Sketch to Report: Microbiologically Influenced Corrosion of Stainless Steels in Sea Water – Critical Parameters

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Introduction

As a part of Task 2, research area "Corrosion", a brief literature survey has been conducted focusing on critical data with respect to both the material and the environment. Microbiologically influenced corrosion, MIC, of stainless steels is reported in a large number of case histories, not only in sea water systems, but also in freshwater systems. However, this report focus' on case histories from sea water systems only.

The main purpose of this report is to identify critical parameters in order to provide input data to Task 3, application project "Risk assessment"

Critical environmental parameters

When stainless steels or other passive metals like titanium or platinum, are kept in sea water under conditions allowing microbial activity, the cathodic reaction rate may increase dramatically. The activity within the biofilm that forms on the surface enhances the free corrosion potential from about 0-100 to 300-400 mV SCE (see Figure 1). The ennoblement of occurs after a few days, or up to a couple of weeks of exposure, and is likely due to a catalytic specie developed within the biofilm, that catalyses the oxygen reaction.

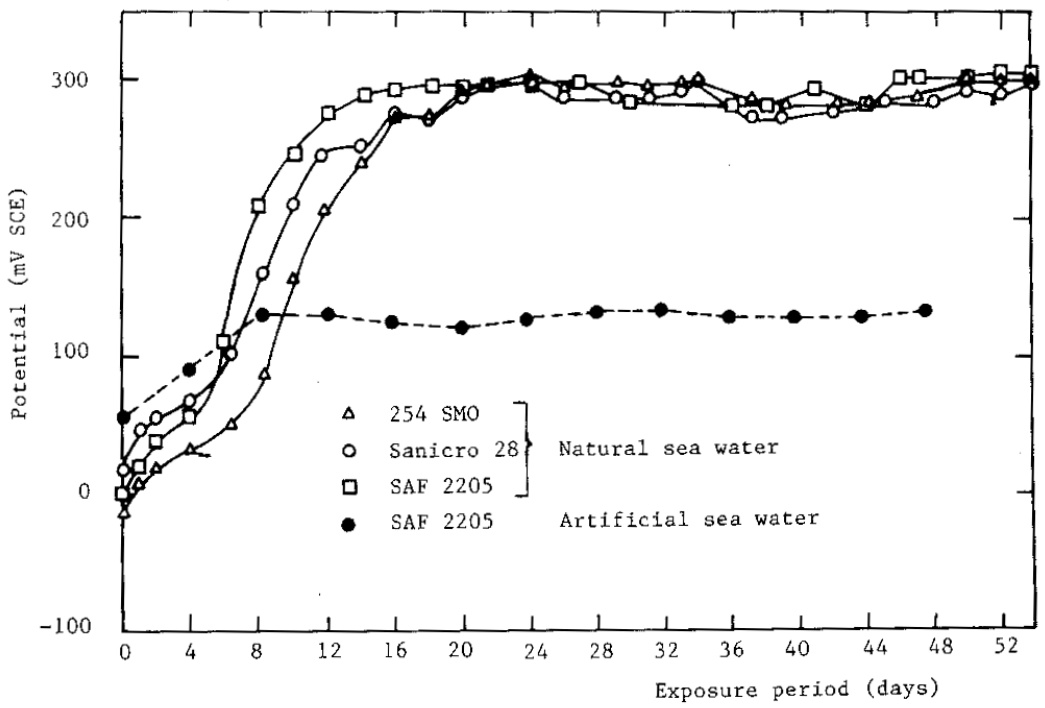


Figure 1 *The potential development for three common stainless steel in nearly stagnant sea water compared to the potential development in artificial sea water. Temperature 8 ± 2°C.*

Studies at CEA-CEREM/SCECF in France have shown that a similar ennoblement as observed on stainless steels (SS) in sea water may be reproduced in the laboratory by addition of glucose oxidase in sterile aerated sea water containing glucose. These tests have demonstrated that the increase in SS free corrosion potential is a result of combined action of hydrogen peroxide and gluconic acid produced by the enzymatic activity. Figure 2 shows the hypothetical mechanism proposed in the French study. Figure 3 shows the potential developments achieved at different temperatures by addition of glucose and glucose oxidase.

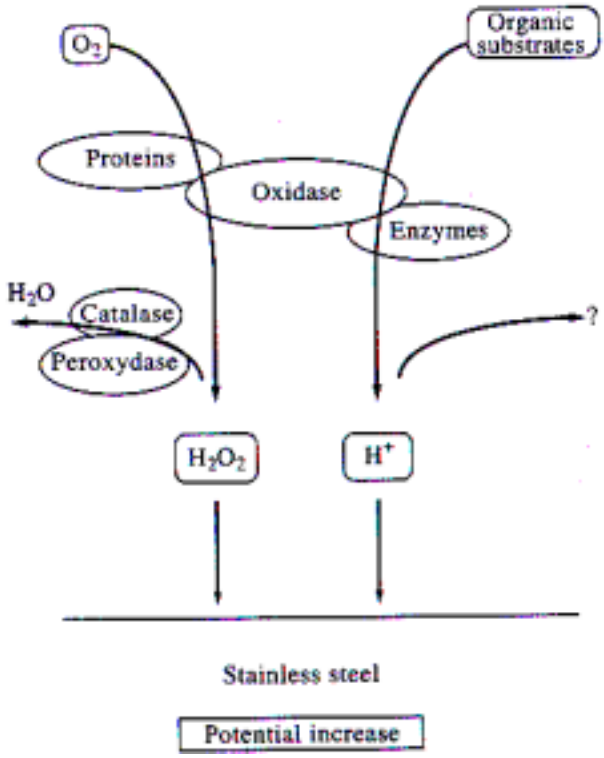


Figure 2 *Hypothetical mechanism of the stainless steel ennoblement in natural sea water.*

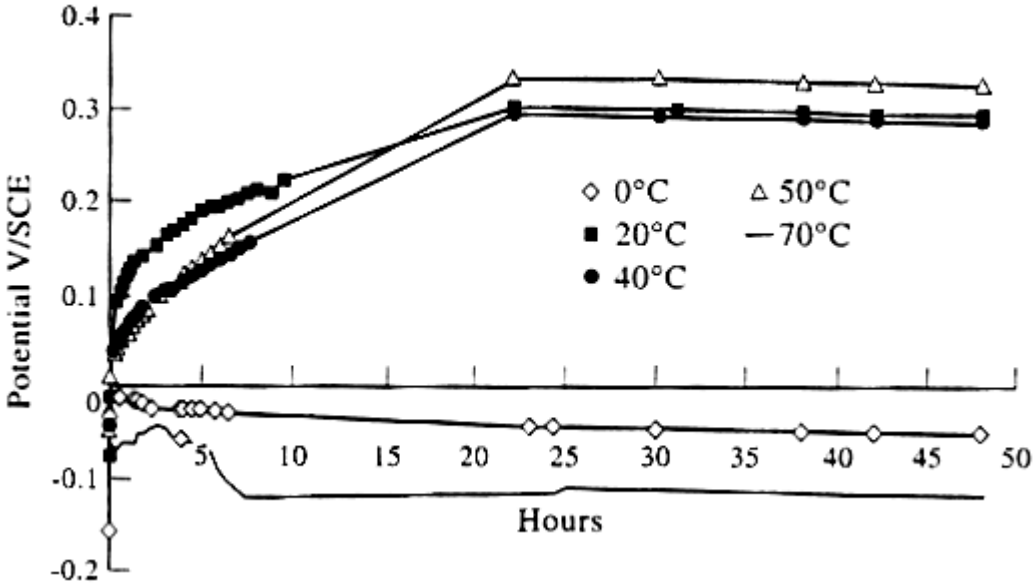


Figure 3 *Potential development for SS in natural sterile sea water after addition of glucose and glucose oxidase at different temperatures.*

Figure 3 shows that in the CEA laboratory tests there was an ennoblement even at 50°C. This is however not the case in natural seawater. Several studies performed at SINTEF/NTNU in Norway have shown that at about 30°C the catalytic effect of the biofilm is strongly reduced. Figure 4 shows cathodic current density as a function of time for four different temperatures. The potential developments for the same temperatures are shown in Figure 5.

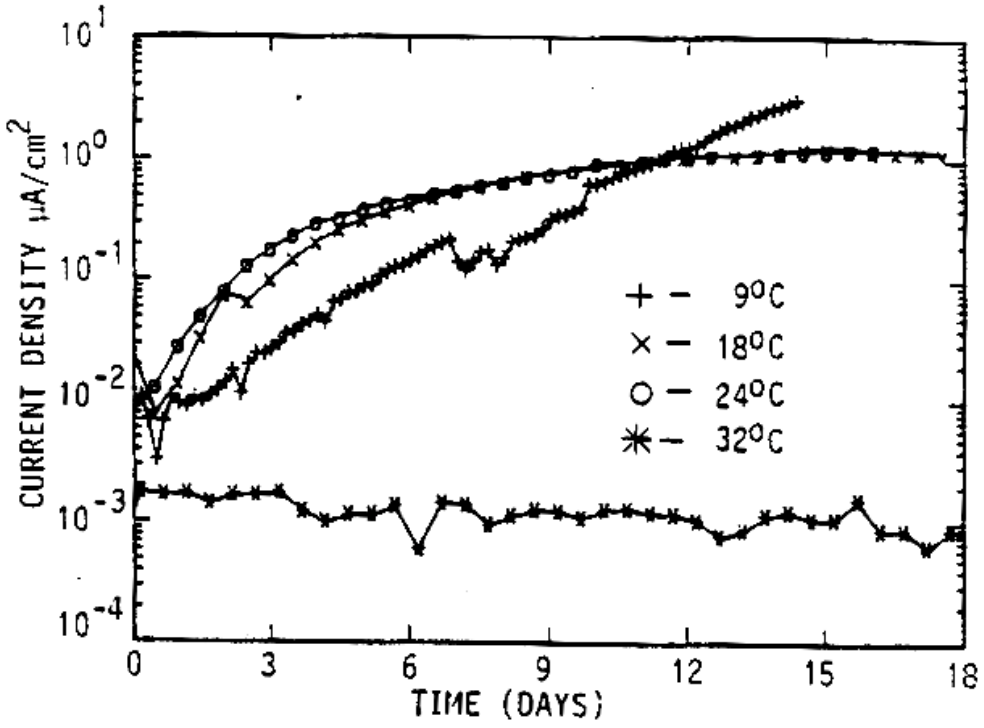


Figure 4 *Development of cathodic currend density on 254 SMO at +100 mV SCE (0 mV at 32°C). Preexposed for 14 days of free corrosion potential. Nearly stagnant conditions.*

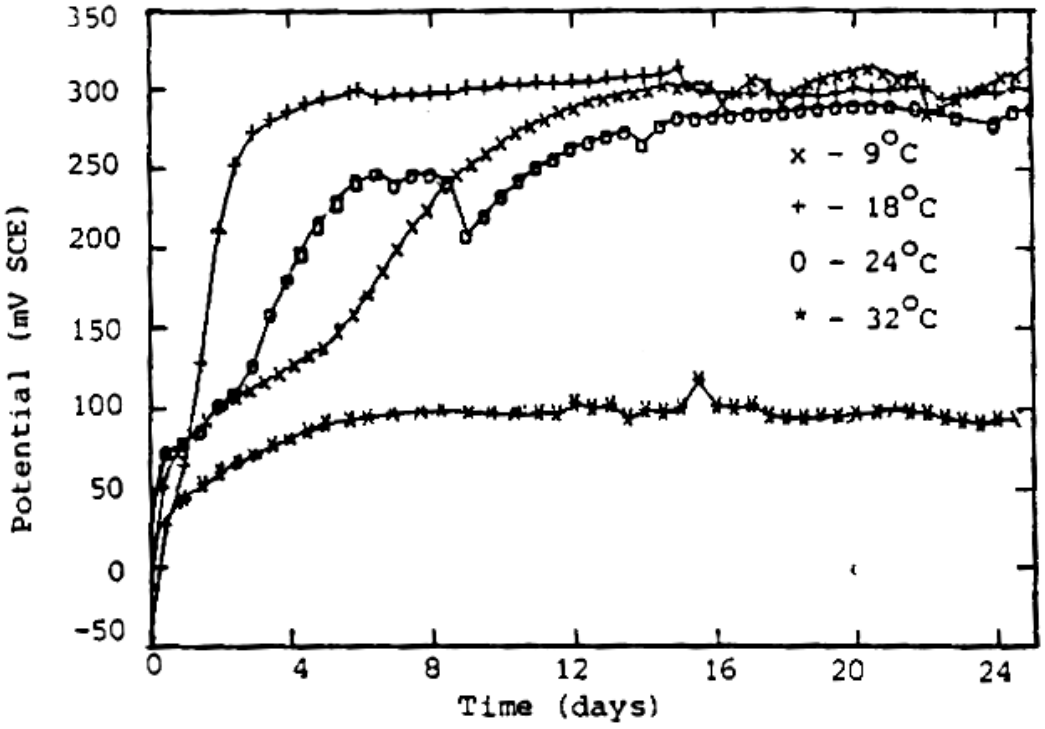


Figure 5 *Potential development of 254 SMO in nearly stagnant sea water.*

Figure 6 shows how the potential is influenced by increasing the temperature from 25 to 30°C. The figure indicates that the critical temperature for the sea water from the Trondheimsfjord in Norway is close to 30°C.

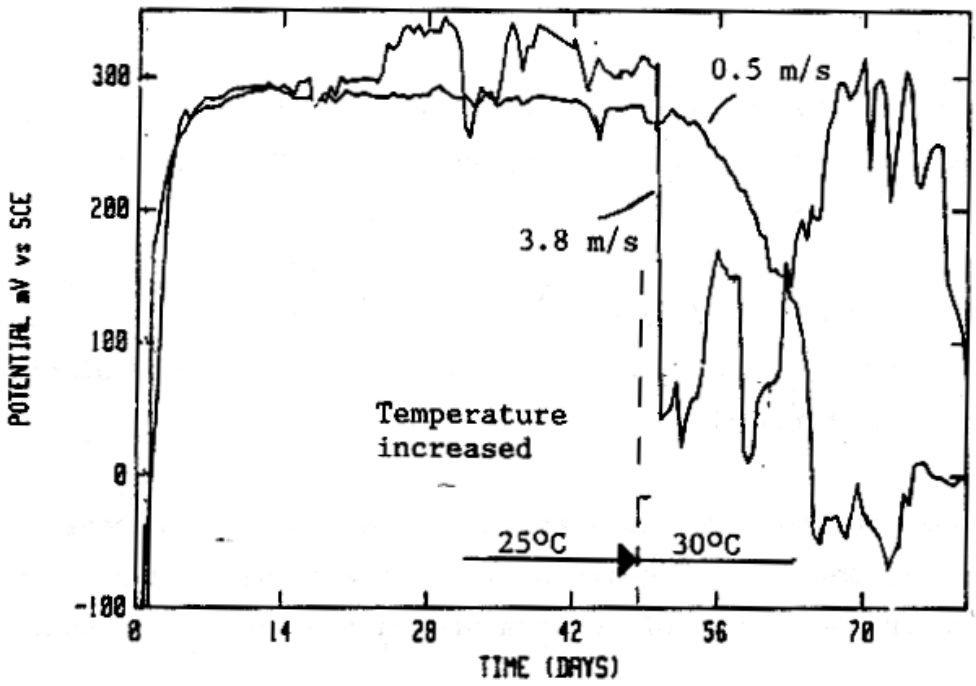


Figure 6 *Effect of an increase in temperature from 25 to 30°C at two different flow rates.*

Scotto et al. found that at temperatures above 30°C the potential drops about 30 mV for each degree celsius until the effect of the biofilm is totally vanished at 40°C. These results are slightly different from the Norwegian results and may be due to a different microbial fauna in the Mediterranean Sea, where Scotto et al. conducted their experiments, than in the Trondheimsfjord. Previous joint European MIC studies have also shown that the results are strongly influenced by location (see Figure 7). This is of course not only due to differences in the microbial fauna, but also due to variations in factors like temperature and salinity. The effect of salinity will be further discussed in the section for countermeasures.

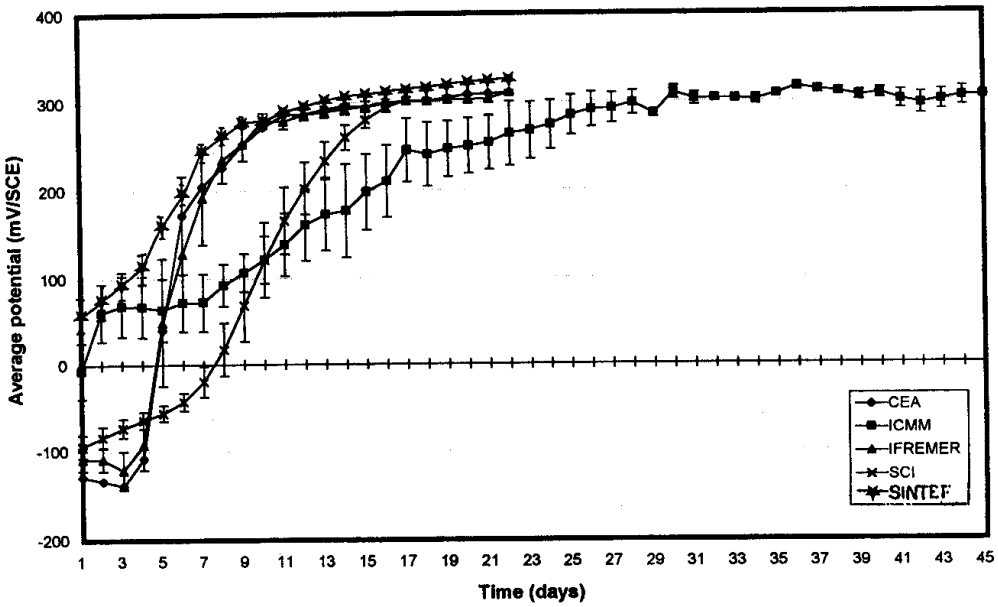


Figure 7 Potential development at different locations in Europe.

Pedersen has found that the biofilm productivity is significantly influenced by temperature. As the temperature was raised from 5 to 15° there was a five-fold increase, and from 15 to 25°C there was a two-fold increase. Tests performed by SINTEF have shown that this effect is of significant importance, as the initiation of crevice corrosion is to a great extent dependent on the incubation time before the ennoblement starts and how fast the potential is increased. Crevice corrosion was not observed in a test performed during the spring, while in the summer test, were ennoblement is faster (see Figure 8), all samples of AISI 316 L initiated crevice corrosion.

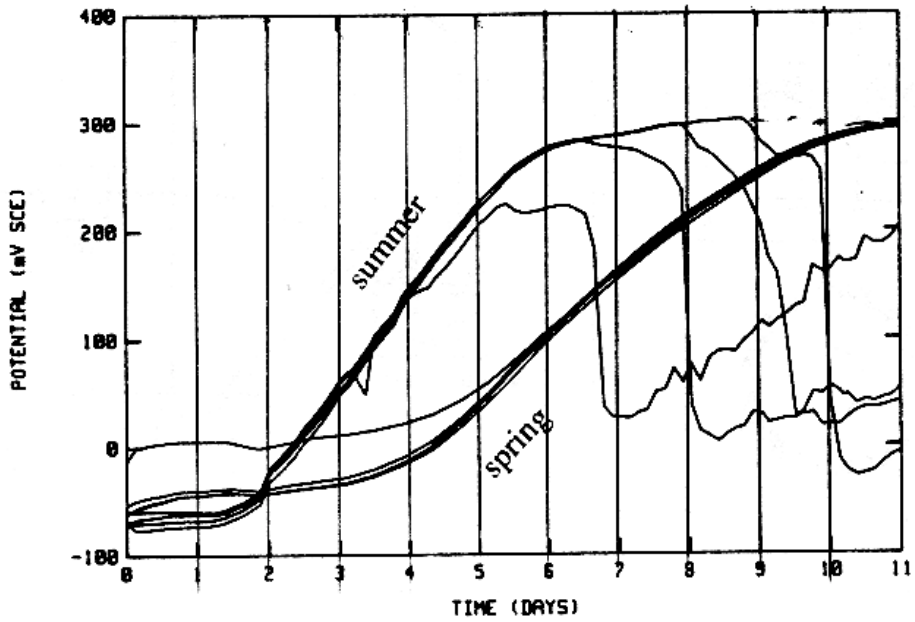


Figure 8 Exposure of AISI 316 L in natural sea water. Crevice corrosion was initiated during the summer test but not during the spring test.

There has been performed a few studies on the effect of the flow rate. Both Bryers et al. and Bakke concluded that biofilm formation and thickness was quite independent of Reynolds number in turbulent tubular flow. However, Mollica et al. proposed a critical flow rate around 0.8 m/s for macro fouling settlement and 1.9 m/s for microbiological film formation. In total contradiction to the findings of Mollica et al., has Johnsen and Bardal shown that biofilm is formed even at a flow rate of 4.5 m/s (see Figure 9). These findings have been supported by Holthe. In the extensive study performed by Holthe there was observed ennoblement of stainless steel 254 SMO at 3.8 m/s. This was the highest flow rate in his test series. In this study both the temperature and the flow rate was varied. The free corrosion potentials after 30 days of exposure at different temperatures and flow rates are summarized in Figure 10.

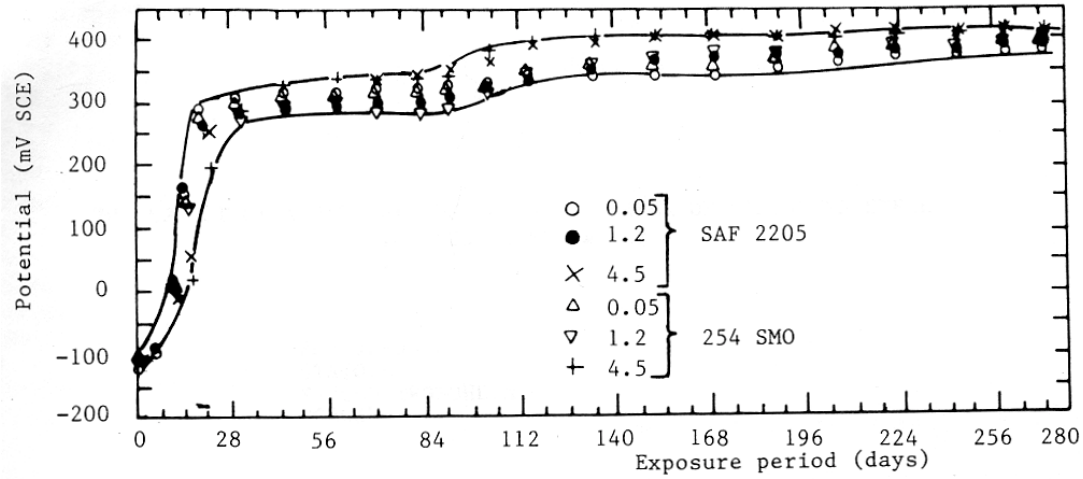


Figure 9 *Potential development of two different stainless steels tested at three different flow rates. Temperature: 11 ± 1°C.*

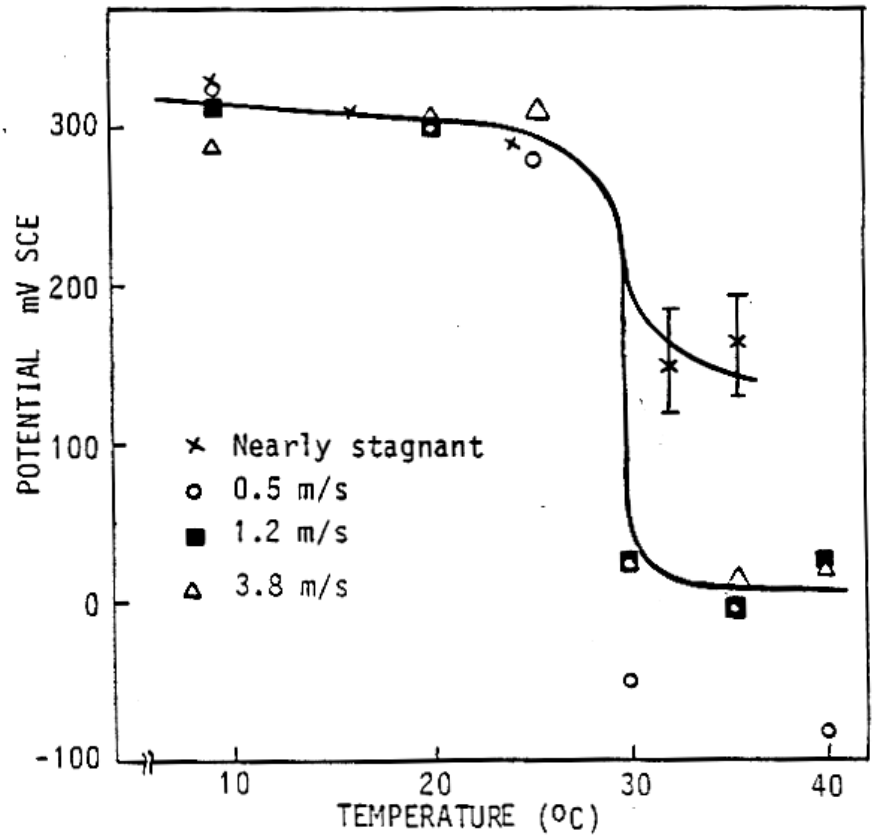


Figure 10 *Potentials after 30 days exposure in natural sea water for tubular samples of 254 SMO.*

The higher tendency to MIC of welds compared to unwelded material has been explained by differences in surface roughness or/and chemical composition that facilitates the colonization of the surface by microorganisms. Experiments performed by Holthe have, however, shown that the increase in potential is just slightly more rapid on a rough than on a polished sample (see Figure 11)

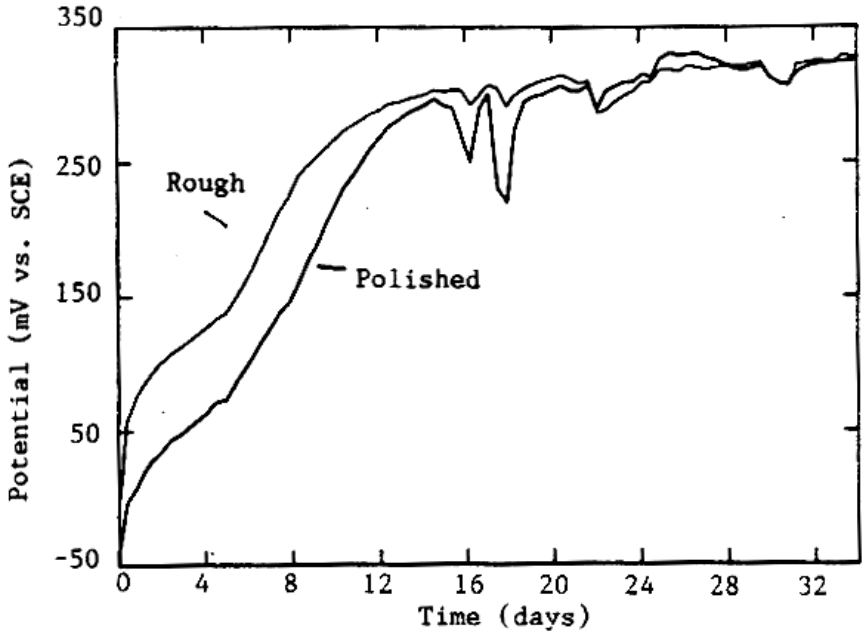


Figure 11 *Potential development for rough and polished samples of 254 SMO. Temperature: 7 ± 1°C.*

Critical material data

As the potential rise in the presence of a biofilm is connected with changes of the cathodic reaction rather than the anodic, most materials being in the passive state will experience a similar potential rise. The exception is copper alloys, possibly due to the poisoning effect of the copper ion. Figures 1 and 9 have already shown that 254 SMO, SAF 2205 and Sanicro 28 behave fairly similar in sea water.

The practical consequence of the bioactivity is that there will be an increased risk of local corrosion initiation due to the potential rise. Highly alloyed stainless steels and superduplex do not normally corrode in natural sea water at temperatures up to 30°C, but more conventional SS like AISI 304 or 316 are not resistant enough to withstand a potential rise up to 300-430 mV SCE, even in rather cold sea water.

The enhancement of the cathodic reaction has serious implications, as the high cathodic efficiency results in large corrosion rates. Tests performed at SINTEF have shown that with area ratios as low as 5:100 between crevice samples of AISI 316 and an outer cathode, the corrosion rate became 1-3 mm/year when a biofilm was being formed. In substitute sea water the corrosion rate was about two decades lower, even with the much larger area ratio of 2000:1.

Below there are listed statements, tables and figures found in literature that are related to corrosion of different stainless steels in sea water. Till the meeting in London September the 15th these data will be systematized.

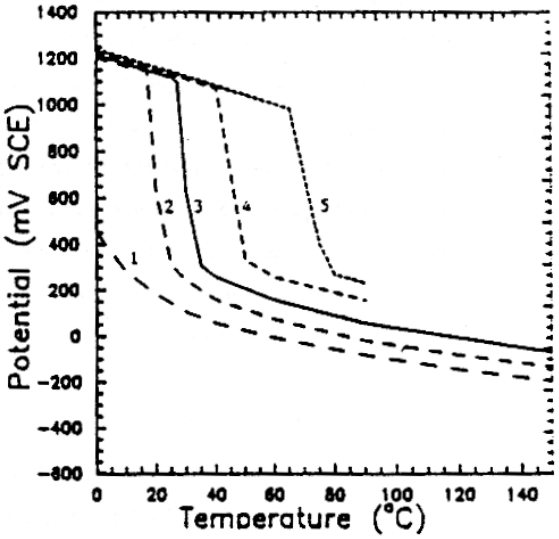
A.A. Stein:

- Sensitization of the 300 series does not affect their susceptibility to MIC.

Audouard et al.:

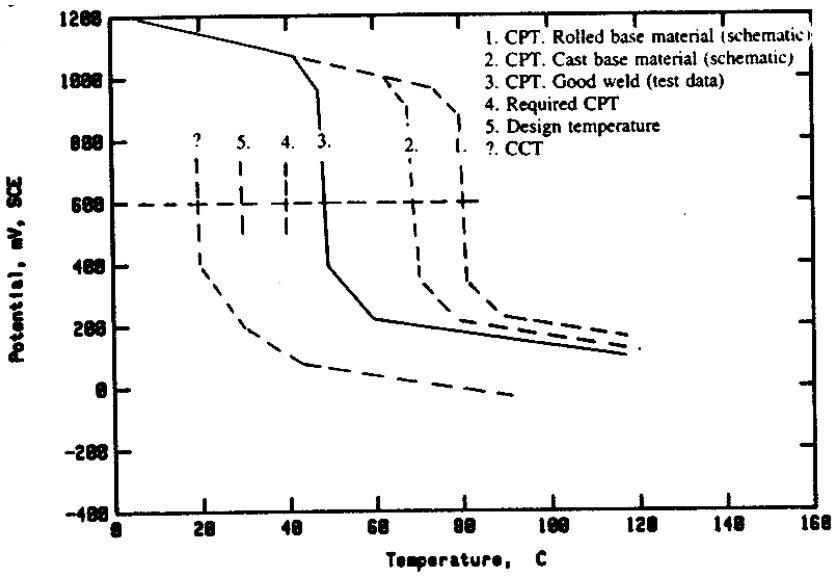
- The ennoblement of the corrosion potential for 654 SMO was observed at all exposure sites and at all seasonal exposures.
- No differences in the corrosion potential versus time curves were found for all investigated alloys (AISI 316L, 254 SMO, 654 SMO, 47 N, 52 N, B 26, SB8, SAF 2205, SAF 2507, SAN 28)) at a given exposure site and season.

Bardal, Drugli and Gartland:



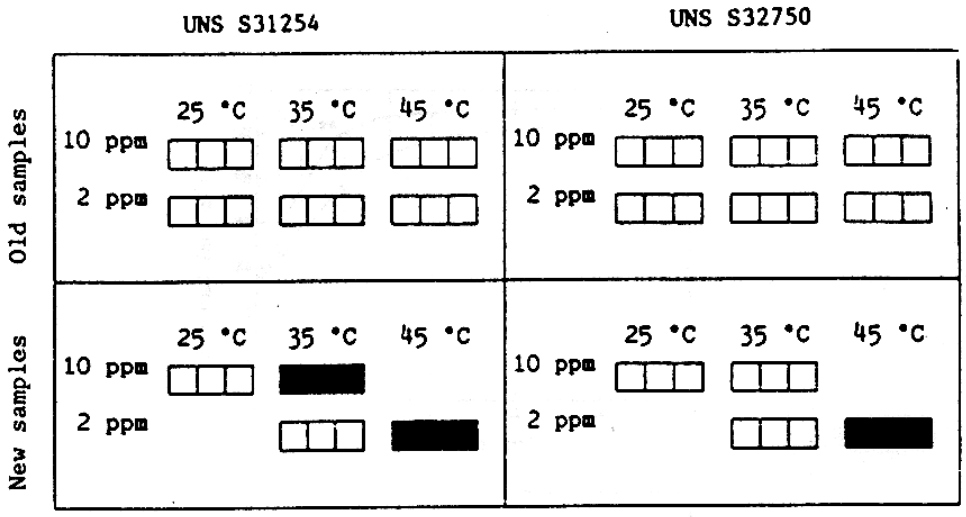
Critical temperature-potential curves for base materials and good welds of different materials. [37, 39, 28].
1. AISI 316L - rolled-annealed. 2. UNS S31803 - welded. 3. UNS S31803 - rolled-annealed. 4. UNS S31254 - welded. 5. UNS S31254 - rolled-annealed.

Drugli and Rogne:



Critical potential vs temperature determined by long duration tests in 3% NaCl, sea water and 6 % $FeCl_3$-solution for UNS 31254. Cl^--concentration: 0.5 - 1.1 M.

Rogne and Steinsmo:



A summary of test results with crevice samples in chlorinated sea water. An open square means a non-corroding sample while a filled square means a corroding sample /7/.

Rogne, Drugli, Knudsen, Olsen and Enerhaug:

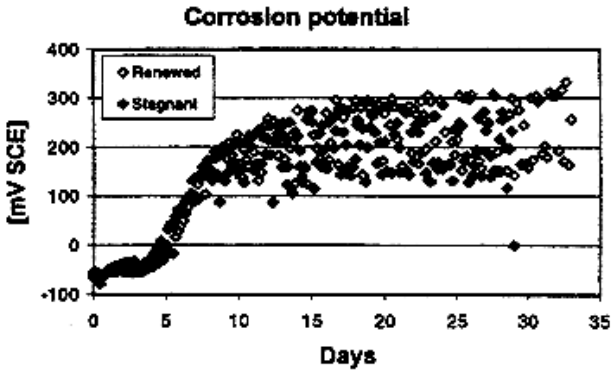
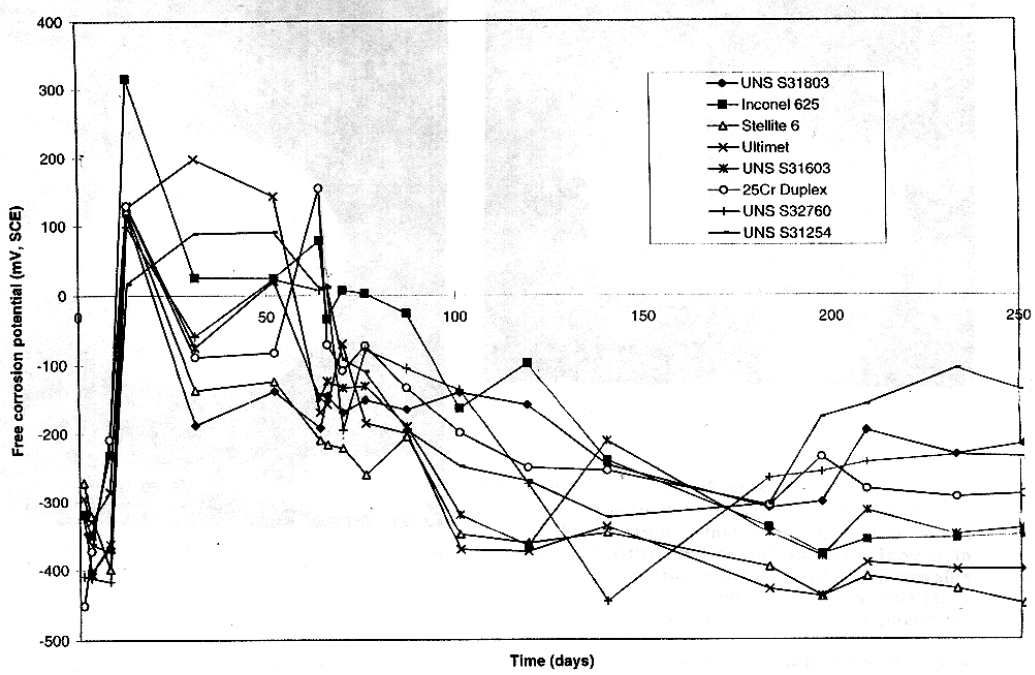


Figure 11. Corrosion potential of 12Cr6.5Ni2.5Mo stainless steel exposed to stagnant and renewed natural seawater.

Neville and Hodgekiss:

112 *Neville and Hodgkiess* Stainless steel and related alloy corrosion in natural sea water



1 *Trends in free corrosion potential of materials tested*

Wallen and Bergqvist:

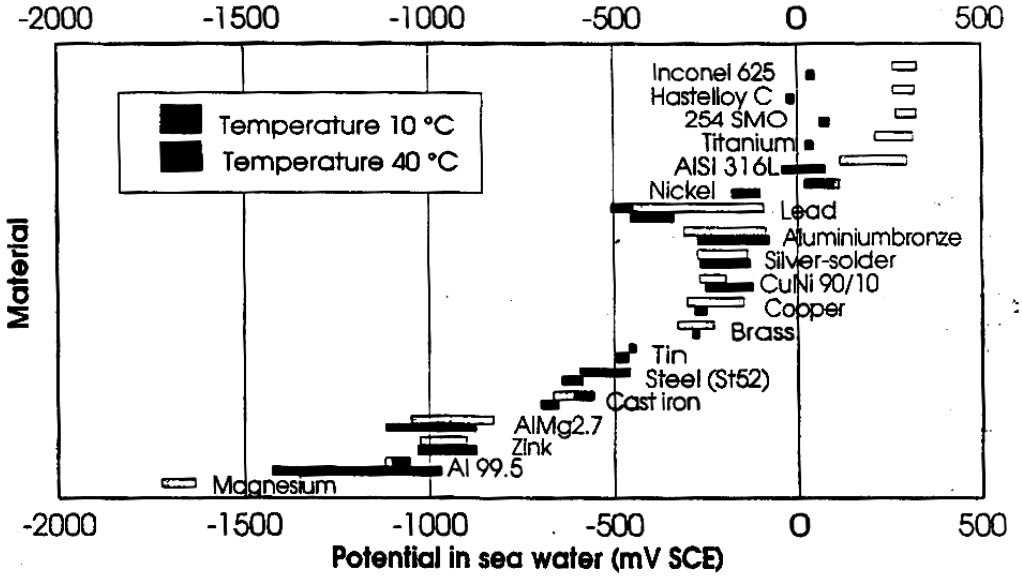
Table 5
Critical crevice corrosion temperatures of flanges used in the piping systems

Flange	CCT, °C	Results in seawater tests
254 SMO, cast	35	Crevice corrosion in Test 1
254 SMO, forged	32.5	Crevice corrosion in Test 2
654 SMO, cast	62.5	Resistant in both tests
654 SMO, forged	62.5	Resistant in both tests
654 SMO, HIP	57.5	Resistant in both tests

Table 6
Critical pitting corrosion temperatures of pipe to flange joint welds used in the piping system

Joint weld		CPT	
Pipe	Flange	°C	Results in seawater tests
654 SMO	654 SMO, forged	65	Pitting in weld defects in both tests
654 SMO	654 SMO, cast	57.5	Resistant in both tests
654 SMO	654 SMO, HIP	52.5	Resistant in both tests
254 SMO	654 SMO, forged	52.5	Resistant in both tests
254 SMO	654 SMO, cast	55	Resistant in both tests
254 SMO	654 SMO, HIP	Not tested	Resistant in both tests

Valen et al.:


-2000
-1500
-1000
-500
0
500
Temperature 10 °C
Temperature 40 °C
Material
Inconel 625
Hastelloy C
254 SMO
Titanium
AISI 316L
Nickel
Lead
Aluminiumbronze
Silver-solder
CuNi 90/10
Copper
Brass
Tin
Steel (St52)
Cast iron
AlMg2.7
Zink
Al 99.5
Magnesium
Potential in sea water (mV SCE)

Féron, Espelid and Scotto:

Table 3 - Evolution of the free corrosion potentials of stainless steets (UNS 31254 for EFC Test and UNS 32654 for MAST-II Programme)

Test	Test station	Incubation time (days)		Potential increase rate (mV/day)		Final potential (mV/SCE)	
		Test I	Test II	Test I	Test II	Test I	Test II
EFC Tests	Zagreb Univ., Dubrovnik	120	1.7	48	34	175	350
	SINTEF, Trondheim	1.6	2.3	125	41	450	348
	Marintek, Sandfjord	3.0	3.5	84	79	480	520
	IFREMER, Brest	1.6	2.0	82	74	331	410
	DNV, Bergen	7.5	5.1	41	52	420	380
	CEA, Cherbourg	1.2	2.0	197	144	285	350
	SCI, Stockhlom	7.0	3.7	58	22	440	443
	Naval Coll., Den Helden	3.0	5.0	250	42	450	500
	Force Inst., Copenhagen		1.5		77		550
	CTO, Gdansk	1.7		65	19	420	352
	Helsinki Univ.	1.7	4.2	144	86	500	500
		Winter	Summer	Winter	Summer	Winter	Summer
MAST II Tests	IFREMER, Brest	4±1	2±1	125±10	145±10	250±20	220±10
	ICMM, Genova	8±1	5±1	10±4	10±4	300±10	360±15
	SCI, Kristineberg	6±1	6±1	35±5	50±5	300±10	330±10
	SINTEF, Trondheim	2±1	1±1	25±5	60±10	300±10	300±5
		20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
	CEA, Cherbourg	1.1	2.5	>125	125	40	-	310	280	-110

Table 4 - Crevice corrosion results of the EFC Test [8]

Alloy	UNS 31600		UNS 08904		UNS 31254	
Test stations	Test I	Test II	Test I	Test II	Test I	Test II
Zagreb Univ., Dubrovnik	2/4	4/4	0/4	3/4	0/4	0/4
SINTEF, Trondheim	4/4	3/4	1/4	3/4	0/4	0/4
Marintek, Sandfjord	1/4	2/4[2]	0/4	0/4	0/4	0/4
IFREMER, Brest	0/4	0/4	1/4	0/4	0/4	0/4
DNV, Bergen	0/4	0/4[1]	0/4[2]	0/4[1]	0/4	0/4
CEA, Cherbourg	3/4	4/4	1/4[3]	4/4	0/4	0/4
SCI, Stockhlom	1/4	0/4[1]	1/4	0/4	0/4	0/4
Naval Coll., Den Helden	4/4	3/4	0/4	3/4	0/4	0/4
Force Inst., Copenhagen		4/4		3/4		0/4
CTO, Gdansk	2/4[1]	3/4	0/4[1]	2/4	0/4	0/4
Helsinki Univ.	0/4	0/4	0/4	0/4	0/4	0/4
Total	17/40[1]	22/44[4]	4/40[6]	19/44[1]	0/40[2]	0/44[1]

[1 2 3 4 5 6] In addition 1/2/3/4/5/6 specimens respectively initiated at cable connection. Due to the potential drop, initiation at cable connection might prevent corrosion to occur at the "less severe crevice" created by the plastic crevice former used.

Table 5 - Crevice corrosion results of the MAST-II Programme on UNS 31600 (number of crevice corroded specimens over the total number of specimens)

Station	ICMM, Genova[1]	IFREMER, Brest[1]	SCI, Kristineberg[1]	SINTEF, Trondheim[1]	CEA, Cherbourg[2]		
					20°C	30°C	40°C
Result	5/5	0/4	0/4	4/4	5/5	3/5	0/5

[1] Natural seawater and ambient temperature
[2] natural seawater thermally altered (heated)

Table 6 - Crevice corrosion at low ambient temperature on UNS 31600

Location	EFC Test I		EFC Test II		MAST-II Programme	
	Temp. °C	Crevice corrosion	Temp. °C	Crevice corrosion	Temp. °C	Crevice corrosion
Marintek, Sandefjord	6	1/4	12.5	2/4		
DNV, Bergen	9	0/4	9.1	0/4		
SCI, Stockholm	5	1/4	10.0	0/4		
Helsinki Univ.	6	0/4	10.0	0/4		
SINTEF, Trondheim	11	4/4	9.5	3/4		
SCI, Kristineberg					6.0	0/4
SINTEF, Trondheim					8.3	4/4
IFREMER, Brest					8	0/4

Table 7 - Crevice corrosion at high ambient temperature on UNS 31600

Location	EFC Test I		EFC Test II		MAST-II Programme	
	Temp. °C	Crevice corrosion	Temp °C.	Crevice corrosion	Temp. °C	Crevice corrosion
Zagreb Univ., Dubrovnik	18	2/4	22.0	4/4		
Naval Coll., Den Helder	13	4/4	15.7	3/4		
Force Inst., Copenhagen			15.0	4/4		
CTO, Gdansk	11	2/4	14.5	3/4		
CEA, Cherbourg	12	3/4	16.2	4/4	20.0*	5/5
ICMM, Genova					24.6	5/5

* heated seawater

Table 8 - Influence of the "Incubation time" before the increase of free corrosion potential

Test station	Programme	Temp. °C	"Incub. time"	Crevice corrosion
DNV, Bergen	EFC, Test I	9.0	7.5 days	0/4
	EFC, Test II	9.1	5.1 days	0/4
SINTEF, Trondheim	EFC, Test I	11.0	1.6 days	4/4
	EFC, Test II	9.5	2.3 days	4/4
Marintek, Sandefjord	EFC, Test I	9.0	3.0 days	1/4
	EFC, Test II	10.0	3.5 days	2/4
SINTEF, Trondheim	MAST-II W	8.3	2.0 days	4/4
IFREMER, Brest	MAST-II W	8.0	4.0 days	0/4

Countermeasures

The most common countermeasure towards bioactivity is addition of chlorine. The chlorine kills the living organisms including the bacteria. In this way the biofilm effects will not occur. However, by addition of chlorine new cathodic reactions are introduced and the potential is raised to even higher potentials than in natural sea water (see Figure below).

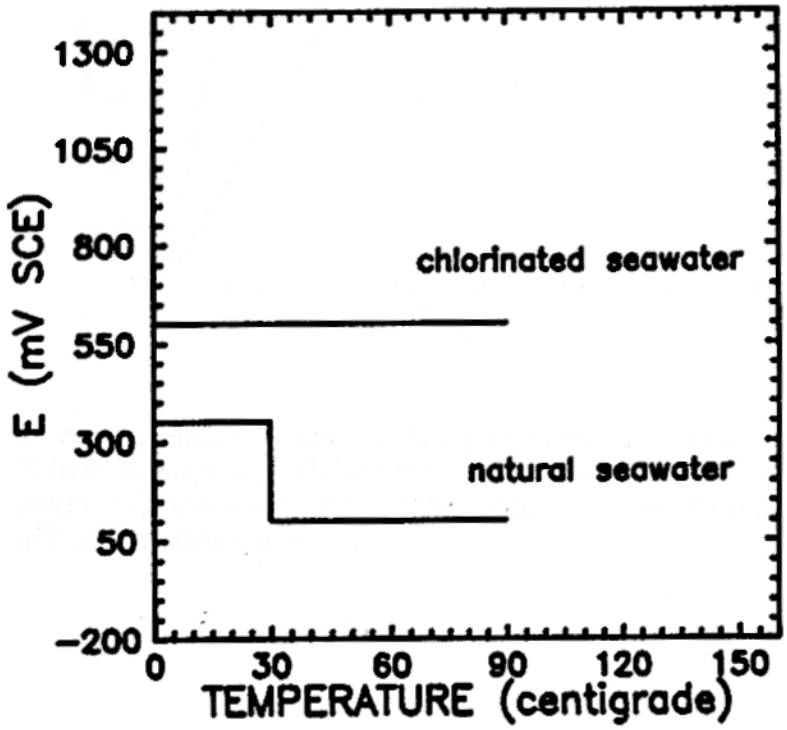


Figure Open circuit potentials for UNS S31254 as a function of temperature after 3 weeks of exposure in chlorinated and natural sea water. Flow rate: >0.5 m/s. Chlorinated sea water: > 1 ppm residual chlorine.

Till the London meeting the effect of chlorinating will be further discussed. Other countermeasures like treatment with copper, will also be discussed in the final report.

References

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