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Stainless steels durability and biofilm formation in potable water: a comparative study with usual materials

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ABSTRACT

Numerous materials have been using in potable water distribution systems depending on their availability and ease to install. Even if these materials have been in operation for decades, both for small diameter and large diameter pipes, they are known to suffer from internal corrosion by water and/or from external corrosion by soils. Due to their high durability properties, stainless steels appear as promising candidates.
To validate their high internal corrosion resistance, a 2 years corrosion study has been developed in a natural potable water loop. The tested stainless steel grades are 444/EN 1.4521, 304L/EN 1.4307, 316L/EN 1.4404, 316LN/EN1.4429, UNS S32304/EN 1.4362 and UNS S32205/EN 1.4462. The behavior of these grades is compared to that of copper, galvanized steel, polyethylene and cement. Different parameters have been followed during the exposure: bio-fouling, scaling, corrosion rate and potential threshold of stainless steels.
First results after 8 months exposure are presented in the present paper: stainless steels are evidenced as an attractive opportunity for water pipes manufacturing.

Keywords: corrosion resistance, stainless steels, potable water

1. INTRODUCTION

The potable water network is a living medium, which evolves continuously due to physico-chemical and microbiological reactions. Most of time, there is a development of a discontinuous scale constituted by biofilm and deposits (calcium carbonate…) or of corrosion products (iron oxide…) [1].

Numerous materials are used in potable water distribution systems depending on their availability and ease to install. Even if these materials have been in operation for decades, both for small diameter and large diameter pipes, they are known to suffer from internal corrosion by water and/or from external corrosion by soils. Selecting the appropriate stainless steel may thus offer several advantages [2].

First of all, because of their passive state in a wide range of waters, stainless steels seem more secure regarding to human health [3,4]. 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 [5,6]. 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 incorporated into NSF/ANSI Standard 61 in addition to types 304, 304L, 316 and 316L [7].

So, stainless steels have been used now for manufacturing, storage and transport of beer, juice soda and wine. In general, they have a good behavior but some localized corrosions on welds or Heat Affected Zone (HAZ) have been reported in the literature and are linked to the presence of a biofilm. Indeed, it is well known that biofilm developed mainly on irregularities, such as welds or non removal heat tints because the chemical composition and the roughness are different on these places than on free surface [8-13].

The objectives of this study are to compare the behavior of different stainless steel grades with four other materials usually used in natural potable water networks (copper, galvanized steel, polyethylene and cement). Different parameters have been followed such as fouling (bio-fouling and scaling), corrosion rate and free potential of stainless steels.

2. EXPERIMENTAL DETAILS

2.1. Materials

Stainless steels used in this work are produced by ArcelorMittal (Industeel and Ugine & Alz). The chemical analysis and PREN value of these alloys are reported in Table 1.

Grade (EN/UNS)		C	Cr	Ni	Mo	N	Mn	Si	S (ppm)	PREN
α	**Uginox F18MT (1.4521)**	0.015	17.62	0.12	2.04	0.017	0.36	0.42	9	26.6
γ	**304L (1.4307)**	0.020	18.41	10.16	0.16	0.074	1.20	0.37	13	20.1
	316L (1.4404)	0.017	16.50	10.07	2.02	0.027	1.86	0.63	9	23.6
	316LN (1.4429)	0.018	17.44	13.45	2.60	0.167	1.19	0.55	6	28.7
α/γ	**UR2304 (1.4362/S32304)**	0.029	22.73	4.29	0.23	0.139	1.33	0.54	3	25.7
	UR2205 (1.4462/S31803)	0.016	22.79	5.45	2.83	0.156	1.84	0.24	4	34.6

Table 1: Elemental composition of the alloy (%wt) and Pitting Resistance Equivalent Number (PREN=Cr%+3.3Mo%+16N%) for ferritic (α), austenitic (γ) and duplex (α/γ) grades

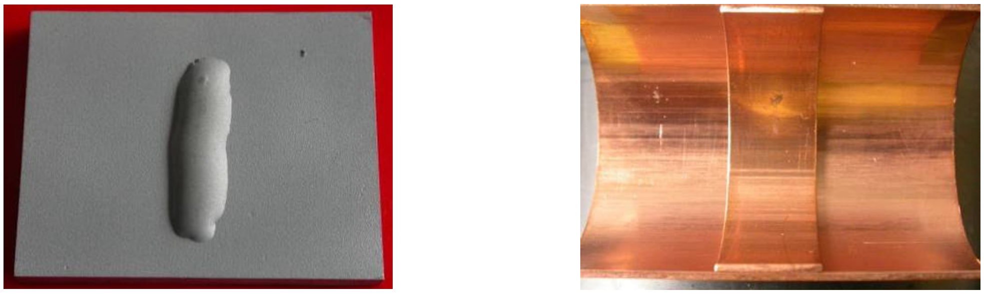
Stainless steels ability for resisting to pitting corrosion may be evaluated by calculation of the Pitting Resistance Equivalent Number (PREN). The formula was developed using a ferric chloride solution ($FeCl_3$), which is an oxidizing chloride containing acid solution [14]. The ranking of stainless steels obtained with this index is valid only in this type of media. In other media where corrosion mechanisms may be different (e.g. neutral chloride containing solution or very acidic solution…), the ranking is not valid.

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 low sulfur content; the risk of sulphur containing inclusions is thus decreased.

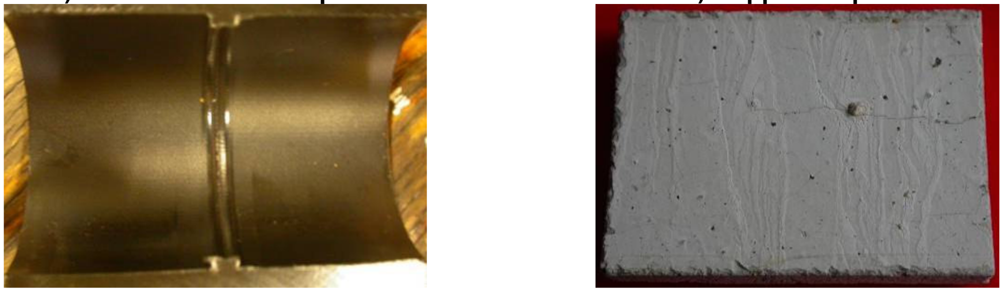
The dimensions of stainless steels coupons were 40 × 50 × 5-6 mm. A bead of weld metal was deposited by automatic TIG welding process on coupons (Photography 1). Then coupons were sand-blasted and pickled in a hot hydrofluonitric (HNO_3 / HF) bath in order to remove heat tints from welding.

The behavior of stainless steels is compared with four other materials usually used in natural potable water networks: copper, galvanized steel, polyethylene (PE) and cement (Photography 1).

As for stainless steel, to disturb water flow and to favor the development of biofilm and/or deposit, polyethylene is butt welding and a socket is realized for copper. For galvanized steel and cement, the roughness is evaluated as sufficient to promote the fouling.



a) Stainless steels coupons **b) Copper coupons**



c) PE coupons **d) Cement coupons**

e) Galvanized steel coupons

Photography 1: Coupons exposed in the potable water system

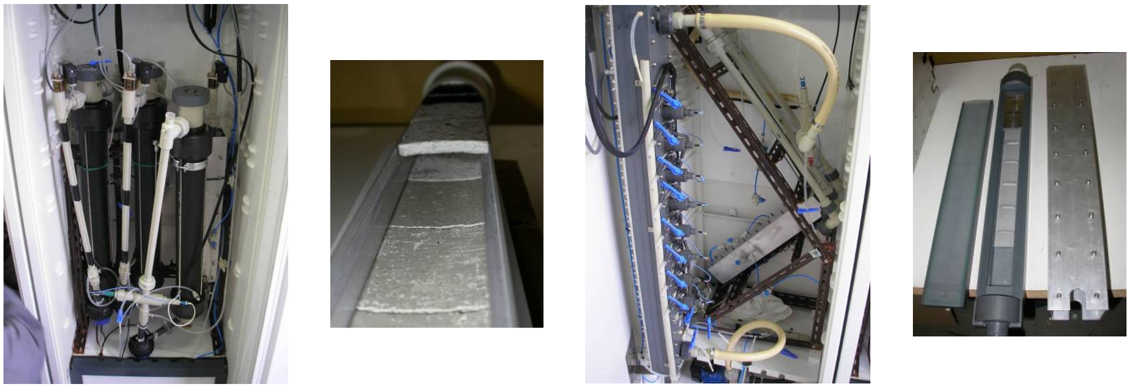
2.2. Pipe loop set up

Four recirculating and thermostated pipe loops were used for each type of material, except for PE and cement for which the same loop was used (Table 2, Photography 2). These water boxes allow a regular, tangential and controlled flow of natural potable water at the surface of the coupons. Free residual chlorine was adjusted and control at 0.3±0.1 ppm; residence time was fixed at 24 hours (Table 3). Each pipe loop contains several water boxes containing set of coupons.

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 electrochemical box

Table 2: Description of the four loops

For stainless steels, each water box contains only two grades: Uginox F18MT/304L, 316L/316LN and UR2304/UR2205. A specific water box is dedicated to the electrochemical measurements on stainless steels. Moreover, depending on the coupons design, cylindrical and flat box are used (Photography 2).



a) Loops 1-3 for PE, copper, galvanized steel and cement: cylindrical box

b) Loop 4 for stainless steels and electrochemical box: flat box

Photography 2: Photos of water boxes in the different loops

The functioning conditions are the following:

Residence time	24 h
Temperature	10 °C
Pressure	0.7 bar
Velocity	0.25 m/s
Free chlorine concentration	0.3 ppm
Iron concentration (Fe^{III})	0.2 ppm
Chloride concentration	100 ppm
Sulfate concentration	35 ppm
pH	8.1
Methyl-orange alkalinity	20 °f
Calcium concentration	20 °f, i.e. 200 ppm $CaCO_3$

Table 3: Functioning conditions

2.3. Typical measurements

During exposure, the following measurements have been realized:

- analytical control of water: conductivity, chlorine and chloride concentrations,
- electrochemical measurements with Ag/AgCl reference electrode: free potential of stainless steel coupons.

At the end of each period of exposure, a set of coupons is retrieved from the water boxes for different analysis and observations. In this paper, the results of 1, 2, 3 and 8 months exposure times are presented.

2.3.1. Fouling and surface contamination

The coupons were sonicated for 2 minutes in sterile ultra pure water; the water suspensions obtained were used for following analysis:

- total solid matter,
- heterotrophic plate count (HPC) on R2A agar (Fluka) after an incubation period of 15 days at 20 °C,
- adenosine triphosphate (ATP), using Hidex Triathler luminometer, Luciferine Luciferase and reagents for extractant mixture from Sigma. ATP content was calculated by the standard addition method,

- enterobacteriae (Coliforms, Salmonella, Shigella) plate count on Chromocult Coliform agar (Merck) after an incubation period of 5 days at 20℃.

2.3.2. Oxides and corrosion rate

Corrosion rate and oxides fraction were deduced from weight loss after pickling following ASTM standards [15,16].

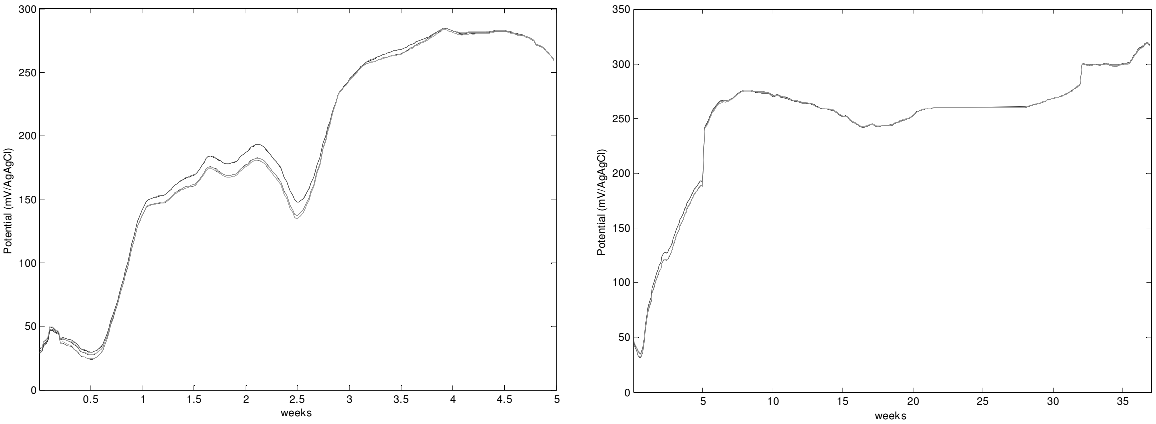
2.3.3. Scanning electron microscopic examination

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

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Free potentials of stainless steels

The free potentials of stainless steels were followed during the test (Figure 1). All stainless steel grades have about the same free potentials.
The first week corresponds to the start up of the loop and to the increase and adjustment of chlorine content; potentials increase until +150mV/AgAgCl.
During the two following weeks, we observe some drops due probably to the adjustment of the system and the evolution of chlorine concentration, but the potential values continue to increase to more anodic value.
It seems that after 3 weeks, the system is stabilized at an average value of +300mV/AgAgCl.
During the 8 months of exposure, we also observed some decreases of free potentials after step of stabilization. This evolution may be due to the evolution of chlorine concentration but also to an evolution of the surface state (increase / release of biofilm, fouling…).



a) Potential evolutions on the five first weeks b) Potential evolution during 8 months

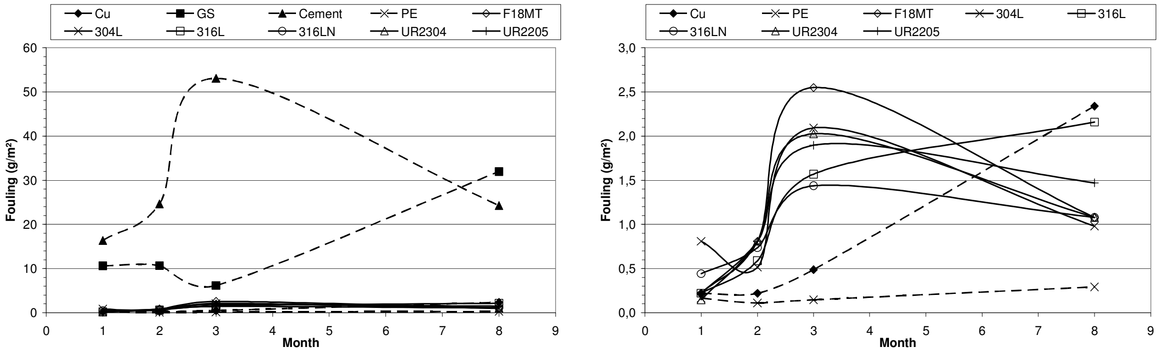
Figure 1: Free potentials of stainless steels during the eight months of exposure

The ennoblement of the free potential is usual on stainless steels immerged in seawater, river water, fresh water… [8,11,17,18]. This phenomenon is still discussed and it is generally associated with the development of biofilm and not on a modification of the passive film (no evolution of passivation current with biofilm development [19]).

3.2. Fouling

Figure 2 shows that materials presenting the highest fouling are galvanized steel and cement. Stainless steels behave similarly to copper, i.e. the fouling is very low. The material which presents the lowest fouling is polyethylene. For stainless steels, the values do not exceed 2.5g/m^2 whereas on cement and galvanized steel, the fouling can be higher than 20g/m^2.

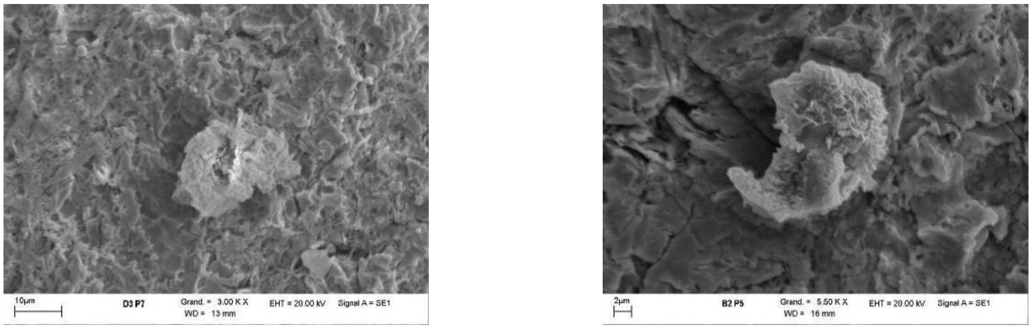
Depending on the material, fouling evolves with time. For galvanized, stainless steels and cement, the fouling presents phases of increase and of decrease, which may imply period of deposits removal. For copper, polyethylene and 316L, no decrease is observed; the fouling is still in a phase of growth.



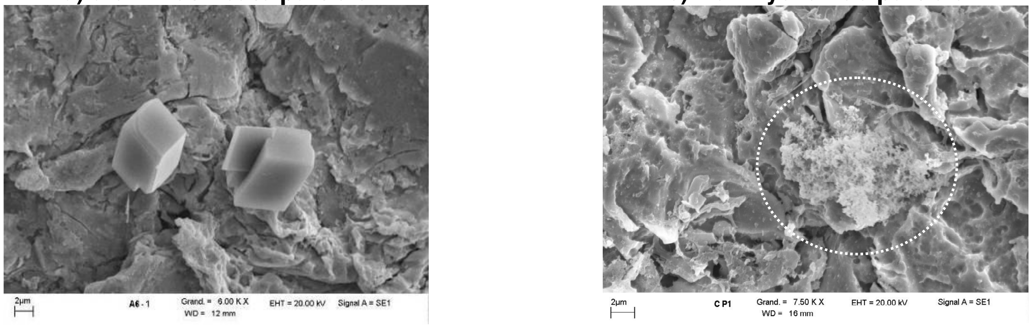
a) **b) zoom**

Figure 2: Threshold of fouling for all materials in function of exposure time

SEM examination revealed the presence of particulate matter fouling of the surface such as: aluminosilicate (Photography 3a), iron hydroxide (Photography 3b) and cubic calcium carbonate particles (Photography 3c). From the third month, very few cubic calcium carbonates are still observed and more coarse flocculent (Photography 3d) is analyzed. It seems that deposit of calcium carbonate is not adherent.



a) aluminosilicate particle **b) iron hydroxide particle**



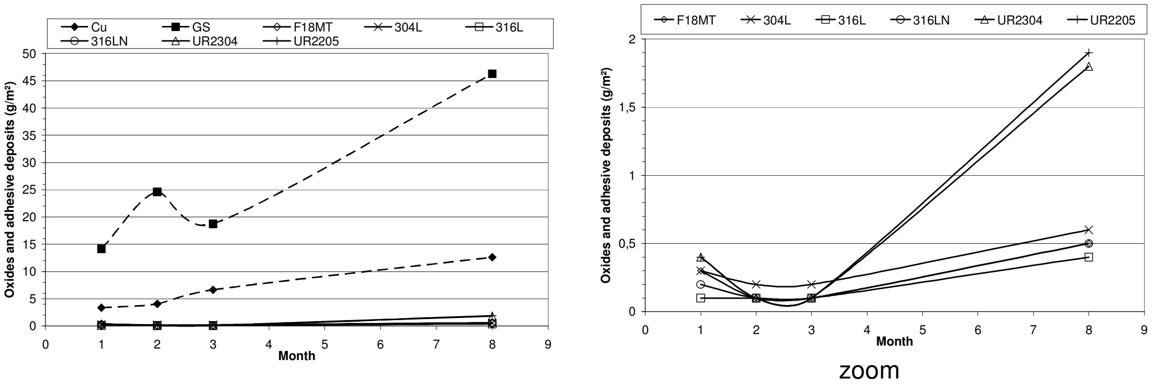
c) cubic calcium carbonate particles **d) coarse flocculent**

Photography 3: SEM observations of particles

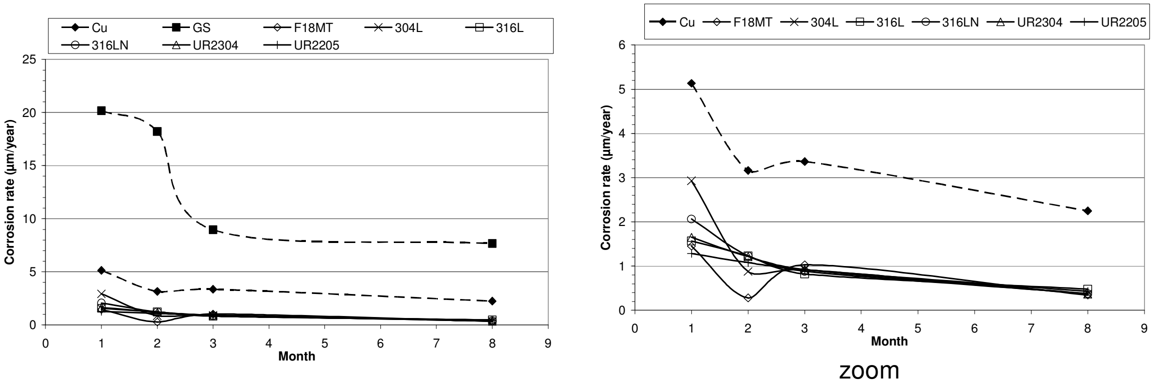
3.3. Oxides and corrosion rate

Figure 3a shows that copper and galvanized steel present the heaviest oxides and adherent deposits. This is well correlated with the corrosion rates. Indeed, these two materials act against corrosion by developing a protective oxide layer on the surface: copper oxide Cu_2O and zinc hydroxycarbonate $Zn_5(OH)_6(CO_3)_2$ [20]. The corrosion rates for copper (3-5 µm/year) and galvanized steel (20 µm/year) are typical values. Moreover, after a period of stabilization during the three first months, the oxides and adherent deposits highly increase, especially for galvanized steel. This increase may not be due to the growth of the oxides layer because corrosion rate decreases.

For stainless steels, these parameters are very low and suggest the absence of corrosion, which is confirmed by visual observation. The species release is near to the limit of detection.



a) oxides and adhesive deposits



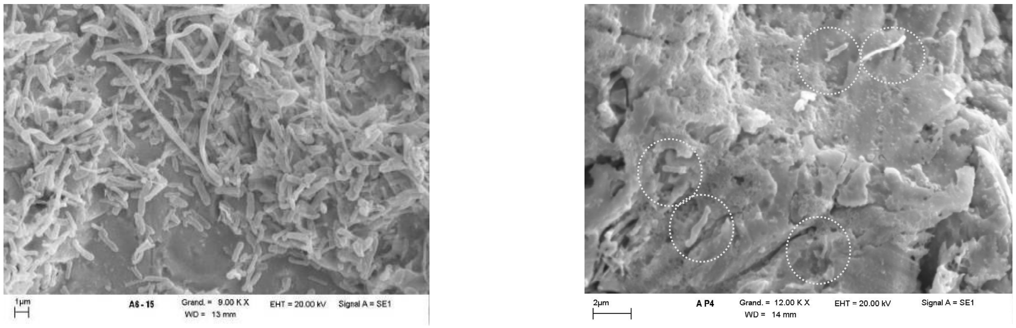
b) corrosion rate

Figure 3: Threshold of oxides and corrosion rate

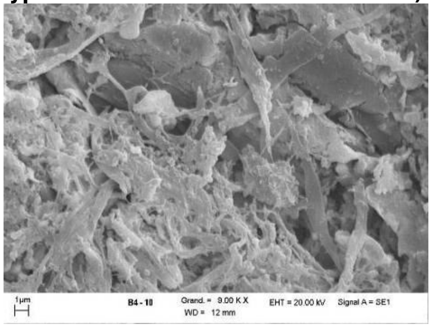
3.4. Surface colonization and biofilm development

The colonization by micro-organisms is dependant on materials but for all of them, colonization takes place and the surface concerned seems to increase with time. Surface colonization presents various aspects (Photography 4):

- single bacteria or small colonies, mainly rod-shaped type,
- filamentous colonies.



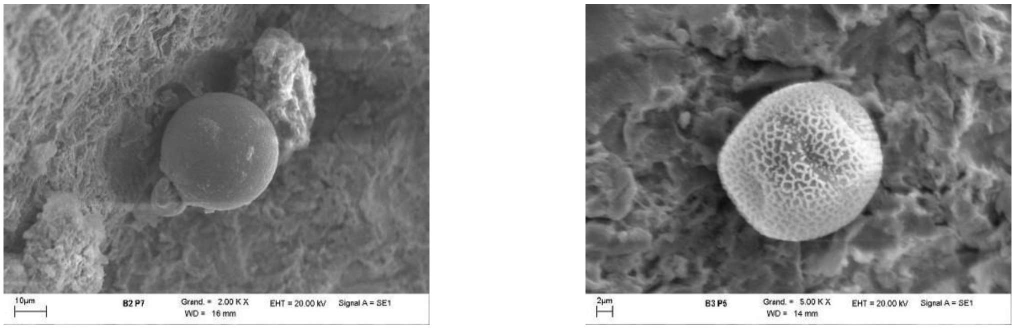
a) colony of rode-shaped type bacteria **b) sparse bacteria**



c) filamentous bacteria in a membrane matrix

Photography 4: SEM observations of different types of bacteria

Other micro-organisms are observed like fungus and protozoa. These last micro-organisms are known to regulate bacteria colonization.



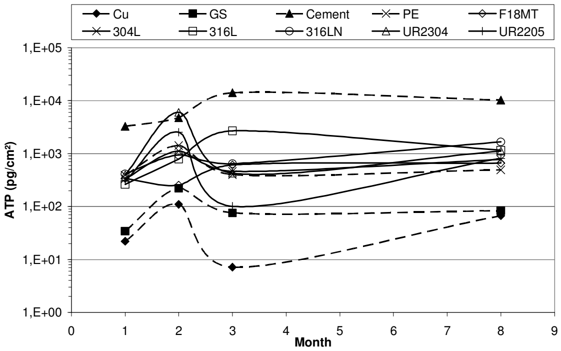
Photography 5: SEM observations of protozoa and fungus

ATP analysis, HPC and enterobacteria cultures and SEM examination show that surface contamination and biofilm development is different following the type of material. Three groups can be distinguished:

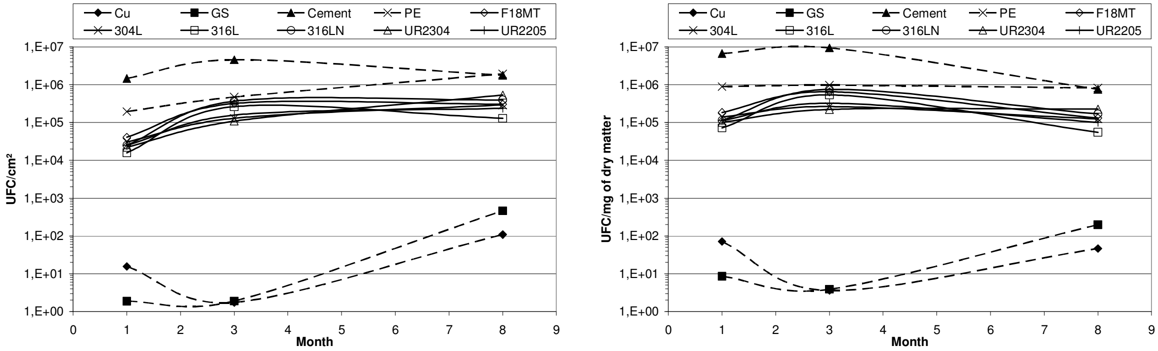
1. Cement is the only material completely recovered with biofilm after the first month, it shows the highest value of ATP,
2. Copper and galvanized steel are known as biostatic materials. At the first month, no development on galvanized steel and only few areas of diameter 20-50µm on copper are observed. The development of micro-organisms is the slowest on these materials,
3. PE and stainless steels have a similar behavior by considering ATP. For stainless steels, the colonization surface was not the same for the different grades during the first months. But it seems that at the eighth month, the biological maturity is at a same level for all grades.

As for fouling, ATP presents phases of increase and of decrease, which can be linked to the release of biofilm. This observation may be also linked to free potential evolution observed for stainless steels.

However, it seems that at the eighth month, aerobic heterotrophic bacteria have reached a stable value for cement and stainless steels (Figure 4b). For copper and galvanized steel, the contamination is still in an increasing phase at the eighth month. Indeed, the value of aerobic heterotrophic bacteria reported to the dry matter increases for copper and galvanized steel, whereas it decreases for the other materials. That could indicate a mineralization of the biofilm, i.e. secretion of bacteria or exogenous component trap.



a) ATP measurement



b) aerobic heterotrophic bacteria measurement

Figure 4: Threshold of surface contamination: evolution of ATP and aerobic heterotrophic bacteria

From the first month, enterobacteria (Salmonella and Shigella) are examined on cement, polyethylene and stainless steels and at a higher level for cement and PE. Some coliforms are detected at the eighth month on galvanized, stainless steels and cement but at a very low level. The presence of this type of bacteria indicates a maturation of biofilm.

4. CONCLUSIONS

Biological activity in potable water networks can raise the free corrosion potential of stainless steels to values similar to those reported for exposure in seawater or river water. This increase of free potential can also have an effect on the risk of pitting.

By taking into account the presence of free chlorine and according to previous studies [3,4], the pitting potential of stainless steels increases in chlorinated media. On the other hand, anaerobic bacteria, growing in the internal deoxygenized part of the biofilm, may have a detrimental effect on pitting potential through sulphur ions [19,21]. Until now, although free potentials of stainless steels are high, no corrosion is observed in the potable water network. At the end of this study, pitting potentials will be measured on each grade to evaluate the risk of pitting.

For copper and galvanized steel, no corrosion is observed visually but significant corrosion rate is measured and depends on the formation of protective oxides on their surface.

Each tested materials have typical behavior and according to the results after eight months, some differences are observed:

- copper and galvanized steel biostatic materials present the advantage of a slow bacteria development but due to their high corrosion rates, they also present the disadvantage to release heavy metals,
- cement shows the highest fouling and development of micro-organisms,
- PE presents a large surface contamination. In addition, fouling and colonization are still in an increasing step,
- stainless steels have reached a stationary state according to fouling and micro-organisms measurements.

The results for longer exposure time may evidence further differences between materials.

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