



Corrosion behaviour of some stainless steels in chlorinated Gulf seawater

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Abstract

The corrosion resistance of conventional and high alloy stainless steels (specifically 316L, 317L, 904L, duplex 2205, 3127hMO, 1925hMO, 254SMO, 654SMO and Remanit-4565) was determined electrochemically in chlorinated and unchlorinated Arabian Gulf Seawater at 25 and 50 °C. The stainless steels 316L and 317L were used as reference alloys. The electrochemical potentiodynamic cyclic polarization method was used to determine the passive film break down potential (E_b), protection potential (E_{prot}) and maximum current attained on scan reversal (I_{max}). It was found that at 25 °C in chlorinated and unchlorinated seawater and at 50 °C in unchlorinated seawater, stainless steels 316L and 317L have poor resistance to corrosion, Stainless steels 904L and duplex 2205 at 25 °C in chlorinated and unchlorinated seawater showed good resistance to corrosion but at 50 °C these steels failed to resist. The high alloy stainless steels such as 3127hMO, 1925hMO, 254SMO, 654SMO and Remanit-4565 showed better corrosion resistance under all the test conditions.

1. Introduction

The application of conventional and high alloy stainless steels in marine environments, which are particularly pertinent to desalination, have been dealt with in a number of review articles [1–5]. The pitting of stainless steels is the single most frequently occurring corrosion phenomenon in seawater processing plants and has been the subject of numerous studies [6–10]. Electrochemical techniques have been applied as a principal tool for characterizing pitting corrosion. Crevice corrosion is another form of localized corrosion which is frequent in marine structures, pipelines, pumps or shafts or any location where there is an occurrence of a crevice or cavity or deposit formation. The behaviour of a crevice had been investigated electrochemically by many workers by determining parameters such as critical crevice solution pH, passive current, critical crevice potential, critical crevice temperature and variation of potential with time [10–12].

A substantial part of the aforementioned electrochemical studies on localized corrosion of steels have been carried out in natural seawater, which has global variations in the dissolved salt contents and temperature. For example, the dissolved salt contents in Baltic, Atlantic and Arabian Gulf Seawater is on average 7000, 35 000 and 43 000 ppm respectively. Seawater temperature also varies widely from 2 °C in the Arctic to 30 °C in the tropics to 45 °C in the Arabian Gulf [13].

The biological activity in seawater may cause practical problems leading to costly production disturbances. For example, a high degree of fouling creates friction losses in a pipeline and may induce erosion in certain metals. Furthermore, even slight fouling lowers the thermal efficiency of a heat exchanger surface. The conventional way to prevent biofouling or to reduce its effects is to chlorinate the water. This is normally done by adding a strong hypochlorite solution or by electrolysis of the water, continuously or intermittently [14]. As the chlorine is a strong oxidizing agent, the study of corrosion behaviour of materials in chlorinated seawater forms an important aspect of corrosion and material selection in seawater handling systems. A limited number of studies have been carried out on the corrosion behaviour of materials in chlorinated seawater [15–17]. The pitting and under deposit corrosion tendencies of stainless steel piping in chlorinated seawater were tested electrochemically and by crevice corrosion exposures [18]. It was shown that except for 254SMO which did not corrode in chlorinated seawater (25 000 to 50 000 ppm Cl^- and 0–10 ppm residual chlorine), all other alloys developed crevices and suffered some degree of corrosion. In another study, Steilsmo et al. [19] tested eleven high alloyed stainless steels for application in chlorinated Norwegian seawater (Salinity 20 000 ppm). The critical crevice temperature (CCT) was determined using a potentiostatic test method. CCT was found to be in the same range for the six austenitic and five duplex stainless

steels. Repassivation of crevice corrosion was found to occur at far lower temperatures than initiation of crevice corrosion. The effect of chlorination on some high alloy grade stainless steels (254SMO, Monit and Sandvik Sanicro 28) in the North Sea was studied [20]. The investigations showed that continuously chlorinated seawater was considerably more aggressive than unchlorinated seawater or intermittently chlorinated seawater and that an increase to higher temperatures increased the risk for localized corrosion at the same chlorine concentration.

This paper presents the results of a study carried out to determine the effect of temperature, residual chlorine and dominant alloy additions, Cr, Mo, Ni, on the localized corrosion of conventional and high alloy stainless steels in Arabian Gulf Seawater.

2. Experimental details

2.1. Materials

Nine different commercial grade stainless steels namely 316L, 317L, 904L, 3127hMO, 1925hMO, 254SMO, Duplex 2205, Remanit-4565 and 654SMO were used. The seawater and chlorinated (0.2 ppm residual chlorine) seawater mentioned in this paper is as Arabian Gulf raw seawater unless otherwise mentioned. The compositions of the seawater and that of alloys are given in Tables 1 and 2, respectively.

Table 1. Composition of Gulf seawater, pH = 8.2

Ions		Concentration/mg L ⁻¹
Calcium	Ca ²⁺	580
Magnesium	Mg ²⁺	1618
Sodium	Na ⁺	13440
Potassium	K ⁺	483
Strontium	Sr ²⁺	17
Bicarbonate	HCO ₃ ⁻	176
Chloride	Cl ⁻	24090
Sulfate	SO ₄	3384
Bromide	Br ⁻	83
Fluoride	F ⁻	1
Total dissolved solids	TDS	43800

Table 2. Composition of alloys

Alloys	Elements/wt % (balance Fe)						
	Cr	Mo	Ni	C	Cu	Mn	Others
316L	16	3	11	0.02	0.2	1.0	0.054P, 0.02S, 1.0Si
317L	18	3	13	0.02	0.2	2.0	0.054P, 0.02S, 1.0Si
904L	20	5	24.5	0.02	1.0	1.5	0.054P, 0.02S
3127hMO	27	6.5	32	0.02	1.0	2.0	0.003S, Nb, Pb
1925hMO	21	6	25	0.01	0.9	0.9	0.2N, 0.002Si
254SMO	20	6	18	0.02	0.7	–	0.2N, 0.002Si
Duplex2205	22	3	6	0.02	0.2	1.5	0.15, 0.6 (Cb+Ta)
Remanit4565	22–25	4–6	16–18	0.02	0.1	0.5	0.5N, 0.003Si, 0.1Nb
654SMO	25	7	22	0.015	0.4	0.5	0.5N

2.2. Sample preparation

For potentiodynamic cyclic polarization (PCP) experiments, round samples, ~15 mm dia. and 3–5 mm thick, were machined from sheets and were abraded sequentially on 120, 180 and 320 grit SiC paper to simulate service conditions. The abraded samples were cleaned in ethanol in an ultrasonic cleaner. All the specimens were abraded for one hour before each experiment.

Rectangular coupons of the size 100 mm × 20 mm by 3–5 mm were cut from the sheets and were ground by a surface grinder for open circuit potential measurements. The surface finish was ~0.12 μm r.m.s. The ground samples were cleaned with ethanol in an ultrasonic cleaner.

2.3. Open circuit potential measurements

Open circuit potential (OCP) measurements of nine different alloys were carried out in chlorinated (0.20–0.65 ppm residual chlorine) seawater at 25 °C and raw seawater at 50 °C. In the experiments with chlorine dosing the residual chlorine was monitored every day except weekends. A special test cell was designed and fabricated in the laboratory for measuring the OCP. Two multipen chart recorders of 6 and 3 pens were electrically connected to the specimens. The change in voltage, against the SCE, used as reference electrode, was plotted versus time. Everyday the data were transferred in the computer and a combined graph was drawn to study the change in potential for each of the alloys.

2.4. Potentiodynamic cyclic polarization experiments

Potentiodynamic cyclic polarization (PCP) experiments were carried out in seawater at room temperature (25 °C) with and without dosing of sodium hypochlorite (NaOCl) solution and in raw seawater at 50 °C.

The potentiodynamic cyclic polarization experiments were carried out using a computer controlled EG&G model 273 potentiostat with a saturated calomel electrode (SCE) as reference and graphite rods as the counter electrode. The details of the experimental set up are given previously [10].

2.5. Residual chlorine degradation measurements

The degradation of different levels of residual chlorine (0.20–0.7 ppm) with time was monitored at 25 °C in open and closed systems. Initially the residual chlorine level was raised to a predetermined value, and the degradation with time was monitored at short intervals during the first few hours and later at increased intervals. Figure 1 shows the change in the concentration of residual chlorine in an open and closed system with time. It is evident that initially the degradation of chlorine was very fast and later slowed down.

Some trial experiments were carried out to investigate the degradation of chlorine in presence of some alloys. It was found that the maximum effect of chlorine dosing on the open circuit potential of the alloy was observed after 15 min. The corrosion potential becomes more noble and reaches a maximum value after ~15 min of chlorine dosing. 20–25 min after the chlorine addition the potential starts decreasing and after more than 10 h, reaches to same potential as prior to chlorine dosing.

On the basis of the results obtained from the aforementioned trial experiments carried out on chlorine degradation, the potentiodynamic cyclic polarization experiments were set up in such a way that the effect of chlorine on alloys could be studied. A scan rate of 60 mV min⁻¹, after 15 min of sample immersion, appeared to provide polarization curves which gave adequate information about the requisite corrosion parameters. Recently, Latha and Rageswari reported results for stainless steels at the same scan rate [21].

For the materials showing passive behaviour in static seawater on increasing the potential from the free corrosion potential value E_{corr} in the anodic direction, low currents were observed up to a potential, E_b . E_b represents the potential at which the current starts to rise significantly, indicating a loss of passivity or film breakdown. The anodic polarization scan was reversed once the current reached 100 $\mu\text{A cm}^{-2}$. The current, I_{max} , represents the maximum attained should it not begin to fall immediately after scan reversal. E_{prot} is called the repassivation potential, at which the current

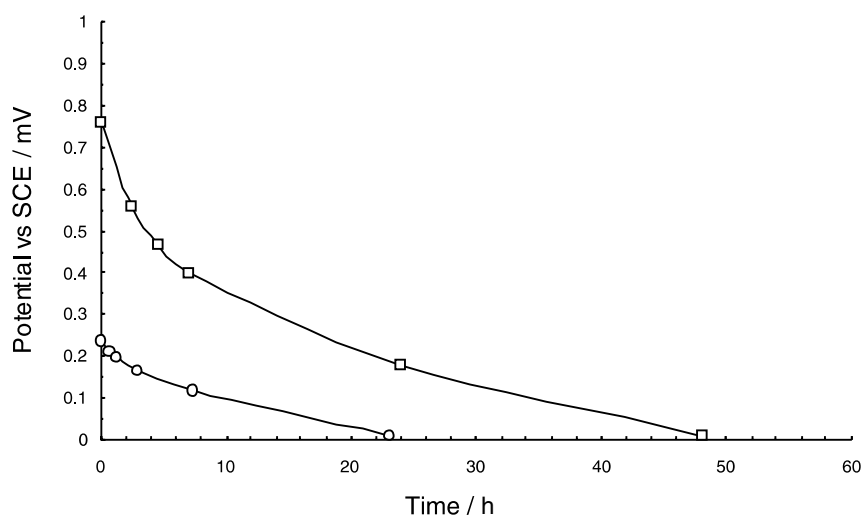


Fig. 1. Degradation of residual chlorine in seawater with time 25 °C. Key: (□) 0.76 ppm and (○) 0.24 ppm.

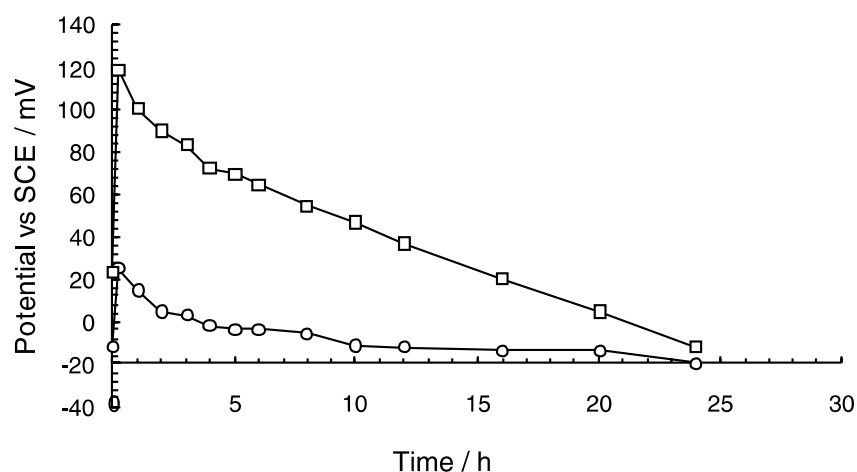


Fig. 2. Degradation of residual chlorine in the presence of SS 316L at 25 °C. Key: (○) 0.23 ppm and (□) 0.65 ppm.

falls to the small value recorded during the forward scan [11].

3. Results and discussion

3.1. Potentiodynamic cyclic polarization studies

Figures 3 and 4 show two typical potentiodynamic scan plots chosen from scans of all nine alloys under study. The values of breakdown potential (E_b), protection potential (E_{prot}) and maximum current density (I_{max}) attained after the start of the reverse scan (at $100 \mu\text{A cm}^{-2}$) at 25°C with and without chlorination and at 50°C in seawater are given in Table 3. The E_b of different alloys at 25°C in seawater follows the sequence:

$$316\text{L} < 317\text{L} < 254 \sim 3127 \sim 1925 \sim 654 \\ \sim 2205 \sim 904\text{L} \sim 4565$$

The E_b values for all the alloys except 316L and 317L are in the range 900–1000 mV vs SCE. A similar trend was also observed in chlorinated seawater. In chlorinated seawater the values of E_b were slightly lower as compared to raw seawater. At 50°C , the E_b of all alloys follow the following sequence:

$$316\text{L} < 317\text{L} < 2205 \sim 904\text{L} \sim 654 \sim 3127 \\ \sim 925 \sim 4565 \sim 254$$

The lower E_b value indicates a higher probability of breakdown of the passive film and an early start of pitting and crevice corrosion. The lowest E_b values were found at 50°C followed by corresponding values in chlorinated and unchlorinated seawater at room temperature. The E_b values of high alloy stainless steel and 904L in chlorinated or unchlorinated water at 25°C fall in the range 905–1016 mV and those of E_{prot} in the range 822–1002 mV. The E_b and E_{prot} values for conventional stainless steels 316L and 317L are about 600–700 mV lesser than for high alloy stainless steels. Amongst the high alloy stainless steels, the E_b values of all alloys except Duplex 2205 at 50°C are in the range 870–921 mV. The maximum I_{max} value is recorded for 316L at 50°C followed by Duplex 2205 and 904L. At room temperature, in chlorinated and unchlorinated seawater, 316L and 317L show slightly higher current densities as compared to the rest of the alloys under test. An increase in I_{max} indicates the possibility of general corrosion under the test condition. At room temperature in both the chlorinated and unchlorinated condition, the current density I_{max} of all the alloys except 316L and 317L lie in the same range. At 50°C the I_{max} follow the sequence:

$$316\text{L} < 2205 \sim 904\text{L} \sim 317\text{L} < 1925 \sim 3127 \\ < 654 \sim 254 \sim 4565$$

A sharp decrease in E_b of all the alloys was observed. It is interesting to note that E_b of Duplex 2205 steel was reduced drastically from 1010 mV SCE at 25°C to 354 mV vs SCE at 50°C . A negligible difference was found in the I_{max} values of 3127hMO, 1925hMO, 254SMO, Remanit-4565 and 654SMO alloys in all the experimental conditions. Duplex 2205 steel showed the maximum difference in I_{max} at 50°C as compared to both the room temperature condition, followed by 904L, 316L and 317L steels.

A small decrease in E_b was observed for 3127hMO, 1925hMO, Remanit-4565 and 654SMO alloys. Therefore these alloys are less prone to crevice and pitting corrosion in seawater and chlorinated seawater at 25°C and in seawater at 50°C . Stainless steels 316L and 317L

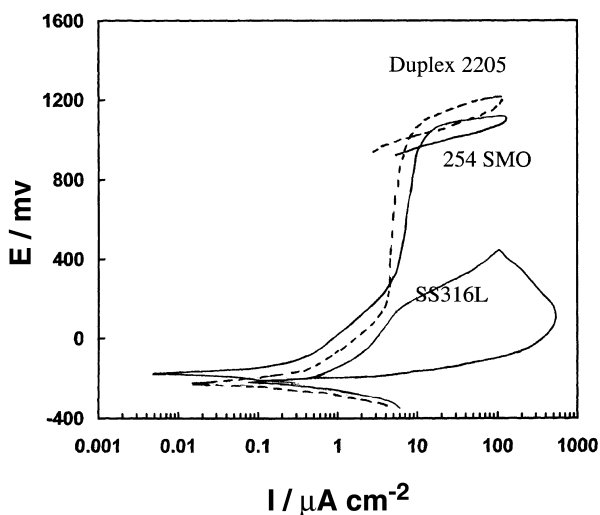


Fig. 3. Potentiodynamic cyclic polarization (PCP) plot for stainless steels 316L, 254SMO and Duplex 2205 in raw Arabian Gulf seawater at 25°C .

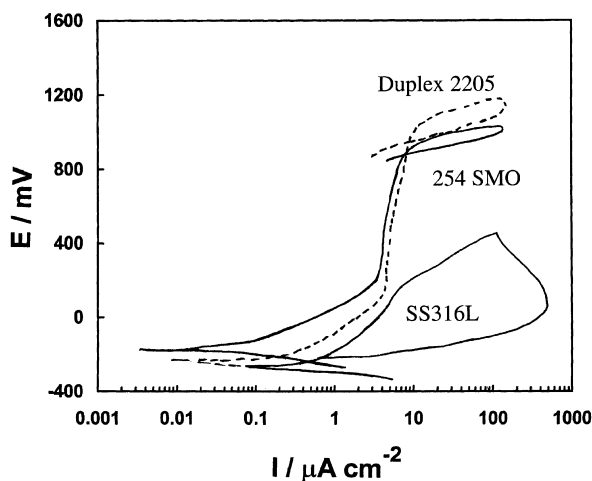


Fig. 4. Potentiodynamic cyclic polarization (PCP) plot for stainless steel 316L, 254SMO and Duplex 2205 in chlorinated (~ 0.2 ppm) Arabian Gulf seawater at 25°C .

Table 3. Breakdown potential (E_b), and protection potential (E_{prot}) vs SCE and maximum current after scan reversal (I_{max}) of nine different alloys in Arabian Gulf water at 25 °C, chlorinated (0.20–0.25 ppm) Arabian Gulf water at 25 °C and Arabian Gulf water at 50 °C

Alloys	PRE _N	25 °C			25 °C (chlorinated)			50 °C		
		E_b /mV	E_{prot} /mV	$I_{max}/\mu A\ cm^{-2}$	E_b /mV	E_{prot} /mV	$I_{max}/\mu A\ cm^{-2}$	E_b /mV	E_{prot} /mV	$I_{max}/\mu A\ cm^{-2}$
316L	25	228	-209	541	97	-220	479	43	-102	1607
317L	30	524	-173	180	300	-165	423	159	-90	816
904L	35	1016	1002	130	905	822	122	647	-114	1230
3127hMO	48.5	950	849	204	905	852	146	879	798	424
1925hMO	41	968	950	135	989	884	146	907	778	515
254SMO	43.5	918	909	141	911	866	142	923	923	128
Duplex2205	24	1010	968	124	1003	957	145	354	-203	132
Remanit4565	40	1039	929	127	952	914	1140	921	921	126
654SMO	57	1001	908	155	948	878	144	870	870	130

at 25 °C, and 904L and Duplex 2205 at 50 °C can suffer from general as well as crevice and pitting corrosion due to their low E_b and high I_{max} values.

An increase in E_b value is observed above a PRE_N value of 30 and at 50 °C an increase in E_b is noted in steels having a PRE_N above 35 (Table 3). From these observations, it can be concluded that the alloys having a PRE_N value of 30 or above at 25 °C in seawater with and without chlorine and alloys having PRE_N value of 35 in unchlorinated seawater at 50 °C can be used safely for seawater applications.

The results of potentiodynamic polarization studies indicate excellent corrosion resistance by 6Mo steels in natural seawater (25 °C and 50 °C) and chlorinated seawater (25 °C). The findings are in agreement with the results reported by others from similar studies on these alloys in Atlantic and Norwegian seawaters [15, 16, 19].

3.2. Open circuit potential studies

Figures 5 and 6 show OCP against time plots of 316L and 254SMO, respectively with different levels (0.23–0.60 ppm) of residual chlorine at 25 °C. A significant

ennoblement in OCP at different concentrations of residual chlorine was observed in all the alloys. The OCP increases with increase in residual chlorine at 25 °C (Figure 7). Figures 8 and 9 show OCP against time plots for 316L, 254SMO and Duplex 2205, respectively, in raw Gulf seawater at 50 °C. They represent typically the OCP against time plots for conventional and high alloy stainless steels. At 50 °C, the OCP of 1925hMO, 254SMO, 654SMO, 3127hMO and Remanit-4565 reached zero value within 10 h of the immersion, while 316L, 317L and 904L take about 15 h to reach this value. In the case of Duplex 2205, a frequent change in potential from anodic to cathodic and vice versa was observed (Figure 10) indicating that some corrosion phenomenon is active at the metal/solution interface.

The use of stainless steels 316L, 317L at 25 °C in seawater applications is unsafe. Because of their very low E_b and high I_{max} values, a further decrease in E_b values in chlorinated seawater increases the risk of their use. The OCP at high levels of residual chlorine is very near to the E_b , especially for 316L and 317L at 25 °C and duplex 2205 at 50 °C in seawater (Table 3). In fact a sharp decrease in E_b from 1095 mV vs SCE at 18 °C to

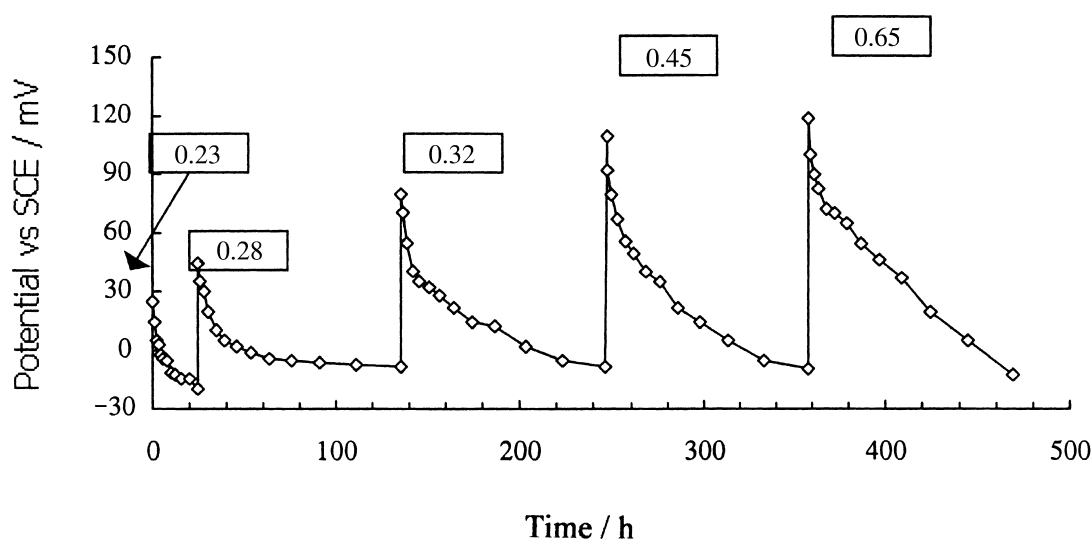


Fig. 5. Open circuit potential (OCP) of stainless steel 316L in Gulf seawater with different levels (left to right: 0.23, 0.28, 0.32, 0.45 and 0.65 ppm) of residual chlorine at 25 °C.

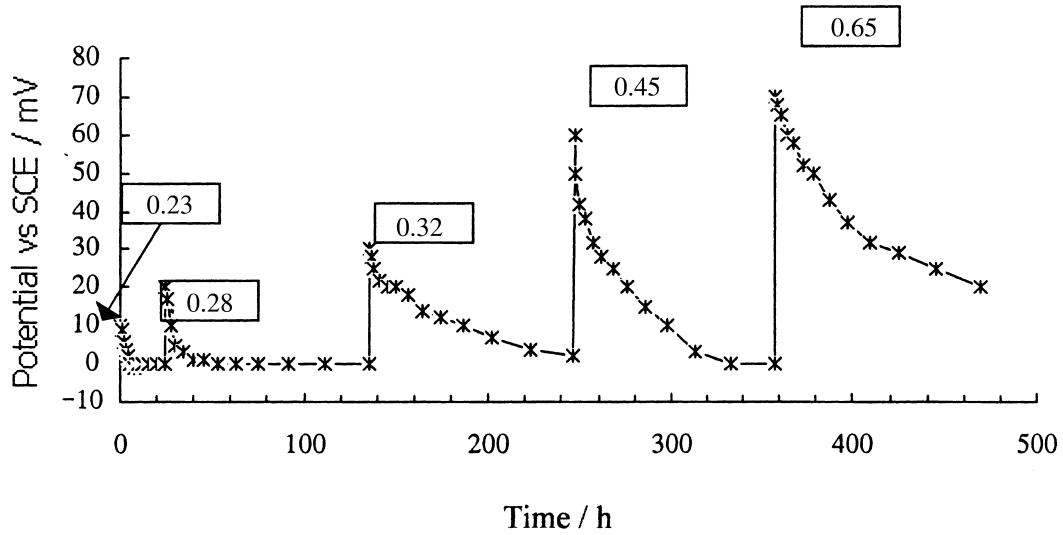


Fig. 6. Open circuit potential (OCP) of stainless steel 254SMO in Gulf seawater with different levels (left to right: 0.23, 0.28, 0.32, 0.45 and 0.65 ppm) of residual chlorine at 25 °C.

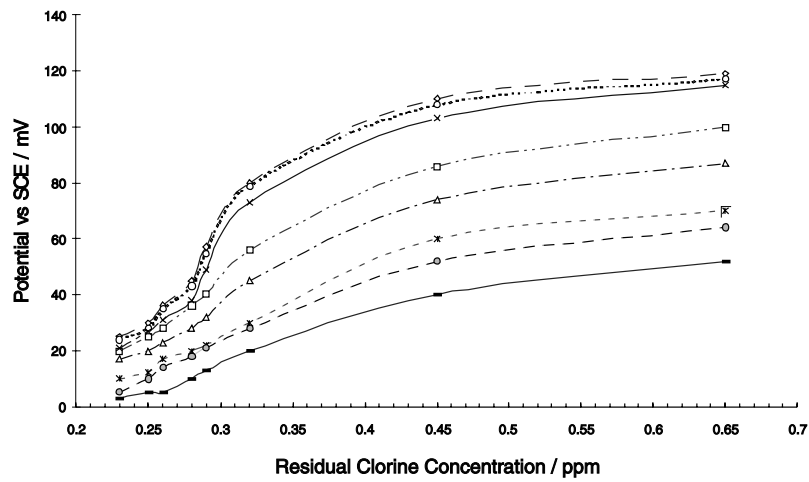


Fig. 7. Plot of maximum open circuit potential (OCP) attained at different levels of residual chlorine for all the alloys at 25 °C. Key: (Δ) 1925hMO, (□) 3127hMO, (—) 4565 Remanit, (○-○) SS 317L, (x-x) 254SMO, (○-○) 654SMO, (◇-◇) SS 316L and (x-x) SS 904L.

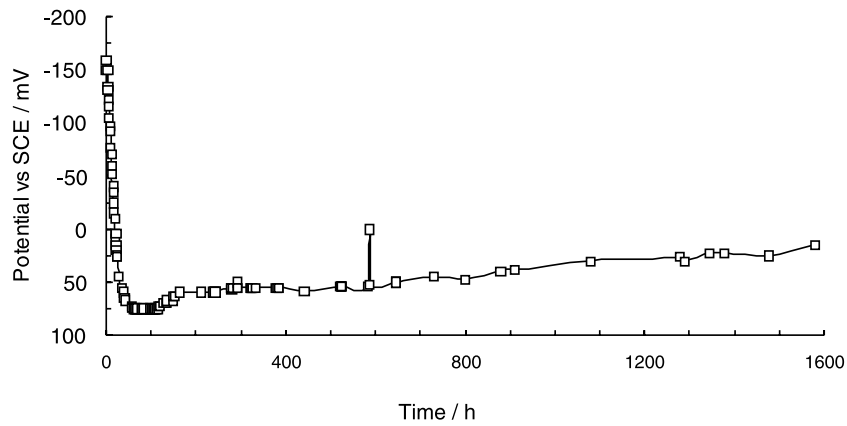


Fig. 8. Open circuit potential (OCP) of stainless steel 316L in raw Gulf seawater at 50 °C.

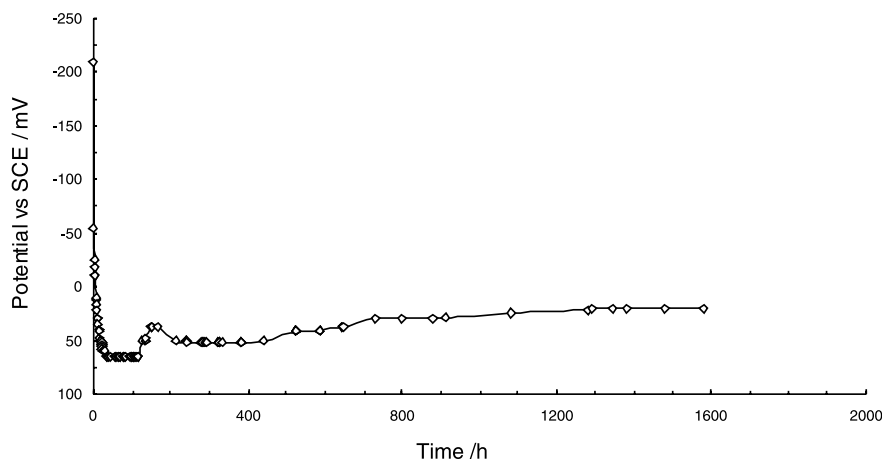


Fig. 9. Open circuit potential (OCP) of stainless steel 254SMO in raw Gulf seawater at 50 °C.

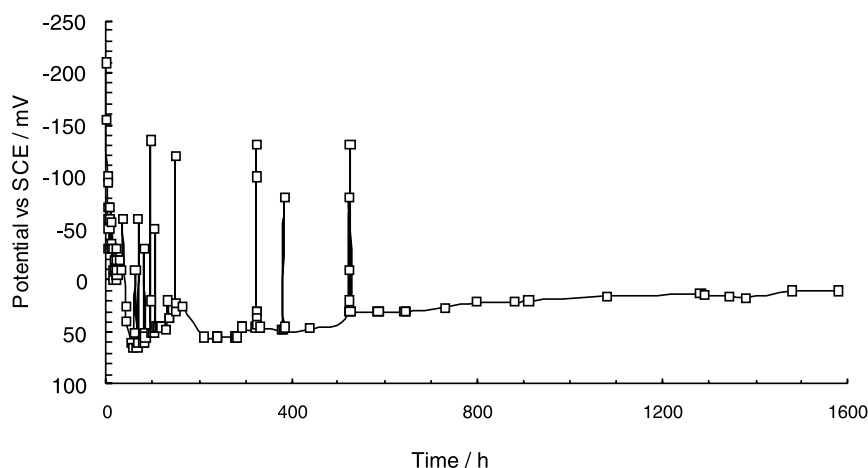


Fig. 10. Open circuit potential (OCP) of stainless steel Duplex 2205 in raw Gulf seawater at 50 °C.

417 mV at 30 °C was reported for this steel [11]. Frequent changes in the OCP, pit formation and sharp decrease in E_b value provide strong evidence that the duplex 2205 steel is not a suitable alloy for high temperature seawater applications.

4. Conclusions

The following conclusions can be drawn:

- (i) The E_b values of stainless steels 316L, 317L and 904L at 25 °C in seawater follow the sequence: 25 °C > 25 °C (chlorinated) > 50 °C.
- (ii) Duplex 2205 steel shows a drastic reduction in E_b from 1010 mV at 25 °C to 325 mV at 50 °C, therefore its use should be restricted to low temperature applications.
- (iii) Alloys having a PRE_N value greater than 35 showed E_b values in a narrow range, for example, 950–1016 (at 25 °C), 905–1003 (at 25 °C, residual chlorine 0.2–0.25 ppm) and 879–923 (at 50 °C).
- (iv) All the stainless steels under test show an increase in open circuit potential in presence of residual chlo-

rine. The ennoblement in open circuit potential increases with increase in the quantity of residual chlorine.

- (v) High alloy stainless steels such as 3127hMO, 1925 hMO, 254 SMO, 625 SMO and Remanit-4565 have very little tendency to crevice and pitting corrosion in normal seawater at 25 and 50 °C and chlorinated seawater at 25 °C.

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