EFFECT OF HIGH CONCENTRATIONS OF CHLORINE AND SULPHIDE ON STAINLESS ALLOYS IN SEAWATER

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CONTENTS

ABSTRACT

A range of stainless steels and nickel base alloys has been tested for crevice corrosion in strongly oxidising or reducing seawater environments: (i) natural seawater with high chlorine concentration (10 mg/l^{-1} residual) at 45°C; (ii) natural seawater with high sulphide concentration (1 g/l^{-1}) at ambient temperature. In sulphide polluted seawater, the tested stainless steels (S31254, S32654, S31803 and S31603) were immune from crevice corrosion after 95 days of exposure. In chlorinated water, only the S32654 steel (654 SMO™⁽¹⁾) was unaffected by crevice corrosion. The other materials (S31254, S32750, N06625 and N10276) were attacked by crevice corrosion.

1. INTRODUCTION

The corrosion resistance of stainless alloys in natural seawater has been the subject of many studies during the last two decades. The increased use of these alloys, especially of the stainless steels, and the need for reliable seawater systems, have led to the development of several "new" seawater resistant stainless alloys by different suppliers. Even if these materials exhibit good corrosion resistance in natural seawater at ambient temperature, the risk of failure remains important in extreme conditions such as high temperature, high concentrations of chlorine or of pollutants like sulphides.

It is well known that biological activity in seawater may cause many practical difficulties due, for instance, to the increase of friction losses or to the decrease of thermal efficiency. Chlorination is often used to prevent or at least lessen biofouling formation. Chlorine, however, is a strong oxidant which increases the risk of pitting and crevice corrosion. Some investigations have been made regarding the corrosion behavior of stainless steels in chlorinated seawater but few data are available concerning nickel base alloys.

If biological activity in seawater develops, it leads to modified chemical conditions due to the metabolites. For instance, the activity of sulphate-reducing bacteria is associated with the an increased presence of sulphides.

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It is noticeable that in a natural environment, there are both biotic and abiotic sources of sulphides. Very few data are available concerning sulphide effects on the corrosion of highly alloyed stainless steels or nickel base alloys.

The aim of this study is to evaluate the crevice corrosion behavior of these highly alloyed stainless materials (superaustenitic and superduplex stainless steels, nickel base alloys) under "extreme" seawater conditions. Two conditions have been selected, which correspond to strongly oxidising or reducing environments: (i) natural seawater with high chlorine concentrations (10 $mg.l^{-1}$ residual) at high temperature (45°C) on the one hand, (ii) natural seawater with high sulphide concentration (1 $g.l^{-1}$) at ambient temperature on the other.

2. EXPERIMENTAL PROCEDURE

2.1. Test Conditions

The seawater exposure was performed at La Hague peninsula (Normandy, France). The seawater was taken from the sea surface, near the coast, in the tidal zone. The two tests were carried out in the SIRIUS facility which is mainly made of titanium, and which is capable of reproducing many seawater treatments (decarbonization or deoxygenation) or pollutants. For these two experiments, tested specimens were immersed in 100 liter titanium vats. The seawater used for these tests had the following characteristics: pH = 8.1 (standard deviation: 0.1); total conductivity = 7.8 (0.2) $mS.cm^{-1}$; chloride concentration = 20 (1) $g.l^{-1}$. The two experiments lasted 95 days.

When investigating sulphide pollution, the seawater was polluted by the addition of 1 $g.l^{-1}$ of sulphide as Na_2S at the beginning of the test (750 g of Na_2S, $12H_2O$ added in the 100 l titanium vat). The polluted seawater was recirculated at a flow rate of 30 - 40 liters per hour. The pH was planned to be maintained between 6 and 8 by additions of hydrochloric acid or sodium hydroxide if necessary. The evolution of sulphide concentration in the 100 l titanium vat was followed by chemical analyses. Sulphides were analyzed with the methylene blue method(2), by photometric measurements at 665 nm: the results are expressed as S^{--}, but include HS^- and S^{--}.

The seawater was chlorinated by addition of a sodium hypochlorite solution into a 5 m^3 tank. The residual chlorine concentration was planned to be 10 mg/l^{-1}. The chlorine concentration in the 5 m^3 tank was checked at least each 100 hours and sodium hypochlorite added if needed. The chlorinated seawater was pumped from this tank to a 100 liter titanium vat a flow rate of around 10 liters per hours, so that the retention time was approximately 10 hours: the conditions are nearly stagnant but with a renewed chlorinated seawater. Electric heaters maintained the seawater temperature at 45°C. Residual chlorine was determined with the p-phenylenediamine method(3), by photometric measurements at 557 nm.

During both experiments, the free corrosion potentials (E_{cor}) were measured against an Ag-AgCl reference electrode but are reported versus Saturated Calomel reference electrode (E_{cor}/SCE = E_{cor}/Ag-AgCl + 44 mV). The measurements which included not only free corrosion potentials, but also redox potentials, pH and temperature, took place each hour. The electrical connection on stainless alloy electrodes consisted of an insulating wire which was attached to the electrode by welding. The welded area and the part of the wire without electrical insulation were masked by a rubber primer. This electrical insulation was checked at the beginning and at the end of each experiment.

2.2. Test Material

Five stainless steels and two nickel base alloys, the chemical compositions of which are shown in Table 1, have been investigated. The choice of material has not been the same for the two tests but has been made according to the expected corrosivity of the environment. The chlorinated water was judged to be the most corrosive and here only the highest alloyed stainless steels and nickel base alloys were tested:

- the stainless steels consisted of a superaustenitic 6Mo steel (S31254), a further development of that type of steel (S32654) and a superduplex steel (S32750).
- the nickel base alloys were those most commonly in use for corrosion resistance today (N06625 and N10276).

In the sulphide polluted seawater, only stainless steels, ranging from S31603 and 22Cr duplex steel (S31803) to the two superaustenitic grades, were used.

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(2) Spectroquant®-MERCK

(3) Spectroquant®-MERCK

Table 1
Chemical composition of the test material

Alloy	Chemical composition %										
UNS #	C	Si	Mn	P	S	Cr	Ni	Mo	Fe	N	Cu	Other
S 31603	.023	.47	1.48	.015	.001	16.80	11.19	2.16	Bal	-	-	
S 31803	.018	.45	1.43	.021	.003	21.76	5.67	3.01	Bal	.170	-	
S 32750	.022	.16	.35	.015	.001	24.29	6.62	3.74	Bal	.284	-	
S 31254	.014	.34	.43	.022	.001	20.06	17.89	6.11	Bal	.198	.80	
S 32654	.017	.26	1.97	.023	.001	24.24	22.25	7.09	Bal	.460	.45	
N O6625	.017	.29	06	.007	.002	21.30	Bal	8.52		-	-	Ti .34, Nb 3.46
N 10276	.006	.02	.021	.005	.004	15.9	Bal	16.50	7.6	-	-	W 3.1

The test specimens were taken from commercially produced, cold rolled material, the thickness of which was approximately 3 mm for all alloys except for N06625 (1.25 mm). The material was tested with as delivered (pickled) surfaces with the exception of S32750 which had a ground (220 grit) surface.

Two kinds of test specimens were used: coupons and electrodes. The coupons were rectangular specimens (200x70 mm) as shown in Figure 1. When fabricating the coupons, two plates were butt welded (GTAW) to form the specimen. The welding was done in one pass using filler materials, the chemical compositions of which are given in Table 2. The gas protection consisted of pure argon except for S32654 where argon plus 10% nitrogen was used for torch protection and argon plus 10% hydrogen for root protection. In order to remove any oxide, the welds and surrounding areas were sand blasted and the specimens were briefly pickled. The second type of specimens (electrodes) was intended for corrosion potential measurements. The electrodes which were unwelded had a flag shape, as shown in Figure 1.

Both coupons and electrodes were equipped with crevice formers taken from a commercial gasket material (Klinger Sil C-4400), consisting of rubber bound aramid fibre. The crevice formers were punched from a 2 mm thick sheet and had a diameter of 24 mm and a 12 mm hole in the center. They were applied on both sides of the specimens and were fixed into position by PTFE insulated bolts and nuts made of titanium. The bolts were torqued to 40 Nm immediately before the exposure of the specimens. The ratio between bold and creviced areas was approximately 40:1.

In both experiments, three coupons and one electrode of each alloy were tested. The specimens were mounted on titanium rods which were insulated by PTFE. The electrodes had part of the "flag staff" above the liquid level in order to avoid problems with corroding electrical connections.

2.3. Corrosion Evaluation

After the tests, the specimens were photographed before cleaning which was accomplished by a short (60 seconds) pickling. The weight losses were then determined to a precision of 1 milligram and the specimens were carefully inspected in a stereo microscope at 20x magnification. If localized corrosion was detected, the depth of the attack was measured by means of a needle point micrometer or a microscope with a calibrated fine-focus knob. In a few

Table 2

Welding parameters and chemical composition of filler materials

Alloy UNS #	Filler	Arc Energy kj/mm		Chemical composition %				
			Cmax	Cr	Ni	Mo	N	Other
S 31603	316 L	1.0	.025	18.5	12.5	2.7	-	-
S 31803	2205	0.8	.020	22.5	8	3	.14	-
S 32750	2507/P100	1.2	.020	25	10	4	.25	-
S 31254	P 12	1.2	.035	21	Bal	9	-	Nb
S 32654	P 16	1.2	.025	23	Bal	16	-	-
N 06625	P 12	1.2	.035	21	Bal	9	-	-
N 10276	C-276	1.2	.020	16	Bal	16	-	W

Notes : P 12, P 16 and 2507/P 100 are trademarks of Avesta Welding AB.

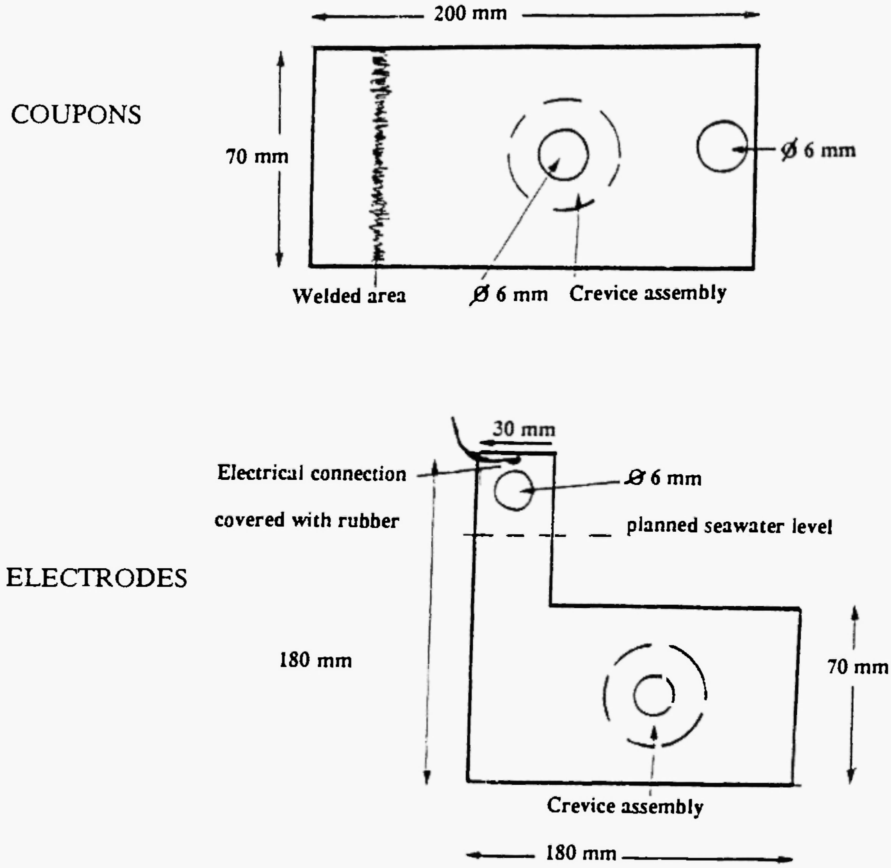

Fig. 1: Specimen configuration

cases, a metallographic investigation was also carried out.

Besides the microscopic examination, a profilometric survey was performed on one coupon of each alloy tested in the chlorinated seawater. The profilometry was accomplished by means of a scanning tactile microscope. With this method, the shape of crevice attacks can be reproduced. Semi-quantitative analyses were also performed on the specimens at the end of the experiments, using a scanning electron microscope equipped with an EDX analyser.

3. RESULTS

3.1. Temperature

The temperatures were fairly constant during the two tests as indicated by the low standard deviation values in Table 3, where the mean values with the standard deviations are reported. The sulphide pollution test was performed at a mean temperature of 17.6°C. It can be seen that the chlorination test had a mean temperature slightly higher (46.5°C) than expected (45°C).

3.2. Chemical and Electrochemical Measurements

The measurements related to the chemistry of the two tests (i.e. pH and sulphide or chlorine concentrations) are also reported in Table 3, and their evolution is shown in Figures 2 and 3. The mean redox and free corrosion potentials are also reported in Table 3.

3.2.1. Chlorinated Seawater. Chemical parameters were fairly constant during the chlorination test, as shown in Figure 2. The pH of the chlorinated seawater was maintained between 8.0 and 8.1. The residual chlorine concentration was the more fluctuating parameter, with values between 7.6 and 13 $mg.l^{-1}$, the mean value being 9.2 $mg.l^{-1}$ in the 5 m^3 tank. At the beginning of the test, residual chlorine was also analysed at the outlet of the titanium vat: with a residual chlorine concentration of 10.8 $mg.l^{-1}$ in the 5 m^3 tank, i.e. at the inlet of the titanium vat, the chlorine concentration at the outlet of the titanium vat was 9.2 $mg.l^{-1}$. This shows that there was a decrease of residual chlorine concentration during the stay of the chlorinated seawater in the titanium vat (approximately 10 hours at 45°C), but this decrease was limited to about 15%.

The redox potential was very high and very constant during the test (Figure 4): +719 mV/SCE, with a standard deviation of 11 mV.

The free corrosion potentials varied as shown in Figures 4 and 5. The S32654 steel had a stable potential from the beginning of the test to its end: around +400 mV/SCE. The free corrosion potential of N10276 nickel base alloy was more noble and very stable, except during the first 350 hours when instabilities and lower values were recorded. The value of N10276 mean potential was 453 mV/SCE; it was the highest obtained during this test, but its standard deviation (70 mV) was greater than the standard deviation of

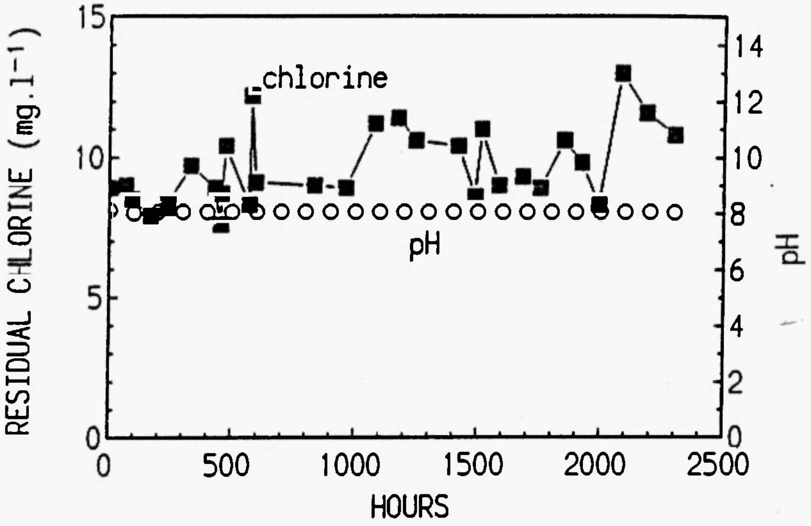

Fig. 2: pH and residual chlorine evolution

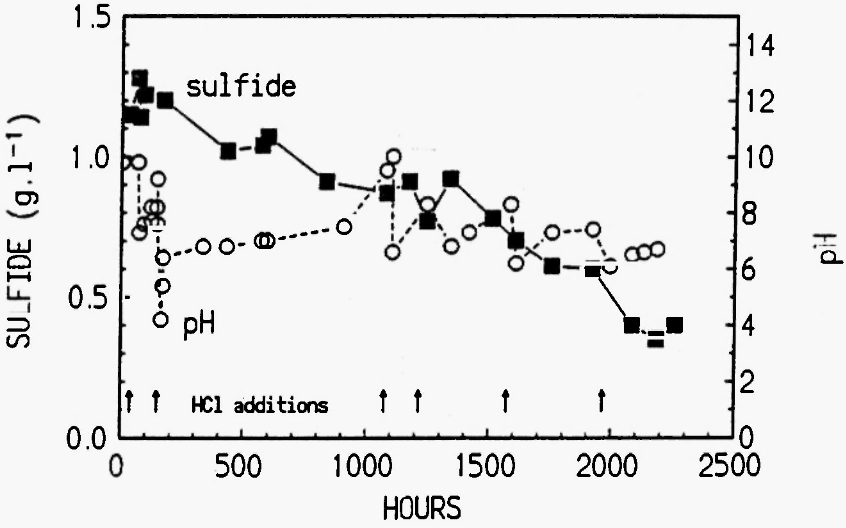

Fig. 3: pH and sulphide evolution

the S32654 potential (25 mV), meaning that the N10276 potential was less stable. The free corrosion potentials of the three other alloys had nearly the same evolution: instabilities during the whole test, lower values at the

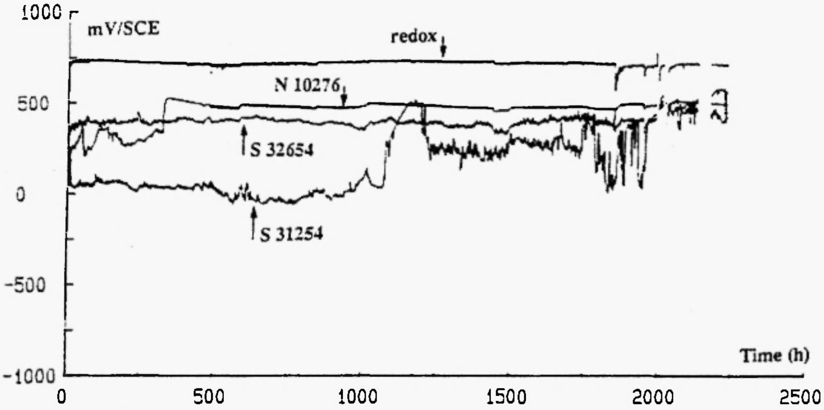

Fig. 4: Evolution of the redox and the corrosion potentials of S31254, S32654 and N10276 during the chlorination test

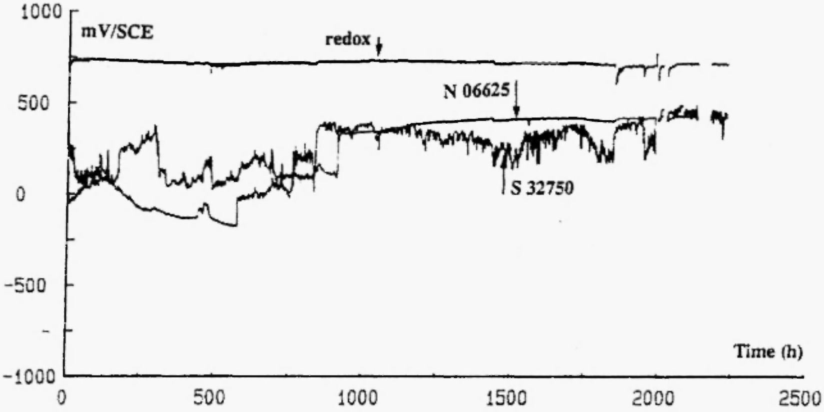

Fig. 5: Evolution of the redox and the corrosion potentials of S32750 and N06625 during the chlorination test

beginning and higher values after 800 h to 1100 h. The lower mean potential, 175 mV/SCE (standard deviation 177 mV) was obtained with S31254 superaustenitic stainless steel; the potentials of the S32750 superduplex stainless steel, and of the N06625 nickel base alloy, were nearly the same: respectively, 257 mV/SCE and 231 mV/SCE, but the standard deviations were different: 127 mV for the S32750 and 212 mV for the N06625. It was noticed that the N06625 potential was very stable at the end of the test.

Table 3

Mean values (standard deviations) of the main test parameters

	Sulfide pollution	Chlorination
Temperature	17.6 (1.4)°C	46.5 (1.2)°C
pH	7.45 (1.27)	8.05 (0.07)
$S^{=}$ ($g.l^{-1}$)	0.81 (0.26)	-
Residual Cl_2 ($mg.l^{-1}$)	-	9.2 (1.6)
Redox potential (mV/SCE)	- 494 (40)	+ 719 (11)
Free Corrosion Potential (mV/SCE)		
S 31803	- 514 (26)	-
S 32750	-	+ 257 (127)
S 31603	- 505 (31)	-
S 31254	- 506 (26)	+ 175 (177)
S 32654	- 515 (29)	+ 396 (25)
N 06025	-	+ 231 (212)
N 10276	-	+ 453 (70)

3.2.2. Sulphide Polluted Seawater. Difficulties were met in pH measurements and in maintaining pH values between 6 and 8: sulphide poisoned the pH electrode which was inside the 100 l titanium vat for continuous measurements; so only discontinuous pH measurements were made on samples of sulphide polluted seawater. The pH mean value was 7.45, but large fluctuations were observed: between 4.2 and 10.0.

Because sulphide was added as Na_2S, the formation of H_2S in the gaseous phase led to the alkalinization of the solution (seawater) due to the following reactions:

$$S^{--} + H^+ \rightarrow HS^- \text{ and } HS^- + H^+ \rightarrow H_2S$$

HCl additions decreased the pH as shown in Figure 3, but also led to the formation of H_2S. The pH increases during the test were due to H_2S escapes. This was in accordance with the decrease of sulphide concentration in seawater (S^{--} + HS^-) (Figure 3). The sulphide mean concentration was 0.8 $g.l^{-1}$, but sulphide decreased regularly from 1.2 $g.l^{-1}$ at the beginning of the test to 0.4 $g.l^{-1}$ at the end.

Redox potential was low, nearly -500 mV/SCE, but fairly constant (standard deviation 40 mV), even if its variations are correlated with HCl additions (Figure 6). The free corrosion potentials of all the tested alloys are in the same range, between -500 mV/SCE and -515 mV/SCE. They also have the same evolution as shown in Figure 6: slight increases of less than 80 mV when HCl is added, and slow decreases between the HCl injections.

3.3. Corrosions

3.3.1. Chlorinated Seawater. As expected, there was no slime or biofouling on specimens after the test. The stainless steel specimens had a very clean appearance but on those specimens that had been attacked by crevice corrosion, dark brown rust staining spread downwards from the mouth of the crevice. The nickel base N06625 had a dense gray-bluish discolouration and a very pronounced rust staining coming from the crevices. The N10276 specimens were grayish and had a few rust spots on the bold surfaces as well as close to the crevice formers. The immersed parts of the electrodes had the same appearance as the coupons. At the liquid level, however, there was light rust staining on all specimens except on N06625 where a distinct, black line existed.

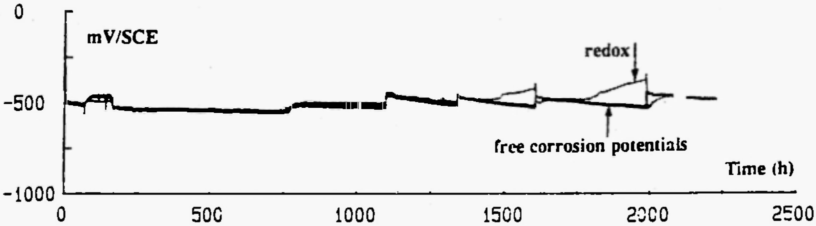

Fig. 6: Evolution of the redox and the corrosion potentials during the sulphide pollution test

The observations made on the coupons and electrodes are summarized in Table 4 and illustrated by photographs shown in Figures 7 to 13. Besides crevice corrosion under the gaskets, all alloys except S32654 were attacked by other types of corrosion.

In the gas phase above the water level, all alloys except S32654 and N10276 were slightly etched at the mounting holes of the electrodes. The gas phase attack was more severe on N0-6625 electrode (Figure 11): the whole area above the water line was etched but the attack was most pronounced at the water level.

Both nickel base alloys exhibit a very distinct corrosion circle around and exactly at the mouth of the aramid crevice (Figures 9 and 10). This type of corrosion existed on all nickel base specimens. A profilogram showing this type of attack is presented in Figure 13. As can be seen in Figure 9, areas covered by corrosion products (from the crevice) are etched too on N06625. Quite unexpectedly, a few pits were observed on N10276 specimens in places where rust spots could be seen after the exposure. A section of such a pit is shown in Figure 14.

3.3.2. Sulphide Polluted Seawater. At the end of the test, there were white but not adherent deposits on specimens exposed to sulphide polluted seawater. These deposits were removed simply by washing the specimens with deionised water. The coupons and the immersed parts of the electrodes did not show any discolouration at all, with the exception of the S31603 specimens where a few distinct dark brown spots existed in the weld areas. In those parts of the electrodes exposed to gas phase, grey spots were found on S31803 and dark grey spots on S31603.

As shown in Table 5, there was no crevice corrosion on any alloy and the

Table 4

Main corrosion results of the chlorination test

Alloy UNS#	Highest weight loss $g/m^2.h$	Crevice corrosion under gaskets	Corrosion in the gas phase	Other types of corrosion
S 32654	< 0.001	0/8 -	No	No
S 31254	0.002	7/8 , 0.98 mm	Yes	No
S 32750	< 0.001	2/8 , 0.09 mm	Yes	No
N 06625	0.004	8/8 , 0.47 mm	Yes	Yes
N 10276	0.001	7/8 , 0.31 mm	No	Yes

Note : 7/8, 0.98 mm means crevice corrosion under 7 of 8 gaskets. Max. depth = 0.98 mm

Table 5

Main results of the sulphide pollution test

Alloy UNS#	Highest weight loss $g/m^2.h$	crevice corrosion under gaskets	corrosion in the gas phase	other types of corrosion
S 32654	< 0.001	0/8	No	No
S 31254	< 0.001	0/8	No	No
S 31803	< 0.001	0/8	No	No
S 31603	0.001	0/8	Yes	Yes

Note : 0/8 means no crevice corrosion under any of the 8 gaskets.

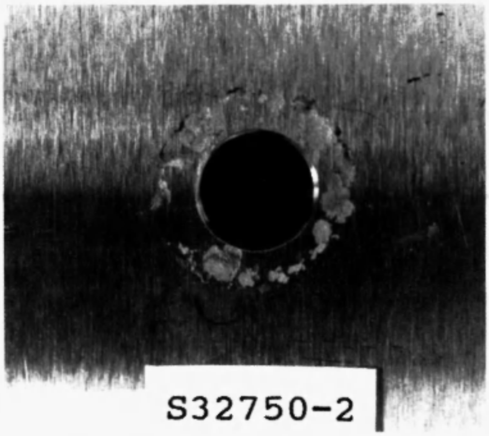

Fig. 7: Crevice corrosion on S32750 superduplex steel

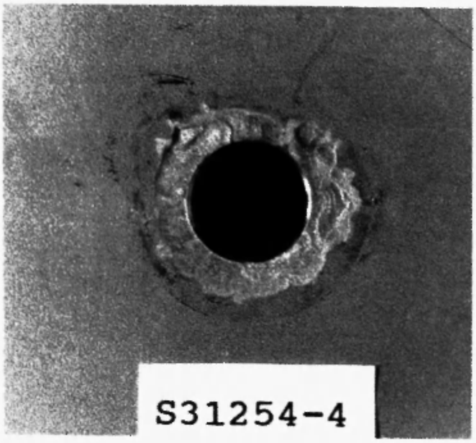

Fig. 8: Crevice corrosion on S31254 superaustenitic 6 Mo steel

weight losses were negligible in all cases. On the other hand, attacks were observed in a few places on S31603. On the immersed parts of the S31603 specimens, localized attacks were only detected in connection with welds, at places where the dark brown spots existed before cleaning. The deepest attack (0.18 mm) existed in the fusion line and is shown in Figure 15. On

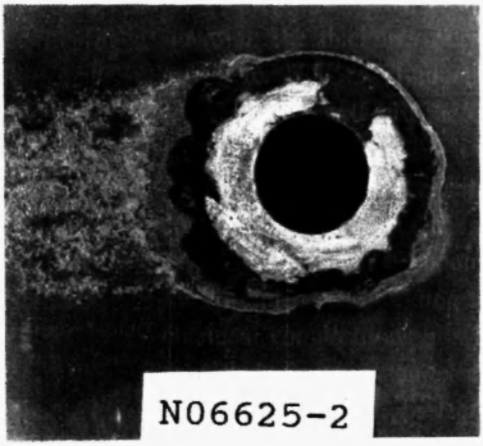

Fig. 9: Crevice corrosion on N06625 nickel base alloy

Fig. 10: Crevice corrosion on N10276 nickel base alloy

the S31603 electrode, pitting was detected above the water level, on places where the dark gray spots existed (Figure 16): the edges were especially prone to corrosion.

Semi-quantitative analyses showed that sulphur was present (absorbed or deposited) on the surfaces outside the crevices: the amount of sulphur varied

Fig. 11: Vapor phase corrosion on N06625 nickel base alloy

Fig. 12: Vapor phase corrosion on S32750 superduplex steel

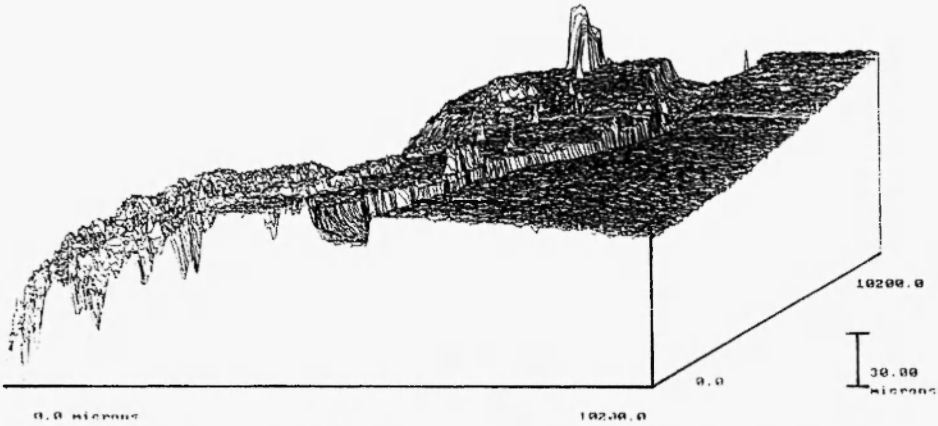

Fig. 13: Profilometry of N06625 crevice: notice the attacks just at the mouth of the crevice and inside the crevice.

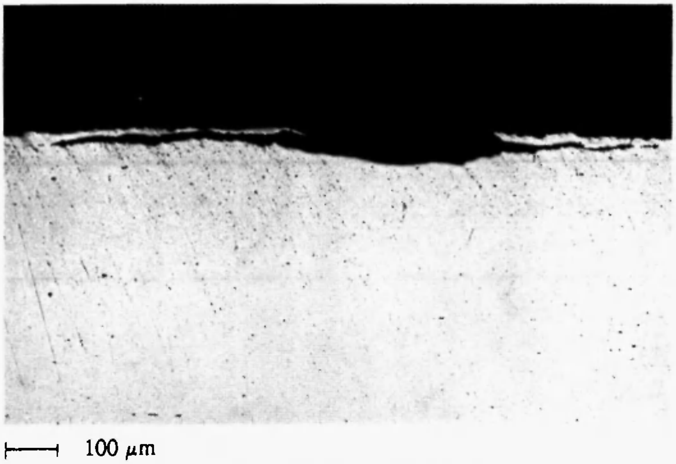

Fig. 14: Localized attack on N10276

between 0.76 weight % on S32654 surfaces and 0.30% on S31603, but on steel surfaces inside the crevices, no sulphur (less than 0.01%) was found.

4. DISCUSSION

4.1. Chlorinated Seawater

As reported in Table 4, all the alloys except for S32654 were attacked by

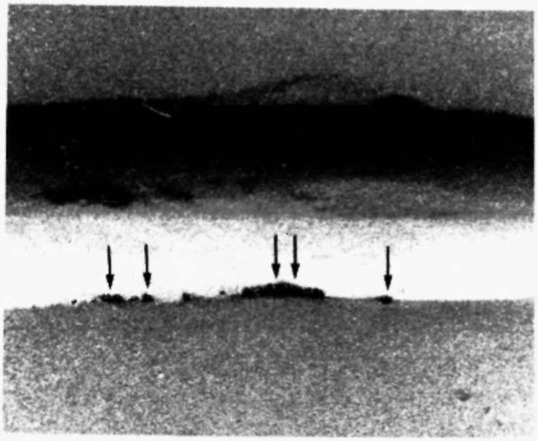

Fig. 15: Localized attack in the fusion line on S31603 coupon

Fig. 16: Pitting in the gas phase on S31603 electrode

crevice corrosion under the gaskets. These results are not unexpected, however. Earlier investigations have shown that, under similar conditions, crevice corrosion is to be expected on S32750 and S31254 if the temperature or the chlorine concentration exceeds certain limits: thus, at 45°C, 2 $mg.l^{-1}$ chlorine will cause crevice corrosion on both these alloys /1,2/. As shown in other tests, N10276 is not immune to crevice corrosion in natural, unchlorinated seawater at ambient temperature /4/ and etching has been reported on N06625 in seawater containing 4 mg/l^{-1} of chlorine at ambient temperature /3/. It could be seen that on the nickel base alloys, but not on the stainless steels, crevice corrosion occurred not only inside the crevice, but also at the mouth of the aramid crevices (Figures 9, 10 and 13).

The gas phase corrosion observed on S31254, S32750 and N06625 electrodes might have been caused by chlorine gas evaporating from the water and forming a highly corrosive condensate. This type of corrosion is common in chlorine stage filter washers in pulp bleaching plants /5/.

The localized attack observed on N10276 coupons (Figure 14) did not appear to be pitting corrosion but seems to have been caused by superficial slag inclusions which have been removed during the test. After removal, the attack most likely stopped.

The potential measurements (Figures 4 and 5) show that the redox potential is very high and almost independent of the variations of chlorine concentrations (8-13 $mg.l^{-1}$). The free corrosion potentials of stainless steels and nickel base alloys are more than 150 mV lower, a difference which is explained by the higher catalytic activity of platinum /1/. The S32654 electrode has a high and stable potential during the whole experiment, while the other electrodes have potentials which are lower and unstable, at least during the first part of the exposure.

All electrodes, except S32654, were attacked by crevice corrosion, and this is reflected in the free corrosion potential curves. While S32654 has a high and stable potential from the very beginning of the exposure, the other alloys start at lower and unstable potentials indicating a probable onset of crevice corrosion. The potential increase of N10276 after around 300 hours is considered to be due to the repassivation of the crevice. The very unstable curve of S31254 indicates incomplete repassivation and the state of the crevice area seems to alternate between active corrosion and passivity.

The conditions of this test, 10 mg.l^{-1} of chlorine at 45°C, have obviously been very corrosive and only S32654 has resisted corrosion completely. However, the specimens were exposed to the warm and chlorinated seawater from the start. As shown by others /6/, stainless steels become more resistant to crevice corrosion if they are exposed to a less corrosive environment some time before contact with the aggressive environment. One way to accomplish this could be to increase chlorine concentration from zero to the nominal value in a couple of days. Treated in this way, S31254 and S32750 have been resistant to crevice corrosion in seawater containing 10 mg.l^{-1} of chlorine at 45°C, i.e. the same conditions as in the present test /6/.

4.2. Sulphide Polluted Water

This environment was been particularly corrosive: crevice corrosion did not occur even on S31603.

The attack in the fusion line of S31603 specimens (Figure 15) was metallographically investigated: the structure was quite normal and did not reveal the reason for corrosion initiation. One possible explanation for the attack might be if all welding oxide was not removed by the sand blasting but that oxide spots remained in "inaccessible" areas like the edge along the weld bead and minor irregularities on the weld bead. The surface under the oxide is depleted in chromium and consequently less corrosion resistant.

The pitting in the gas phase on the S31603 electrode (Figure 16) occurred in unwelded plate material where no oxide or scale existed. The explanation for this attack might be that gaseous hydrogen sulphide, which evaporated from the water especially during pH reductions, condensed on the specimen surface, forming a corrosive solution (acid solution saturated with hydrogen sulphide).

The free corrosion potentials of the stainless steels had nearly the same values as the redox potential, around -500 mV/SCE, and were very stable. This is in accordance with the fact that corrosion did not occur on the immersed part of the electrodes.

Several investigations show that hydrogen sulphide stimulates the anodic reaction in the corrosion process of stainless steels and that pitting potentials decrease with increasing sulphide concentration /7-9/. However, more than 10^{-2} M (320 mg.l^{-1}) seems to be needed to impede the stability of the passive film and to decrease the pitting resistance of type 316 and 304 steels in neutral chloride solutions /10/. The sulphide concentration in the present test was around 800 mg.l^{-1} but still the corrosivity of this environment is much lower than that of natural or chlorinated seawater: in these latter environments, numerous tests and practical experiences show that type 316 steel will suffer severe crevice corrosion and pitting. The reason for the lower corrosivity in the test may be due to the reducing properties of the sulphide ions and to the fact that the inside of crevices is less influenced by sulphide than the outside, as shown by others /12/, and as found by surface analyses in this work (no sulphur was detected on surfaces inside the crevices while some sulphur was present outside). In this way, the sulphide ions bring chemical cathodic protection to the crevice area of stainless steels. It has been reported by others /11/ that no crevice corrosion was observed on the stainless steel specimens which were immersed in anaerobic sediments with high sulphur content and with the same free corrosion potentials as in the present test.

5. CONCLUSION

10 mg.l^{-1} of chlorine in seawater at 45°C obviously creates a very corrosive marine environment: only S32654 superaustenitic steel resisted corrosion completely after 95 days of exposure. The other tested alloys (S31254, S32750, N06625 and N10276) suffered crevice corrosion. This result is reflected in the free corrosion potential evolution; while the S32654 had a high (400 mV/SCE) and stable potential from the very beginning, the other alloys had lower and more unstable potentials.

1 g.l^{-1} of sulphide in seawater at ambient temperature was not particularly corrosive: crevice corrosion did not occur on S32654, S31803, S31254 and S31603 after 95 days of exposure. Only attacks in the gas phase and in the welding area were observed on S31603 specimens. The free corrosion potentials (-500 to -520 mV/SCE) were stable and had nearly the same value as the redox potential.

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