2CrMoTi18-2)	0.015	17.62	0.12	2.04	0.017	0.36	0.42	26.6
γ	**304L** (1.4307) (X2CrNi18-9)	0.020	18.41	10.16	0.16	0.074	1.20	0.37	20.1
	316L (1.4404) ((X2CrNiMo17-12-2)	0.017	16.50	10.07	2.02	0.027	1.86	0.63	23.6
	316LN (1.4429) (X2CrNiMoN17-13-3)	0.018	17.44	13.45	2.60	0.167	1.19	0.55	28.7
α/γ	**UR 2304** (1.4362) (X2CrNiN23-4)	0.029	22.73	4.29	0.23	0.139	1.33	0.54	25.7
	UR 2205 (1.4462) (X2CrNiMoN22-5-3)	0.016	22.79	5.45	2.83	0.156	1.84	0.24	34.6

Sample size is 40 x 50 x 5-6mm. A bead of weld metal deposited by an automatic TIG welding process on the coupon simulates an obstacle to water flow (Table 2). Stainless steel coupons were sand-blasted and pickled in a HNO_3/HF bath at 55°C to eliminate heat tint oxides from the welding. They are compared to four other materials commonly used in drinking water network:
- copper as hemi-cylindrical coupons with a socket (NF EN 1057 - for drinking water application),
- polyethylene as hemi-cylindrical butt welded coupons (NF114 - from "blue strip" tube for drinking water application),
- galvanized steel as hemi-cylindrical coupons: hot galvanizing was applied to low alloyed steel in order to obtain an homogeneous deposit on the sample, particularly on the edges (NF EN A49-700 galvanizing produces between 80 and 100μm with a guaranty of a minimum 4g/dm² Zn and an upper layer Zn - eta phase),
- coupons of cement (from a new cast iron pipe coated with CPA type cement; excess alkalinity was eliminated before exposure using a typical lixiviation step).
Surface roughness properties of cement and galvanized steel are considered sufficient to induce fouling without using an additional obstacle.

Table 2 Coupons used for exposure in natural drinking water pilot.

Copper

Polyethylene

Galvanized Steel

Stainless steel

Cement
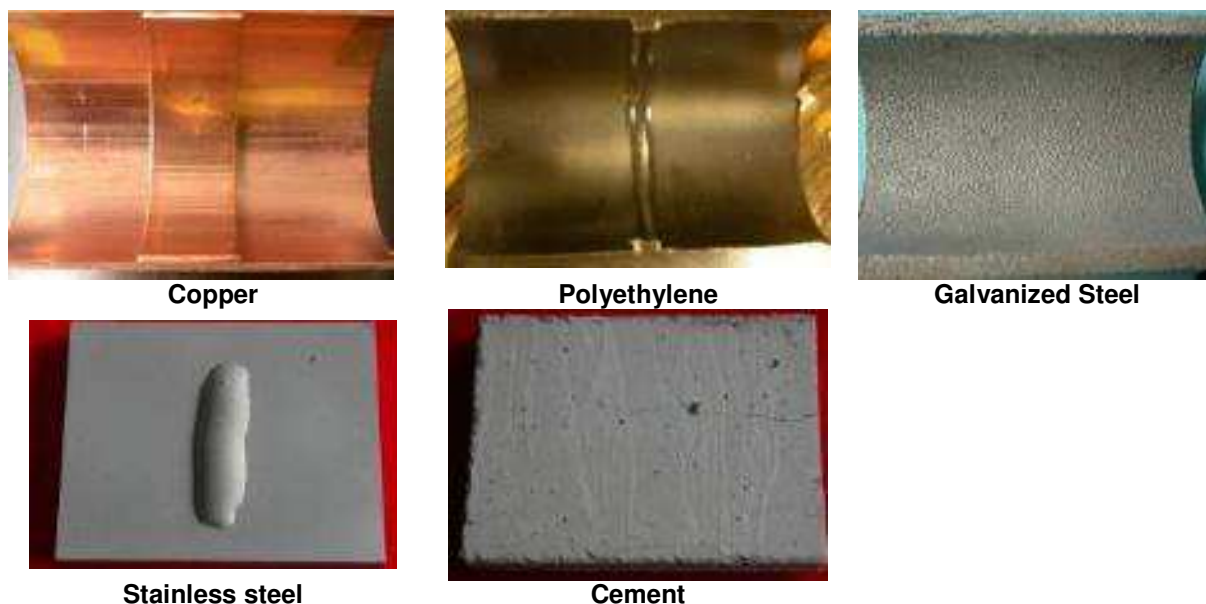
2.2 Pilot simulating drinking water network

Each material family is exposed in an individual loop allowing the:
- simultaneous exposure of several coupons with possible sequential removal,
- regulation of water residence time in the loop,
- adjustment of the free residual chlorine concentration in each loop,
- reproduction of specific operating conditions of drinking water networks like temperature, pressure and controlled flow rate (Table 3). These last two flow characteristics are fundamental parameters for matter transportation and sloughing. They also influence structure as well as organisation of a biofilm [24-26].

Table 3 Drinking water characteristics.

Water residence time in one loop	24 h
Temperature	10 °C
Pressure	0.7 bar
Velocity	0.25 m/s
Free chlorine residual	0.3 ppm +/- 0.1 ppm
Conductivity	700 µS/cm
$[Fe^{III}]$	0.2 ppm
$[Cl^-]$	100 ppm
$[SO_4^{2-}]$	35 ppm
pH	8.1
Total alkalinity	20 °f
$[Ca^{2+}]$	20 °f i.e. 200ppm $CaCO_3$
pH_s	7.4

The pilot is made of:
- storage tanks for chlorinated water,
- monitoring and data acquisition chain,
- four independent thermostated loops (Table 4) containing water boxes (Table 5) with, for each loop, sufficient coupons to allow several characterizations, one circulation pump and solenoid valves for blow-off and regulation.

Copper, galvanized steel, and stainless steels are exposed in independent loops while the cement and polyethylene are installed in the same one.

Table 4 Description of the 4 independant loops.

Loop 1	1 water box for copper
Loop 2	1 water box for galvanized steel
Loop 3	1 water box for cement and 1 for polyethylene
Loop 4	6 water boxes for stainless steels and 1 box for electrochemical measurements

Table 5 Water boxes for flat and hemi-cylindrical coupons.

Water box for flat coupons

Cement water box   *Water box ready for use*

Water box for hemi-cylindrical coupons

*Galvanized steel water box*   *Water box ready for use*

In the stainless steel loop a specific electrochemical box is dedicated to OCP measurement on all grades (Table 6). Each stainless steel coupon is electrically insulated from the others by a 5 mm-thick polycarbonate connecting piece. Each reference electrode is common to two coupons. Reference electrodes are regularly checked to ensure their reliability.

Table 6 Electrochemical box of stainless steels.

Stainless steel coupons

Insulating connecting piece

Counter and reference electrodes

External part of the electrochemical box with reference electrodes
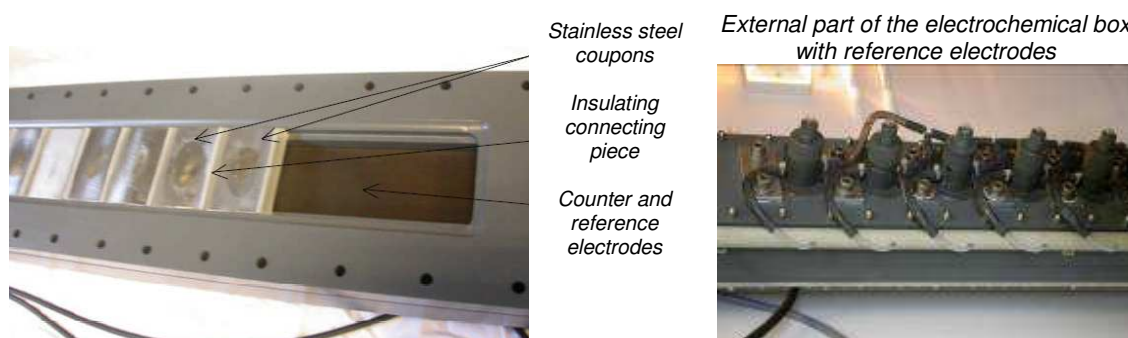
2.3 Measurement and analysis

During exposure the following measurements are performed:
- analytical controls of water (conductivity and chloride),
- chlorine content by N,N'-diethyl-p-phenylenediamine (DPD) spectrophotometric method,
- redox potential with a platinum electrode versus Ag/AgCl reference electrode,
- OCP values (vs. Ag/AgCl) recorded on stainless steels every 2 minutes in the box for electrochemical measurement via a multichannel digital voltmeter.

After 1, 2, 3, 8, 15.5 and 26.5 months of exposure a set of coupons is removed from the water boxes for analysis and observation. They are immediately immersed in sterile water and sonicated to remove biofilm.

The following analyses are obtained from water suspensions.

Fouling and surface contamination
- total solid matter (fouling) by gravimetry,
- total biomass by adenosine triphosphate (ATP) quantification using a bioluminescence method after extraction with standard additions (extractant and Luciferine Luciferase from Sigma),
- heterotrophic plate count (HPC) - culture on R2A agar (Fluka) after 15 days at 20°C,
- enterobacteria count (Coliforms, Salmonella, Shigella, Escherichia Coli, etc) - inoculation on Chromocult® Agar (Merk) - incubation 5 days at 20°C.

Chemical analysis of biofilm
- Ni, Cr and Mo content in the biofilm are evaluated using anodic stripping voltamperometry with standard addition method,
- total calcium content and its $CaCO_3$ proportion with step-by-step selective extraction and spectrophotometry with standard addition method.

The following analyses are performed on coupons.

Oxides and corrosion rate
Corrosion rate and oxides fraction are deduced from coupon weight loss after pickling following ASTM G1-03 and D2688-05 standards.

Scanning electron microscopy (SEM) examination

SEM examinations are performed on a coupon after classical treatment of fixation, dehydration, drying and gold sputtering. Observations are performed with a Leo 1455 VP SEM coupled with Oxford EDS Analyzer.

3 Results and discussion

3.1 Free potential measurement

OCP of the stainless steels are reported in Figure 1. All grades have about the same OCP evolution during the 26.5 months of exposure. Bardal and al. also related no influence of chemical composition of stainless steels in their passive state [27].
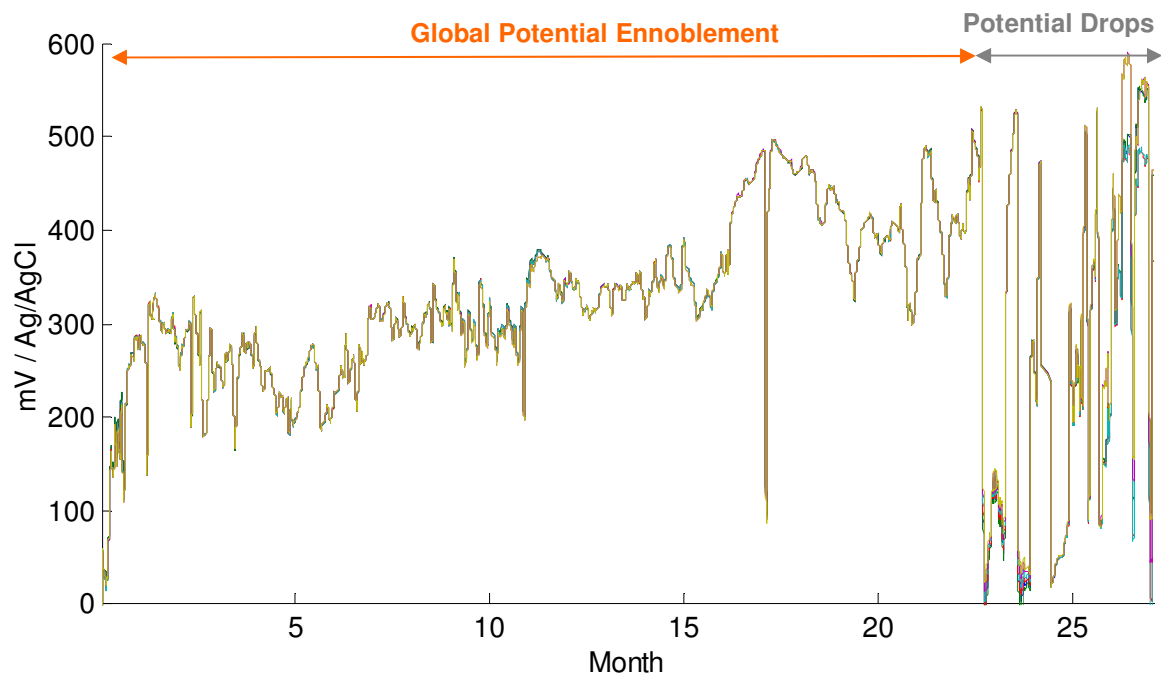
Figure 1 Stainless steel free potential (mV / Ag/AgCl) evolution during 26.5 months.

Up to about 22 months a global potential ennoblement is observed (from 0 and up to ~ 500mV / Ag/AgCl) with the latency period identical for all stainless steel grades. A magnification of the 16th month is given as an example in Figure 2. This phenomenon correlates well with results obtained in natural fresh water reported in the reference literature. In fact potentials after ennoblement are generally measured between 200 – 400 mV/ECS in several natural fresh waters (lakes, estuaries, rivers…) and are not dependent on grade, location and season but mainly on temperature [15;28-30]. Grade independence including microstructure and chemical composition are confirmed by this study. From the 22nd month until the end of the exposure, free potential of all stainless steels was found to decrease drastically to very low potential (~ 0 - 50mV / AgAgCl) and to fluctuate as illustrated in Figure 3 and 4.
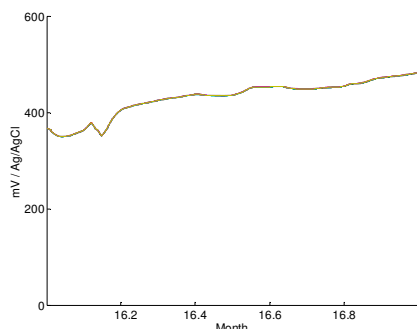
Figure 2 Zoom of 16th month.
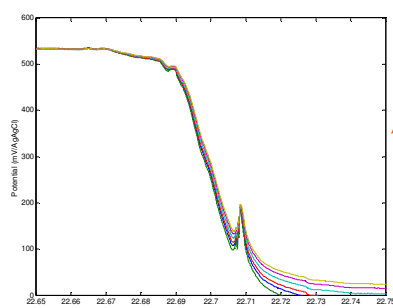

Figure 4 Zoom of potential fall (about 22nd month)
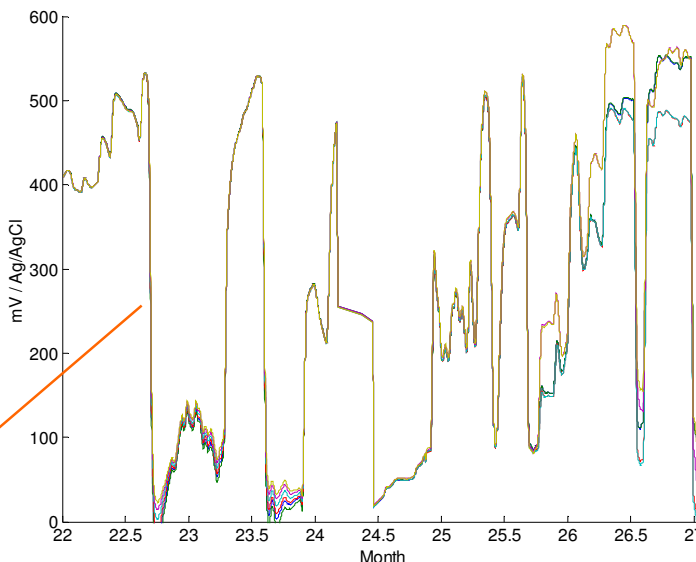
Figure 3 Zoom of potential fall and increase from 22nd to 27th month.

Such an evolution, from our knowledge never previously quoted in the literature, cannot be due to residual chlorine level modification. During the free potential drop, chlorine content was checked with a higher frequency than usual and always remains between 0.3 +/- 0.1 ppm.
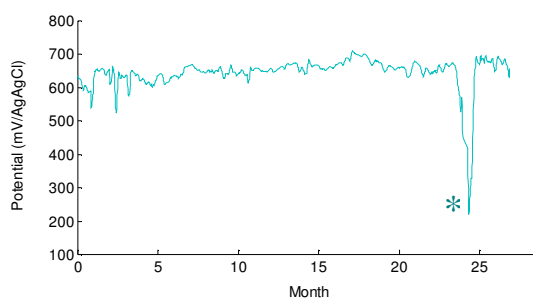
Figure 5 Evolution of redox potential in stainless steel water box during 26.5 months (Pt and Ag/AgCl electrodes). (*)=Accidental shutdown.

According to Figure 5 no specific redox potential evolution was determined. As a consequence, a potential decrease linked to the disinfectant content in the water is not a valid hypothesis. Moreover, potential drops when observed were at times measured over a 2 day period showing the continuity of the phenomena. Taking into account the water residence time of 24h in the loop, the replacement of drinking water from the network into the storage tank every 5 days and the stability of the physicochemical characteristics of the feed water, the quality of the water could not be directly responsible for the free potential decrease.

The possibility of an electrical issue was also eliminated:
- possible electrical contacts were tested between stainless steel coupons,
- each reference electrode was frequently checked.
In addition detailed observations of OCP vs. time curves show that some minor differences exist. This would not have been the case if samples had been electrically coupled (Figure 3 and 4).

3.2 Corrosion rate

The free potential of stainless steels is generally recorded to follow corrosion events and an abrupt decrease means likely corrosion of the metal. In this case a potential decrease is not explained by a material degradation since corrosion rates remain near the detection threshold: below 1 µm/year for all grades (Figure 6). Moreover no localized corrosion was observed on the stainless steel coupons after exposure while for the galvanized steel, with the highest corrosion rates over the full duration, transverse micrographs shows attack of the galvanized layer up to 43µm-deep (Figure 7).

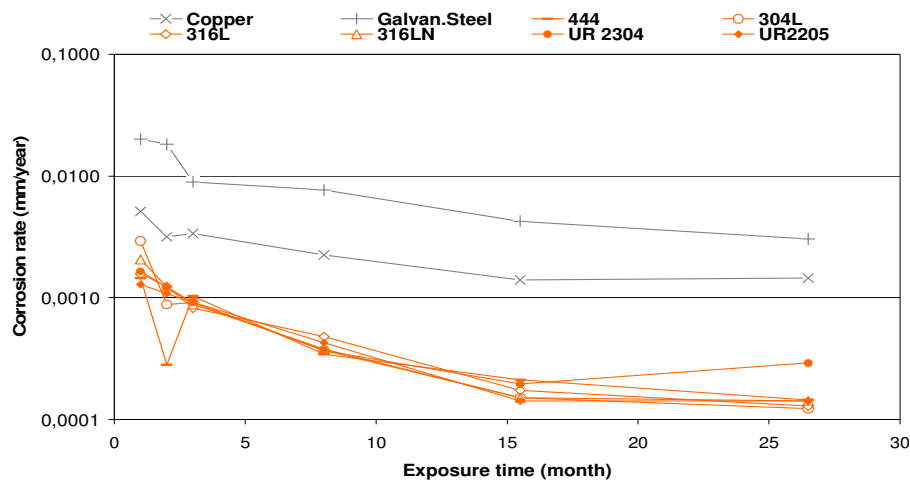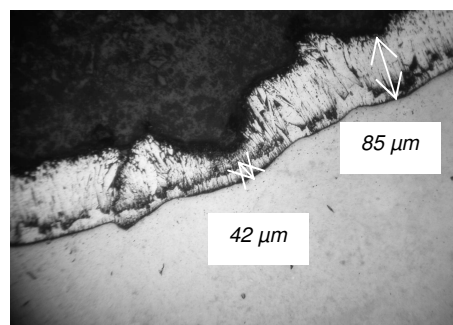**Figure 6 Corrosion rate (mm/year)**

85 µm

42 µm

Figure 7 Transverse micrograph of galvanized steel showing maximum depth of attack

Such negligible corrosion rates on stainless steels correlate well with publications showing negligible release rates for 316L in a solution simulating drinking water [31]. All the release rates are in agreement with requirements in drinking water standards. Moreover duplex stainless steel grades, such as UNS S32205 / EN 1.4462 or UNS S32304 / EN 1.4362, have recently been incorporated into the NSF/ANSI Standard 61 after successful leaching tests [32]. NSF/ANSI Standard 61 also includes grades 304, 304L, 316 and 316L.

3.3 Biocontamination

Microbial contamination reaches a metastable state, in terms of concentration of ATP in the biofilm, after 8 months exposure (Figure 8). Galvanized steel and copper have the lowest levels, while values on cement, PE and stainless steels are higher and nearly the same. On nitrogen containing stainless steel grades, growth rate is higher during the first month of exposure in accordance with Sreekumari who showed a promotion of nitrogen on nitrifying bacterial contamination [33]. No specific nitrogen effect is observed for longer exposures.
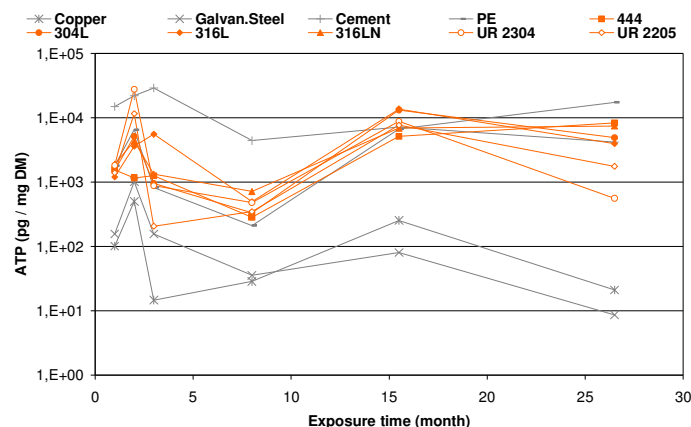

Figure 8 Biomass growth on surface expressed as ATP weight in Dried Matter (DM) of biofilm.

No significant biomass evolution is highlighted between 8, 15.5 and 26.5 months to explain OCP evolution.

3.4 Morphology of biofilm

SEM observations illustrate the fact that biofilms are constituted of bacterial clusters (microorganisms, protozoans) and a significant mineral part constituted of endogen and exogen particles (see Figure 9, 11 and 12). Colonisation area on galvanized steel is limited, but for PE, stainless steels, cement and to a lesser extent copper, biofilms cover the entire surface after 2 years of exposure (Figure 10).

Except for galvanized steel, bacteria are embedded in a complex organic matrix associated with mineral compounds. Indeed particulate matter such as aluminosilicate particles, calcium carbonate precipitates, iron and aluminium hydroxides as well as calcium in a diffuse manner on the surface (associated with organic matter) are all detected. On galvanized steel bacteria are disseminated in the oxide layer. During the final months, a mineralization phenomenon was observed on all materials (Ca, Fe, Si, Al with P and $CaCO_3$ particles, less detected on cement). Moreover, on all stainless steel grades, three zones are observed (Figure 13):
- a network with filaments or membranous structures observed during the whole exposure,
- a new upper layer enriched in $CaCO_3$ and iron at the final withdrawal,
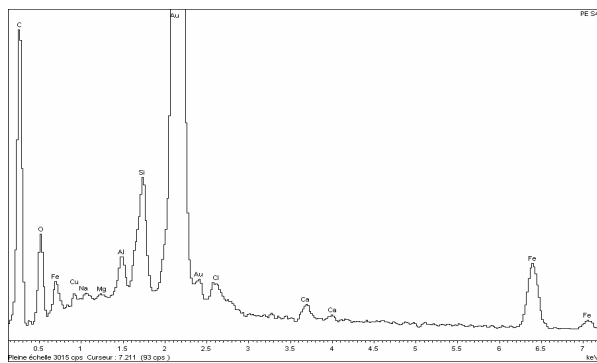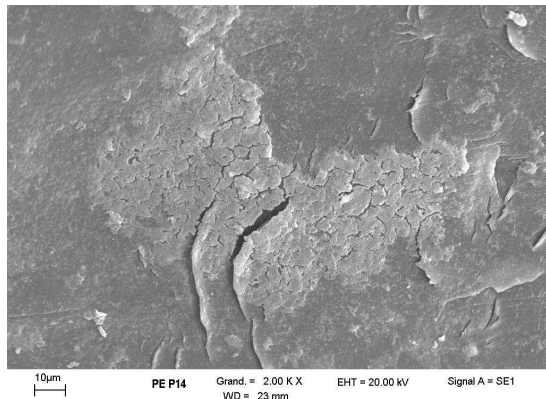- and a colonisation of this new stratum at certain areas by bacteria filaments.

No steady state is reached by the biofilms according to morphology, composition and colonisation areas. These characteristics are dependent on the substrates.
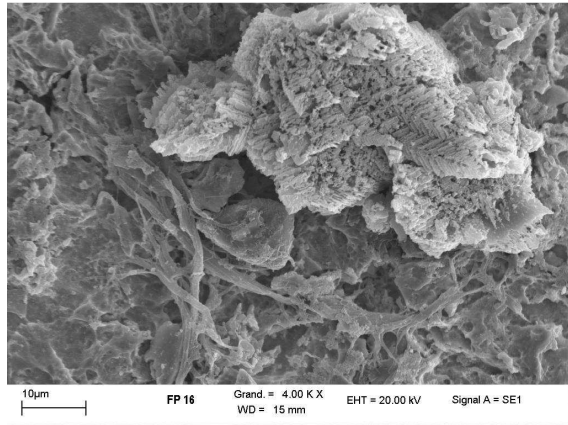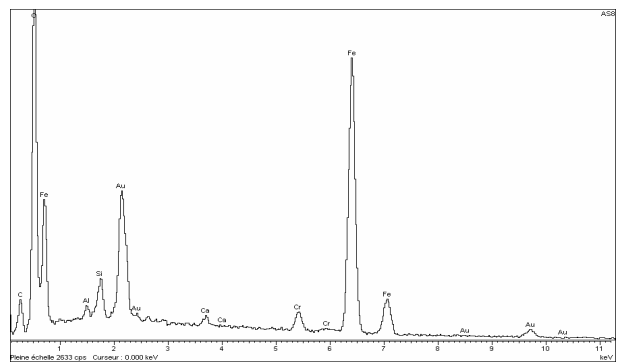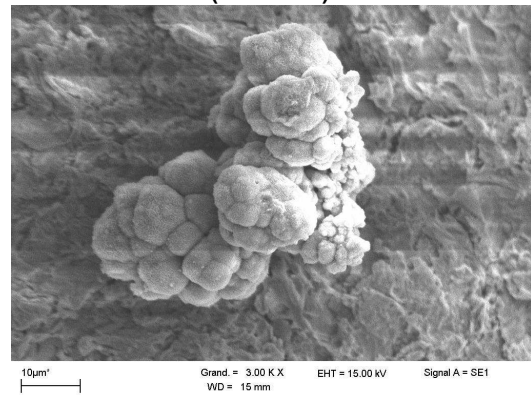

Figure 9 CaCO₃ particle on 2205 (15.5 months).
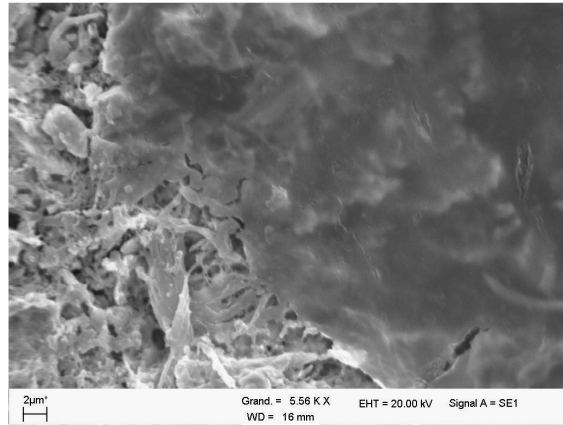
Figure 10 2205 with bacteria under thick membrane (8 months).

Figure 11 Mineral deposit (Si, Al, Fe, O) on PE (15.5 months).

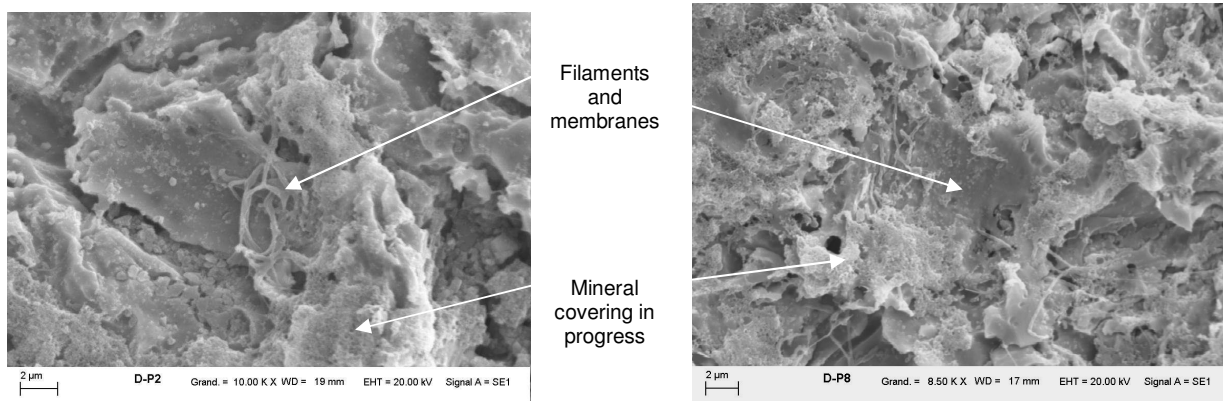**Figure 12 Iron oxohydroxide particle on 444 (8 months).**

Figure 13 Evolution of biofilm morphology : example of 316LN (26.5 months).

3.5 Chemical composition of biofilm

Calcium presence is significant in the deposits as shown by the EDS measurements and SEM observations. Its total concentration increases on all materials during the last year of exposure (Figure 14). Higher concentrations are measured on copper, galvanized steel, cement and PE. Calcium repartition most likely depends on its substrate (Figure 15). On copper, galvanized steel and cement after 26.5 months calcium as carbonate represents 80-97% of the total calcium (35-43% of $CaCO_3$ in dried matter of biofilm). On PE and all stainless steel grades after 26.5 months calcium as carbonate represents 74-80% of the total calcium (10-23% of $CaCO_3$ in dried matter of biofilm). The amount of calcium carbonate increases on all stainless steel grades upon the final withdrawal.
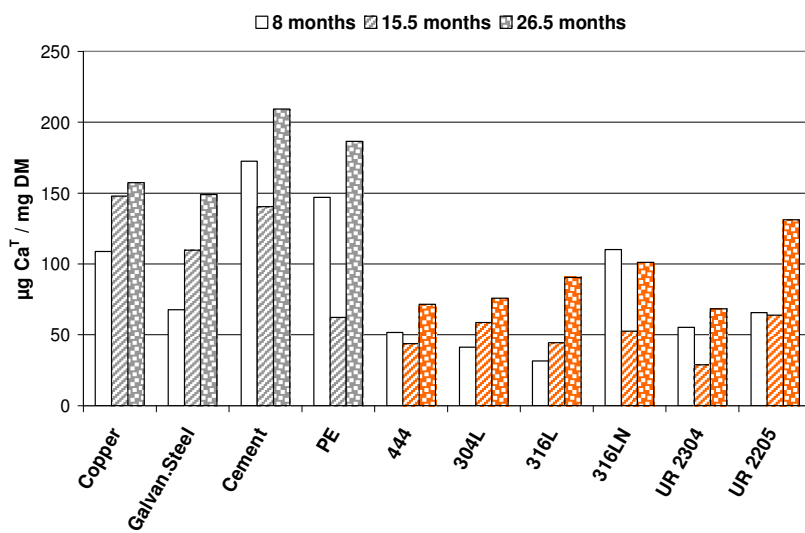

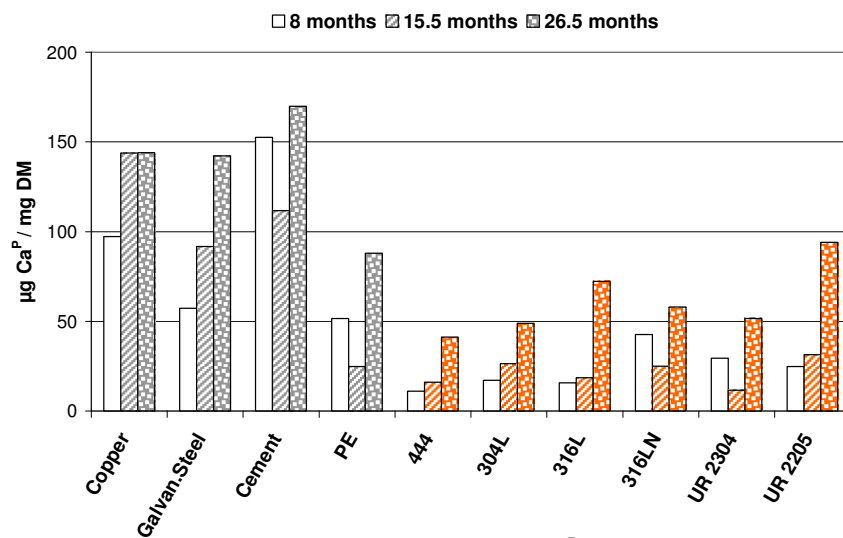Figure 14 Evolution of total calcium (Ca^T) in the biofilm

Figure 15 Evolution of Ca as CaCO$_3$ (Ca^P) in the biofilm

4 Hypothesis on free potential evolution

Ennoblement phenomena in natural fresh water are generally explained by an increase of the cathodic part of the current which is taken into account in the framework of the mixed potential theory to give the OCP:
- by acceleration of the oxygen reduction reaction kinetic,
- by production of one or several new oxidative species in the biofilm.

Manganese oxide produced by biomineralisation cannot be considered since no manganese was detected by EDS analysis.
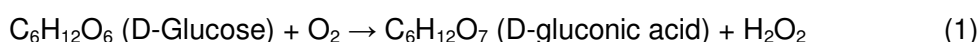
However on the basis of the previous observations and analysis, hydrogen peroxide production may be considered via enzymatic activity.
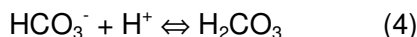
The hypothesis of hydrogen peroxide production, which is an oxidant easier to reduce than oxygen [13], via enzymes may also explain the discontinuity of the phenomena. In fact periods of potential decrease followed by potential ennoblement are often measured.

The ennoblement power of hydrogen peroxide can be affected in several ways.

Buffering power of biofilm

According to some authors only the hydrogen peroxide reduction reaction at low pH (~3) may induce a potential ennoblement [13-34-18]. The increase in calcium carbonate within the biofilm will at least limit such an acidification whatever the glucose oxidase action (1). It can counteract local acidification and exert a powerful buffering effect in a biofilm following equilibrium (2), (3), (4) and (5).

$C_6H_{12}O_6$ (D-Glucose) + O_2 → $C_6H_{12}O_7$ (D-gluconic acid) + H_2O_2 (1)

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (2)$$

$$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^- \qquad (3)$$

$$HCO_3^- + H^+ \Leftrightarrow H_2CO_3 \qquad (4)$$

$$Ca(HCO_3)_2 \Leftrightarrow CaCO_3 + H_2CO_3 \text{ (metastable equilibrium of calcium bicarbonate)} \qquad (5)$$

An increase in calcium carbonate in biofilms may affect activity of hydrogen peroxide in biofilm.

Oxidative radical generation catalyzed by metallic cations and followed by radical scavenging

Some metallic cations like iron, chromium, copper, molybdenum or nickel can catalyze hydrogen peroxide decomposition into very oxidizing hydroxyl radicals (OH°) which increase the cathodic current. The chain of radical decomposition may be interrupted if they react preferentially with carbonate or hydrogen carbonate, both known as radical scavengers, and induce the formation of species with a low oxidation reactivity (see reactions (6) and (7)) [35].

$$OH° + HCO_3^- \rightarrow OH^- + HCO_3° \qquad (6)$$

$$OH° + CO_3^{2-} \rightarrow OH^- + CO_3^{\sigma-} \qquad (7)$$
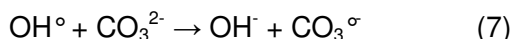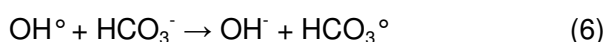
Results from § 3.5 may explain the potential evolution. Calcium carbonate increase in the biofilm during the last year of exposure coincides with potential oscillation instead of constant ennoblement.
Calcium carbonate formation in the biofilm can play an important role on the potential evolution, but other parameters must also be taken in account like catalase and peroxidase actions. Indeed these enzymes decompose H_2O_2 respectively in O_2 and H_2O. Therefore, the presence of catalase can enhance the cathodic part of the current when peroxidase does not. Washishu and al. highlighted catalase and peroxidase action on hydrogen peroxide decomposition and a rapid potential decrease [36].

All parameters linked to hydrogen peroxide production and decomposition are summarized in Figure 16.
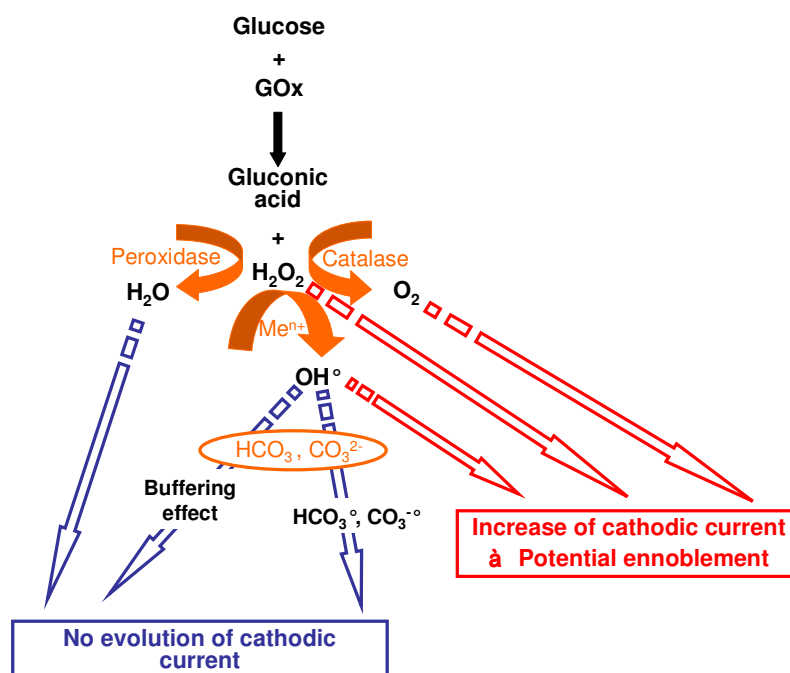
Figure 16 **Summary of parameters influencing hydrogen peroxide generation and decomposition in aerobic biofilm (GOx = Glucose Oxidase, Me^{n+}= metallic cation).**

5 Conclusion

This study was conducted for more than two years in a natural drinking water loop simulating conditions encountered in distribution networks (temperature, pressure, flow velocity and water chemistry). According to our knowledge, it is the first study with various stainless steel grades and other competitive materials exposed in a natural drinking water pilot for so long a duration.

The new phenomena observed during the last months of testing illustrate the successive metastable states of a biofilm and support the necessity to evaluate materials for exposure durations beyond just a few weeks.

After a long potential ennoblement period on stainless steels, free potential drops are observed after 22 months on all grades without any associated corrosion. Indeed, corrosion is only observed on the galvanised carbon steel. For stainless steels negligible corrosion and therefore release rates much below international health requirements, is measured.

From the first months of exposure, more or less developed biofilms were evidenced on all materials. They are composed of bacteria to some degree embedded in an organic matrix, a few protozoan and fungi as well as a consequential mineral part; all these different components constitute complete food chain [37]. After 8 months, a metastable state is reached according to biocontamination. Nevertheless significant changes in terms of morphology and chemical composition of biofilms are reported. Indeed SEM observations and EDS analysis demonstrate a mineralization on all materials with the creation of a new stratum on all stainless steels. In addition, chemical analysis provide evidence of an increase of calcium carbonate concentration in all biofilms between 15.5 and 26.5 months. Concerning the morphology of a biofilm, bacteria

are disseminated in an oxide layer for galvanized steel and in an organic matrix for the other materials. On all stainless steel grades, a new upper layer enriched in $CaCO_3$ and iron is evidenced at the final withdrawal.

It is suggested that the free potential evolution on stainless steels is related to the evolution of the global chemistry and metabolism of the biofilm. The relatively high calcium carbonate content measured at the final withdrawal may explain OCP oscillations after 22 months exposure. Further work will be focused on H_2O_2 production and decomposition mechanisms in relation to OCP values.

References

[1] Hunter PR., *Drinking water and diarrhoeal disease due to Escherichia coli*, 2003, Journal of Water and Health 1(2): 65-72.

[2] LeChevallier MW., Cawthon CD. and Lee RG., *Inactivation of biofilm bacteria*, 1988, Applied and Environmental Microbiology 54, 10: 2492-2499.

[3] Luppens SBI., Reij MW, van der Heijden RWL., Rombouts FM. and Abee T., *Development of a standard test to assess the resistance of Staphylococcus aureus biofilm cells to disinfectants*, 2002, Applied and Environmental Microbiology 68: 4194-4200.

[4] Davey ME. and O'Toole GA., *Microbial biofilms: from ecology to molecular genetics,* 2000, Microbiology and Molecular Biology Reviews 64: 847-867.

[5] Bellon-Fontaine MN. and Briandet R., *Le biofilm, une stratégie de survie du microbe*, 2000, Salles Propres 9: 46-56.

[6] Costerton JW., Geesey GG. and Jones PA., *Bacterial biofilms in relation to internal corrosion monitoring and biocide strategies*, 1988, Material Performance, 27: 49-53.

[7] Chavant P., Martinie B., Meylheuc T., Bellon-Fontaine MN. and Hebraud M., *Listeria monocytogenes LO28 : surface physicochemical properties and ability to form biofilms at different temperatures and growth phases*, 2002, Applied and Environmental Microbiology 68: 728-737.

[8] Mafu AA., Roy D., Goulet J. and Magny P., *Attachment of listeria monocytogenes to stainless steel, glass, polypropylene and rubber surfaces after short contact times*, 1990, Journal of Food Protection 53: 742-746.

[9] Azedevo NF., Pinto AR., Reis NM., Vieira MJ. and Keevil CW., *Shear stress, temperature, and inoculation concentration influence the adhesion of water-stressed Helicobacter pylori to stainless steel 304 and polypropylene*, 2006, Applied and Environmental Microbiology 72: 2936-2941.

[10] Donlan RM. and Costerton JW., *Biofilms: survival mechanisms of clinically relevant microorganisms*, 2002, Clinical Microbiology Review 15: 167-193.

[11] Stoodley P., Wilson S., Hall-Stoodley L., Boyle JD., Lappin-Scott HM. and Costerton JW., *Growth and detachment of cell clusters from mature mixed-specied biofilms*, 2001, Applied Environmental Microbiology 67: 5608-5613.

[12] Scotto (V.), Mollica A., Audouard JP., Compère C., Festy D., Féron D., Rogne T., Steinsmo U., Taxen C. and Thierry D., *The corrosion behaviour of stainless steels in natural seawater : results of a European collaborative project.*

[13] Dexter SC. and Chandrasekaran P., *Mechanism of potential ennoblement on passive metals by seawater biofilms*, 1993, NACE Annual Conference and Corrosion Show, paper 493.

[14] Marconnet C., *Influence de l'adhésion et de l'activité enzymatique du biofilm sur le comportement électrochimique des aciers inoxydables immergés en eau de rivière*, 2007, Thesis of Ecole Centrale Paris.

[15] Féron D. and Roy M., *Corrosion behaviour of stainless steels in natural waters: focus on microbiological and chemical aspect"*, September 2000, Forum Biodétérioration des Matériaux, Toulouse, DAP/SCECF n°256.

[16] Dickinson WH., Caccavo FJ. and Lewandowski Z., *The ennoblement of stainless steel by manganic oxide biofouling*, 1996, Corrosion Science 38: 1407-1422.

[17] Mollica A. and Trevis A., *Corrélation entre la formation de la pellicule primaire et la modification de la réaction cathodique sur des aciers inoxydables expérimentés en eau de mer aux vitesses de 0.3 à 5.2m/s*, 1976, Proceedings of 4th International Congress on Marine Corrosion and Fouling, Juan-les-Pins, Antibes, France.

[18] Dexter SC. and Gao GY., *Effect of seawater biofilms on corrosion potential and oxygen reduction of stainless steel*, October 1988, Corrosion 44: 717-723.

[19] Marconnet C., Dagbert C., Roy M. and Féron D., *Microbially influenced corrosion of stainless steels in the Seine river*, 2006, Eurocorr Conference Proceeding, Maastricht.

[20] Dupont I., *Influence des bactéries et de leur activité sur l'évolution du potentiel des aciers inoxydables en eau de mer naturelle*, 1996, Caen University Thesis, France.

[21] Washizu N., Katada Y. and Kodama T., *Role of H_2O_2 in microbially influenced ennoblement of open circuit potentials for type 316L stainless steels in seawater*, 2004, Corrosion science 46: 1291-1300.

[22] Landoulsi J., Pulvin S., Richard C. and Féron D*., Intérêt d'une approche enzymatique en corrosion microbienne des aciers inoxydables en eaux naturelles*, 2005, Matériaux et Techniques 93: 59-67.

[23] Allion A., Lassiaz S., Peguet L., Boillot P., Jacques S., Peultier J. and Bonnet MC., *Durabilité des aciers inoxydables et développement de biofilms dans les réseaux d'eau potable : étude comparative avec d'autres matériaux couramment utilisés*, 2010, European Journal of Water Quality,

http://www.water-quality-journal.org/index.php?option=toc&url=/articles/wqual/abs/first/contents/contents.html.

[24] Paris T., Skali-Lami S. and Block JC. *Effect of wall shear rate on biofilm deposition and grazing in drinking water flow chambers*, 2007, Biotechnology&Bioengineering, 97: 1550-1561.

[25] Percival SL., Knapp JS., Edyvean RGJ. and Wales DS. *Biofilms, main waters and stainless steel*, 2010, Water Research, 32: 2187-2201.

[26] Simoes LC., Azevedo N., Pacheco A., Keevil CW. and Vieira MJ. *Drinking water biofilm assessment of total and culturable bacteria under different operating conditions*, 2006, Biofouling. 22(1/2): 91-99.

[27] Bardal E., Drugli JM. and Gartland PO, *The behaviour of corrosion-resistant steels in seawater: a review*, 1993, Corrosion Science 35: 257.

[28] Chamritski IG., Burns GR., Webster BJ. and Laycock NJ., *Effect of iron-oxidizing bacteria on pitting of stainsless steel*, July 2004, Corrosion 60: 658.

[29] George RP., Muraleedharan P., Parvathavarthini N., Khatak HS. and Rao TS., *Microbially influenced corrosion of AISI type 304 stainless steels under fresh water biofilms*, 2000, Materials and Corrosion 51: 213-218.

[30] Renner MHW. and Wagner GH., *Microbiologically influenced corrosion of stainless steels*, November 1996, Stainless steel World 8, n°9: 36-43.

[31] *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.

[32] ANSI / NSF Standard 61, Drinking water system components - Health effects, Appendix C. http://www.nsf.org/business/water_distribution/.

[33] Sreekumari KR., Takao K, Ujiro T. and Kikuchi Y., *High nitrogen stainless steel as a preferred substratum for bacteria and other microfouling organisms*, 2004, ISIJ International 44: 858-864.

[34] Franklin MJ. and White DC., *Biocorrosion*, 1991, Current Opinion in Biotechnology 2: 450-456.

[35] Staehelin J. and Hoigne J., *Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions*, 1985, Environmental Science and Technology 19: 1206-1213.

[36] Whashizu N, Katada Y. and Kodama T., 2004, *Role of H_2O_2 in microbially influenced ennoblement of open circuit potentials for type 316L stainless steel in seawater*, Corrosion Science 46: 1291-1300.

[37] Loret JF., Jousset M., Robert S., Anselme C., Saucedo G., Ribas F., Martinez L. and Catalan V., *Élimination des amibes libres par les procédés de traitement de l'eau potable*, 2008, European Journal of Water Quality 39: 37-50.