Field experience - localized corrosion behavior of lean duplex stainless steel DX2202 in urban wastewater treatment plants

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Thanks to their good corrosion resistance and ease to shape and weld, austenitic stainless steel grades (e.g. EN 1.4404 / 316 L / UNS S31603) are used as standard materials for the construction of urban wastewater treatment plants (WWTP). The main factors influencing the corrosiveness of the fluids in WWTP are halide concentration (more specifically chlorides), H_2S, low pH, high temperature and their combined action. Considering the comprehension of moderate material cost, good corrosion resistance and high mechanical properties, lean duplex stainless steels are good alternatives to the commonly used austenitic grades, but they are still too rarely chosen, probably due to a lack of case studies. To define the limit of use of lean duplex stainless steels for urban wastewater treatment units, a European project was initiated, involving stainless steel manufacturers, end-users, corrosion and microbiological laboratories.

The present paper deals with the localized corrosion performance of lean duplex EN 1.4062 / DX2202 / UNS S32202 in solutions simulating pre-treatment unit waters, compared to the austenitic stainless steel 316 L and the more alloyed duplex grade EN 1.4462 / DX2205 / UNS S32205. Crevice corrosion testing was performed using crevice formers defined in ISO 18070:2015. Both laboratory screen tests and field exposure in urban wastewater treatment plants were performed. This study confirms that lean duplex grade DX2202 can be used as an alternative to 316 L in aerated wet atmospheres in case of moderate contamination of H2S (<10 ppm) and chloride (<200 ppm). For higher contaminations (e.g. H_2S around 100 ppm and chloride content around 1000 ppm) the duplex grade DX2205 should be preferred.

> **KEYWORDS:** STAINLESS STEEL, LEAN DUPLEX, URBAN WASTEWATER TREATMENT PLANT, CORROSION RESISTANCE, CREVICE CORROSION, CHLORIDE CONTENT, H_2S;

INTRODUCTION

For several decades, traditional austenitic stainless steel grades (304 L, 316 L) are a material of choice for the water and wastewater industry especially thanks to their very good resistance to localized corrosion in the presence of chlorides [1]. This type of material is used in a high number of related applications: tubing, tanks and machinery for screening, washing, compacting, dewatering and so forth (Figure 1). It is also used in auxiliary equipment, such as stairs and handrails [2,3].

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Fig.1 - Examples of equipment made of stainless steel (from the left to the right): Flotation unit, anaerobic digestion tower, silo decanter, biodigester.

In most cases, the nature of urban wastewater does not present major corrosion issues for these common austenitic grades. However, under specific conditions, the chloride and the H_2S concentrations can reach critical values inconsistent with the use of these alloys.

Chloride is known to be one of the critical agents affecting the stability of protective passive layers for stainless steels [4]. Usually, the chloride content in municipal wastewater streams, around 50-200 mg/L, does not present major issues for austenitic grade such as 3048 L. However, in certain conditions, chloride concentrations can reach 3 000 - 6 000 mg/L and in extreme cases 10 000 mg/L for seaside-located facilities or when de-icing salts are used during winter [5,6] requiring more corrosion resistant alloys.

H_2S is an acidic gas that will, when combined with moisture, acidify moist film at the metal surface. This results in lowering the pitting potential of the material and therefore decreases its corrosion tolerance, especially toward chlorides [7]. Dry H_2S has little impact on stainless 304L and 316L in terms of corrosion. 316 L is the reference material for moist H_2S. But when 316 L is exposed atmospherically to H_2S with chlorides (splash zones, or marine atmosphere), problems can occur and more corrosion resistant alloys shall be selected, including duplex (austeno–ferritic) stainless steels.

Considering the comprehension of economic cost, good

corrosion resistance and higher mechanical properties, the more recently developed lean duplex stainless steel (DX2202) can be a good alternative to the commonly used austenitic grade (316 L) but is still too rarely chosen, due to rare field experiences in the wastewater industry area. In view of defining the limit of use of selected lean duplex stainless steel grades for urban wastewater treatment units, a European project [8] was initiated, involving stainless steel manufacturers, end-users, corrosion and microbiological laboratories. Both laboratory screen tests and field exposure in urban wastewater treatment plants were performed [9,10]. The experiments carried out during this project aim at bringing data for better framing lean duplex stainless steels limits for wastewater applications, and compare them to commonly used austenitic grades.

The present paper deals with the localized corrosion performance of lean duplex DX2202 in solutions simulating pre-treatment unit waters. Results were compared with the austenitic stainless steel 316 L and with the more alloyed duplex grade DX2205. Crevice corrosion testing was performed using crevice formers defined in ISO 18070:2015. Exposures of crevice coupons in field municipal wastewater plants were also conducted for 1 year in a low chloride content unit (Brussels, Belgium) and in a high chloride content unit (Cap Sicié, near Toulon, France).

MATERIALS AND METHODS
Materials
The following lean duplex stainless steel grade was sup-

plied for this project: DX2202 (UNS S32202, EN 1.4062), together with a duplex stainless steel grade DX2205 (UNS S32205, EN 1.4462). The austenitic stainless steel grade 316 L (UNS S31603, EN 1.4404) was used as reference material. All are industrial cold rolled materials with a 2E surface fini-

sh and a plate thickness of 3 mm. Table 1 gives the chemical composition of the tested alloys and their pitting resistance equivalent number (PREN).

Tab.1 - Chemical composition (%w) of the selected grades and PREN (%C + 3.3%Mo + 16%N).

Grades	316 L	DX2202	DX2205
UNS	S31603	S32202	S32205
EN	1.4404	1.4062	1.4462
C	0.0248	0.0225	0.0134
Cr	16.7	23.1	22.7
Ni	10.0	2.6	5.5
Mo	2.0	0.2	3.1
N	0.0498	0.1923	0.1710
Mn	1.2	1.3	1.8
S	0.0016	0.0005	0.0006
P	0.03	0.03	0.03
Fe	Bal.	Bal.	Bal.
PREN	24	27	35

The PREN formula is often used to estimate the localized corrosion resistance ranges of stainless steel from their chemical composition. It is given by PREN = %Cr + 3.3(%Mo) + 16(%N). The PREN must be used with care since this number does not consider other very important parameters, such as the metallurgical state of the alloy, the nickel content, or the surface state. The surface finishes were "as-received" with Ra at 3 ± 1 μm. The metallographic inspections indicated normal microstructures for these materials. The ferrite fraction represents 55% and 50% for DX2202 an DX2205 respectively.

Samples were cut to 150 × 100 mm. All cut edges were polished to P600. Holes were drilled to hold samples and to set crevice formers when needed.

Crevice assembly

The risk of crevice corrosion was evaluated using crevice formers simulating service conditions in confined environ-

ments (e.g., crevice geometry that may be encountered below a given gasket material). Standard crevice assemblies were used for this purpose, according to ISO 18070:2015 [11]. With this assembly, a rather well-defined crevice geometry can be obtained with a controlled pressure at the gasket location. It has the following characteristics: Crevice formers are made of polyvinylidene fluoride (PVDF), all fasteners are made of titanium grade 2, electrically isolated from the tested specimen, and disc springs are used to keep a measurable and constant pressure between the crevice formers and the specimen. The crevice formers were tightened to the test specimens with a force of about 900 N (i.e. a pressure of about 3 N/mm²), which corresponds to a torque of 3 N·m on the used fasteners. A schematic representation and a picture of the crevice assembly are shown in Figure 2. The anode (surface under crevice formers) to cathode (surface in contact with the bulk environment) ratio was about 1:30.
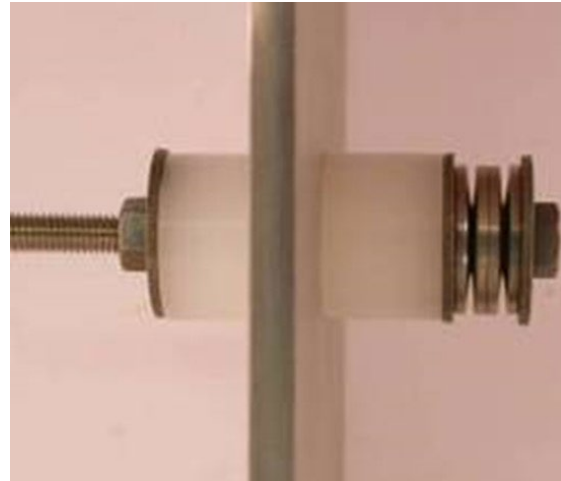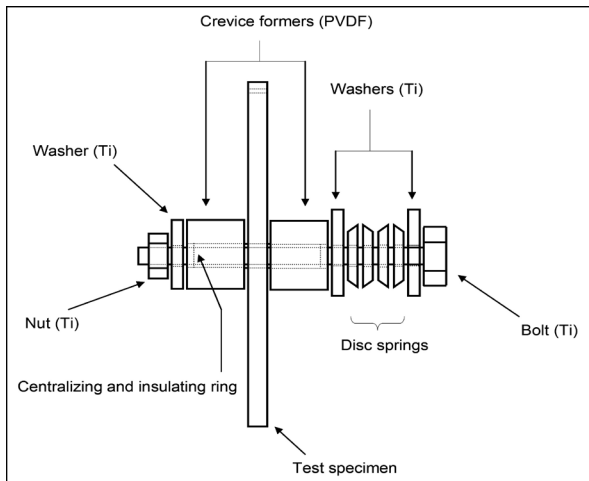
Fig.2 - Schematic representation and picture of the crevice assembly ISO 18070:2015 [11].

EXPOSURE CONDITIONS
Laboratory exposures

a. Corrosion resistance in immersion

All exposures were performed at the open-circuit potential. The tested chloride contents ranged from 200 ppm to 3000 ppm, for two tested temperatures at 35°C and 50°C. All tests were performed at saturated dissolved oxygen using continuous air bubbling. For each test condition, the exposure duration was 30 days. Five replicates were used per tested alloy for crevice samples. Two regulated exposure tanks (1000 L) have been specifically designed for the corrosion tests. The heating was controlled with the use of titanium heaters and the homogeneity in temperature was ensured with permanent stirring pumps. The chloride concentrations were reached by mixing demineralized water (0.1 μs/cm) with NaCl reagent grade. The pH was adjusted and controlled to pH 6.0 ± 0.2 using punctual addition of hydrochloric acid 0.1 N.

b. Corrosion resistance in atmospheric conditions with H_2S

Corrosion tests in the moist environment were implemented to simulate the conditions of exposure of materials in humid units that can generate H_2S gas. The test vessel consisted of a sealed glass cell with the specimens suspended from the cover and exposed to the atmosphere in equilibrium with a saturated K_2SO_4 solution to ensure a relative humidity (RH) of 97% in the headspace of the cell.

The test matrix has been defined from the collected field data (survey from Veolia wastewater plants) in terms of possible ranges in chloride and H_2S contents. The selected conditions are given in Tab. 2. In all cases, the start of the tests was defined as the time when the outgoing gas composition reached the target values. Four replicates have been tested for each test condition and alloy.

Tab.2 - Test conditions for corrosion tests in presence of H2S in moist environments.

	T (°C)	Cl- (ppm)	H_2S (ppm)	Aerated	Concerned application
#A	35	100	100	Yes	Municipal WWTP / gas phase
#B	50	2000	2000	No	Methaniser
#C	35	1000	1000	Yes	Municipal WWTP / gas phase
#D	50	4000	4000	No	Methaniser

Abbreviation: WWTP; wastewater treatment plant.

Field exposures

Two sites have been selected for real condition exposures to represent standard and harsh conditions. These sites are:
- The Brussels municipal WWTP (Belgium)
- The coastal Cap Sicié WWTP (near Toulon, France)

Coupons were exposed in immersed conditions in the pretreatment buildings at the inlet works (screen step to remove large particles) and in wet conditions, at approximately 1 meter above the water level. The main characteristics and environmental conditions of the two units are given in Table 3.

Tab.3 - Main characteristics of the units used for field exposures.

	Brussels WWTP	**Cap Sicié WWTP**
Capacity (eq. inhabitants)	1.4M	0.5M
Year of construction	2007	1998
Temperature range (°C)	10-20°C	10-30°C
pH range	6-8	6-8
Chloride mean/(max) (ppm)	160/(400)	2470/(4100)
H_2S gaseous range (ppm)	2-10	5-100

The concentrations of chloride and H_2S are about 10 times higher in Cap Sicié compared to Brussels WWTP. The samples have been installed on structural modules for exposure in immersion and in atmosphere. For all alloys, five replicates of crevice samples have been tested.

Fig.3 - Illustration of the field exposure of corrosion modules at the Brussels WWTP.

RESULTS – DISCUSSION

Exposures in simulated solutions
Corrosion resistance in immersion
The crevice corrosion results obtained with ISO18070:2015 crevice assembly are given in Table 4 and Table 5. They indicate the total number of corroded specimens (out of the 5 tested replicates) and the maximum corrosion attacks for the less corroded replicates and the most corroded replicate (reported as min. and max. corrosion attack respectively). A typical aspect of the corroded alloys after exposures at 35°C/3000-ppm Cl⁻/pH 6 and 50°C/500-ppm Cl⁻/pH 6 are presented in Figures 3 and 4, respectively.

The results show that localized corrosion, when initiated,

always occurred below gaskets (crevice corrosion) close to the interface with the bulk environment, whatever the tested condition and the alloy.

Tab.4 - Crevice corrosion results using ISO18070:2015 crevice assemblies—the number of crevice samples is indicated (x/5) together with minimum and maximum crevice depth measured on five replicates after 1 month of immersion at 35°C, pH 6.

Grades	Chloride content (ppm)			
	200	500	1000	3000
316 L	0/5 ●	2/5 ⊘ 0 / 15µm	2/5 ✗ 0 / 34µm	3/5 ✗ 0 / 121µm
DX2202	0/5 ●	1/5 ⊘ 0 / 14µm	1/5 ✗ 0 / 41µm	3/5 ✗ 0 / 108µm
DX2205	0/5 ●	0/5 ●	0/5 ●	0/5 ●

✗ Corrosion
● No corrosion
⊘ Superficial corrosion attack (etching)
▬ Not tested (corrosion at lower concentration)

Number of corroded duplicated → x/5 ✗ y µm ← *Min. corrosion attack* / z µm ← *Max. corrosion attack*

Tab.5 - Crevice corrosion results using ISO18070:2015 crevice assemblies—the number of crevice samples is indicated (x/5) together with minimum and maximum crevice depth measured on five replicates after 1 month of immersion at 50°C, pH 6.

Grades	Chloride content (ppm)			
	200	500	1 000	3 000
316 L	0/5 ●	2/5 ⊘ 0 / 15µm	3/5 ✗ 0 / 32µm	▬
DX2202	0/5 ●	3/5 ⊘ 0 / 15µm	2/5 ✗ 0 / 26µm	▬
DX2205	0/5 ●	0/5 ●	0/5 ●	1/5 ✗ 0 / 31µm

✗ Corrosion
● No corrosion
⊘ Superficial corrosion attack (etching)
▬ Not tested (corrosion at lower concentration)

Number of corroded duplicated → x/5 ✗ y µm ← *Min. corrosion attack* / z µm ← *Max. corrosion attack*

At 35°C and 50°C, no crevice corrosion initiated on any tested alloys at a chloride content of 200 ppm. For a chloride content of 500 ppm, 316 L and DX2202 showed only superficial attacks. Superficial attack or etching corresponds to limited corrosion pits, below 25µm, without propagation according to the MTI procedure for localized corrosion assessment [12]. Under the same test conditions, DX2205 resisted crevice corrosion both at 35°C and 50°C. At 50°C, the DX2205 only failed at 3000 ppm.
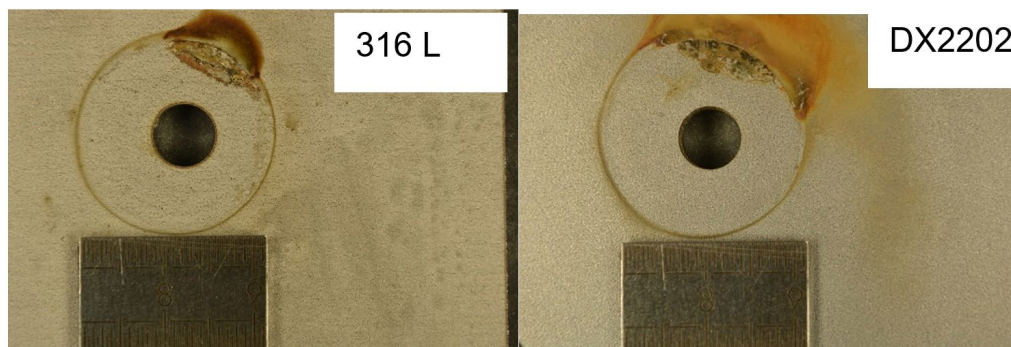
Fig.4 - Typical aspect of corroded samples after exposure in condition 3000ppm Cl⁻, 35°C, pH 6 with ISO18070:2015 crevice assembly.
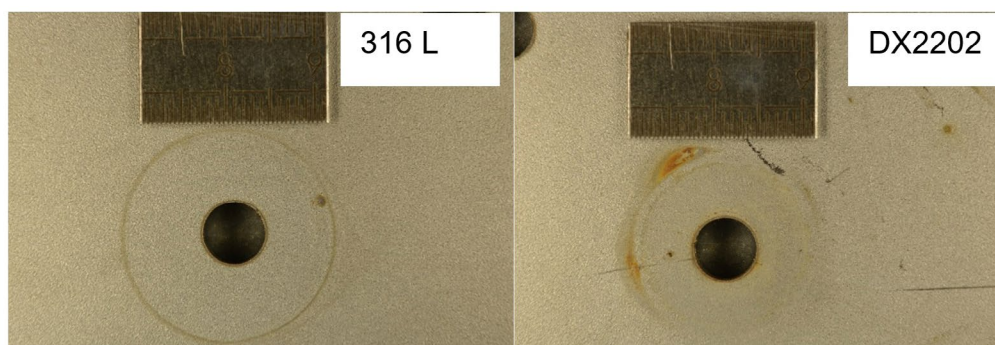

Fig.5 - Typical aspect of corroded samples after exposure in condition 500ppm Cl, 50°C, pH 6 with ISO18070:2015 crevice assembly.

The results draw rather clear trends regarding the limits of use of tested alloys in terms of resistance to localized corrosion, since the corrosion of one replicate is enough to indicate that the alloy is potentially susceptible to localized in the concerned condition. DX2202 presents a moderate crevice corrosion resistance, at the same level that of 316 L for the tested conditions. DX2205 is the grade that exhibits the highest crevice corrosion resistance in the tested experimental conditions.

Corrosion resistance in atmospheric conditions with H2S
The crevice corrosion results for all test conditions in moist H2S are summarized in Table 6.

Tab.6 - Crevice corrosion results after 1 month of exposure in conditions #A, #B, #C, and #D with ISO18070:2015 crevice assembly.

Grades	Aerated moist H₂S		Anaerobic moist H₂S	
	#A	**#B**	**#C**	**#D**
	35°C	**35°C**	**50°C**	**50°C**
	Chloride 1000 ppm	**Chloride 1000 ppm**	**Chloride 2000 ppm**	**Chloride 1000 ppm**
	H₂S 100 ppm	**H₂S 1000 ppm**	**H₂S 2000 ppm**	**H₂S 4000 ppm**
316 L	0/4 ●	4/4 ✖ 25μm 39μm	2/4 ✖ 0 26μm	4/4 ✖ 0 26μm
DX2202	0/4 ●	3/5 ✖ 25μm 37μm	2/4 ✖ 0 22μm	4/4 ✖ 0 25μm
DX2205	0/4 ●	0/4 ●	0/4 ●	0/4 ●

In aerobic tests conditions, at low H_2S content (100ppm), no corrosion occurred. The increase of H_2S content, from 100ppm to 1000ppm significantly affected the crevice corrosion resistance of the tested alloys (316 L and DX2202) except for DX2205 that still resisted to crevice corrosion. In anaerobic tests conditions, the lean duplex DX2202 and the commonly used austenitic 316 L grades showed crevice corrosion; while the duplex DX2205 grade is resistant to crevice corrosion.

Field exposure results

The corrosion results from field exposure tests in Brussels WWTP and in Cap Sicié WWTP are given in Tables 7 and 8 for immersed samples and samples exposed in moist environment respectively.

Corrosion resistance in immersion

Tab.7 - Crevice corrosion results after 1-year exposure in pretreatment units of the wastewater treatment plants (WWTP) in Brussels (mean chloride 160 ppm) and in Cap Sicié (mean chloride 2470 ppm) with ISO18070:2015 crevice assembly; immersed samples.

Grade (UNS)	Brussels WWTP		Cap Sicié WWTP		
316 L	0/5	🟢	5/5	✗	25 32μm
DX2202	0/5	🟢	5/5	✗	25 30μm
DX2205	0/5	🟢	0/5	🟢	

The crevice corrosion resistance of all the alloys is good when samples were immersed in Brussels plant while only DX2205 resisted corrosion when immersed in Cap Sicié plant. One can note that only sludge was observed on samples immersed in Brussels plant
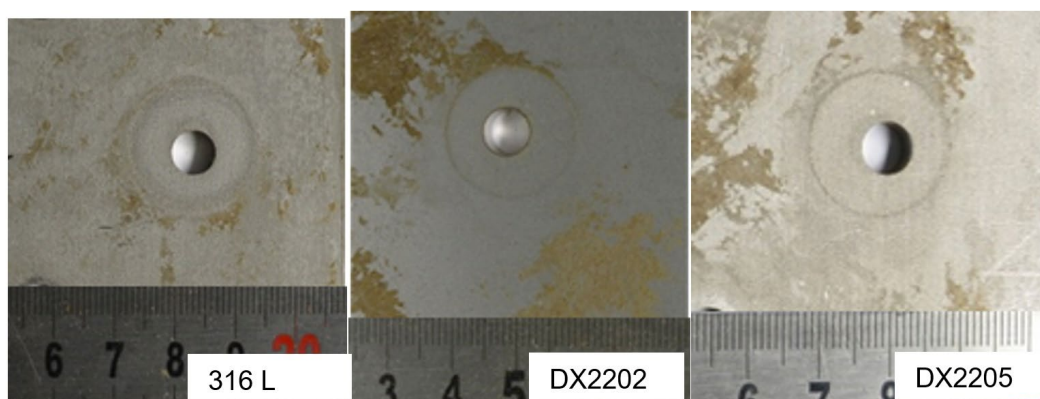

Fig.6 - Typical aspect of samples after 1-year immersion in the pretreatment unit of the Brussels plant.

Fig.7 - Typical aspect of corroded samples after 1-year immersion in the pretreatment unit of the Cap Sicié plant.

The localized corrosion results are in very good line with the ones obtained in simulated waters showing the closest chloride content at 35°C for Brussels and for Cap Sicié, respectively (Table 4).

Corrosion resistance in atmospheric conditions with H_2S

The corrosion results (wet conditions with samples exposed 1 meter above water level) from field exposure tests in Brussels WWTP and in Cap Sicié WWTP are given in Table 8.

Tab.8 - Crevice corrosion results after 1-year exposure in pretreatment unit of the wastewater treatment plants (WWTP) in Brussels (mean chloride 160 ppm) and in Cap Sicié (mean chloride 2470 ppm) with ISO18070:2015 crevice assembly; samples above the water level.

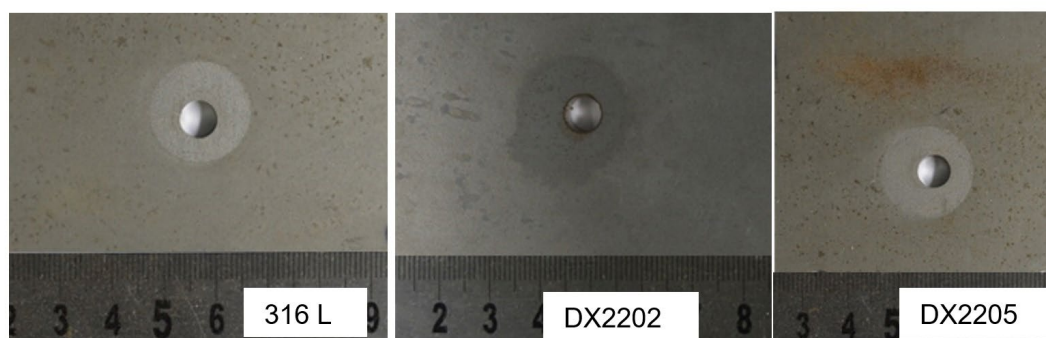| Grade (UNS)	Brussels WWTP		Cap Sicié WWTP		
316 L	0/5	🟢	5/5	❌	510 650µm
DX2202	0/5	🟢	5/5	❌	590 605µm
DX2205	0/5	🟢	0/5	🟢	

Fig.8 - Typical aspect of samples after 1-year exposure in pretreatment unit of the Brussels plant, 1 meter above the water level.
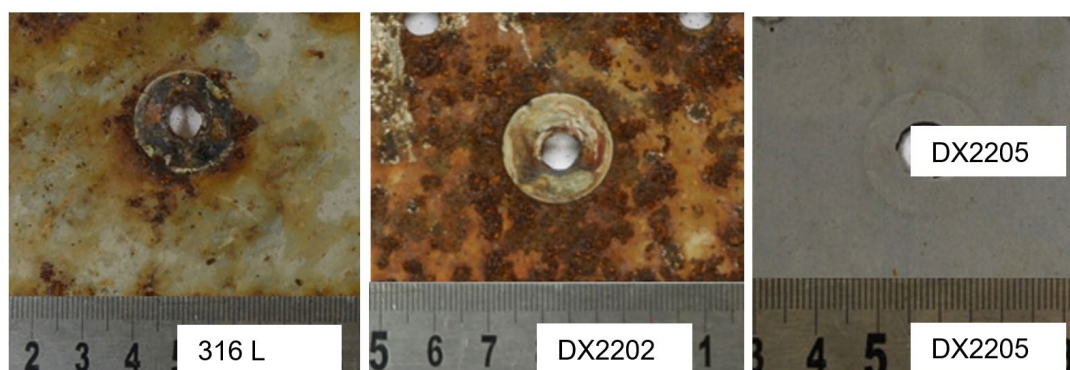
Fig.8 - Typical aspect of samples after 1-year exposure in pretreatment unit of the Cap Sicié plant, 1 meter above the water level.

No corrosion occurred on samples exposed in Brussels WWTP, as predicted from exposures in simulated water containing similar chloride content (Tab. 6). The results from Cap Sicié containing 10 times higher H_2S content (Table 3) were much more severe. A depassivation of the surface occurred on 316 L and DX2202 which showed uniform and localized corrosion. The combination of H_2S and oxygen in a wet atmosphere associated with chloride contamination is a severe cocktail for low-grade stainless steels. The corrosivity and observed depassivations (localized or generalized) might be attributed to the formation of corrosive compounds involving elemental sulfur, thiosulfate, and acidification processes in the presence of chloride. Deeper investigations would be required to assess the relative influence of these parameters and their synergy.

Under these severe conditions, only DX2205 resisted corrosion.

CONCLUSION

For all the tested conditions (immersion or moist environment, laboratory of field exposure), the EN 1.4062 / DX2202 / S32202 lean duplex showed similar corrosion resistance to the austenitic grade EN 1.4404 / 316L / 316 L.
In Brussels where H_2S content is low (2–10 ppm) and chloride below 200 ppm, all tested alloys resisted corrosion. In wet aerated conditions, the presence of H2S combined with NaCl contaminations (in the range of levels encountered in the Cap Sicié WWTP) was extremely severe for EN 1.4404 / 316 L / UNS S31603 but also for the tested lean duplex EN 1.4062 / DX2202 / UNS S32202. These alloys cannot be recommended for harsh environments.

EN 1.4062 / DX2202 / UNS S32202 can be used as alternative alloy to EN 1.4404 / 316 L / UNS S31603 grade in WWTP presenting standard conditions with limited chloride contamination (<200 ppm) and limited H_2S content (<100 ppm) while EN 1.4462 / DX2205 / UNS S32205 should be preferred for harsh conditions.

The results from field exposures (1 year) showed good correlation with the laboratory results in simulated environments, providing confidence in the test method for future investigations.

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