

CORROSION BEHAVIOR OF STEELS IN GULF SEAWATER ENVIRONMENT¹

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ABSTRACT

Due to aggressive environment prevailing in and around Gulf seacoast, the materials of construction are subjected to corrosion of varying degree. There are many factors influencing the initiation of one or several corrosion processes. These factors include nature of material, surface finish, temperature, humidity, wind directions, rainfall, etc. Steels are the predominant constructional materials in seashore structures including desalination plants which are subjected to general or localized corrosion of varying degree. A complete systematic information regarding corrosivity of materials in Gulf seawater is lacking. Keeping in view the importance of the corrosion data of materials particularly steels in Gulf seawater, a systematic study on this subject had been initiated in 1990 and was completed in 1996. This paper provides the results of this study concerning with the corrosion behavior of steels, in Gulf seawater. The steels include carbon steels, stainless steels and super stainless steels (austenitic, ferritic and duplex). The study encompasses the factors influencing general, pitting and crevice corrosion of materials. The effects of TDS in general and chloride concentration in particular and degree of chlorination have been discussed in detail. The role of dominant alloy addition on the corrosion behavior of steels has been emphasized.

Weight loss and electrochemical techniques have been employed in determining the corrosion rates of materials. Potentiodynamic polarization technique has been used to evaluate parameters related to localized corrosion. Both exposure and accelerated tests have been carried out to study crevice corrosion attack. Effect of surface finish

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on crevice attack has been investigated in detail. Rank orders of corrosion rates of steels under different conditions have been presented and their importance vis-a-vis materials selection in desalination plants is discussed.

Key Words: Pitting, Crevice Corrosion, Stainless Steel, Breakdown Potential, Pitting Potential, PRE_N and Chlorination.

1. INTRODUCTION

Steels are the most extensively used structural materials in industry. Mild steel is the most versatile general purpose material due to its good mechanical strength, easy fabricability, formability and weldability, abundance and low cost. In corrosive environment, mild steel structures can be saved by coating and/or cathodic protection. However, in more severe or aggressive environments such as marine or seawater, mild steel may not withstand and austenitic stainless steels such as 304 and 316 have found applications as construction materials. The excellent corrosion resistance, good mechanical properties and reasonable cost are the contributing factors for their application as outstanding structural material. In seawater process industries, which also include desalination plants, 316 type alloys have been formidable material for construction of evaporators, distiller pipes, pumps valves and condensers. These alloy are the most dependable structural materials under dynamic or flow conditions and virtually show no corrosion even on very long exposures. However, these alloys are subject to localized corrosion in presence of chloride ions and under static or stagnant conditions. The pitting of 316 L stainless steel is often encountered in desalination plant and appears to be the most effective factor responsible for corrosion failure in plants. The pits also provide active crevices for a formidable corrosion attack. In most cases, pitting is precursor of crevice corrosion and there are obvious similarities between crevice and pitting corrosion mechanisms. High chromium containing Ni-base alloys (Cr-Ni-Mo) were used as possible replacement for stainless steels to combat localized corrosion. However, the prohibitive cost of Ni-base alloys has severely restricted their application. Based on the fact that Cr and Mo has synergic effect in enhancing the pitting resistance of steel in seawater, 6% Mo containing stainless steels so called high alloy stainless steels were introduced in sixties and the following decades. The application of

conventional and high alloy stainless steels in marine environment have been dealt in a number of review and articles [1-6].

Electrochemical techniques have been the principal tool for characterizing pitting and crevice corrosion. The pitting potential, E_{pit} is a fundamental parameter in evaluating the susceptibility of different materials in different environment to localized corrosion [7]. Some authors [8,9] asserted that due to similarities between crevice and pitting corrosion mechanisms, it would be more appropriate to refer to localized corrosion by a new parameter called breakdown potential, E_b , which is defined as potential where pitting or crevice corrosion or both will initiate or propagate.

Temperature and velocity are the two important factors influencing the corrosion of SS superaustenitic and Ni- and Co- base alloys in seawater [8]. Electrochemical studies explicitly demonstrated the effect of increased temperature in facilitating premature breakdown of passive film on all materials. The effect of high velocity impinging flow was to further shift the passivity breakdown potential to active values but not necessarily to result in greater depth of attack. In general, increase in temperature caused a decrease in pitting potential and an increase in corrosion rate and pitting tendency [10, 11]. However, at a certain temperature, the decrease in Dissolved Oxygen (DO) level could result in reversal of the process.

The Cr, Mo and N contents of the alloy greatly influence their pitting and crevice corrosion behavior. The synergic effect of Cr and Mo in resisting pitting was first shown by Lorenz and Madwar [12] in 1969 and was further investigated by Herbsleb [13] in 1982 who also considered nitrogen. The pitting resistance equivalent, PRE_N is represented by the equation

$$PRE_N = \% Cr + 3.2 \% Mo + 16\% N$$

A PRE_N above 38 is supposed to provide resistance to marine corrosion. Crevice corrosion of highly alloyed SS ($PRE_N > 40$) exposed to seawater, once initiated can propagate at temperature far lower than the initiation temperature. Repassivation

properties of the material are thus important with respect to material selection and control.

This paper incorporates the results of various studies concerning with the corrosion behavior of conventional and high alloy stainless steels in Gulf seawater. A number of studies carried out in recent years signified the importance of PRE_N in assessing the ability of alloy to resist to pitting. Interesting yet useful relationship have been shown between PRE_N and several corrosion parameters such as pitting potential, E_{pit} , pitting induction time, t_i , corrosion rate (CR), etc., [13]. Alloy addition such as Mn appeared to negate the resistance to pitting [14].

Chlorination of seawater is the normal practice to destroy microorganism or microbiological growth, the residual chlorine influences significantly on the corrosion behavior of materials. The results of a number of studies concerning with pitting and crevice corrosion tendencies of conventional and high alloy steels in chlorinated seawater are reported in literature [15, 16]. High alloy stainless steels appear to have good resistance to residual chlorine. In one such study [17] it has been shown that besides 254 SMO which did not corrode in seawater (25,000 to 50,000 ppm Cl^- and 0-10 ppm residual chlorine) all other alloys developed crevice and suffered some degree of corrosion.

Critical crevice temperature and critical crevice index (CCI) have been used for measuring crevice corrosion tendencies of superaustenitic and duplex steels in chlorinated seawater [18] Critical Crevice Temperature (CCT) was found to be in the same range. No significant difference in CCT for metal-metal and metal-gasket crevices was found. Even the Ni-base alloys, which were supposed to have formidable resistance against crevice attack in seawater, have been found to be vulnerable. Creviced Ni-Cr-Mo-Fe alloys (alloy 625 and C 276) immersed in two different types of seawater, were found to contain concentrated amounts of dissolved Ni^{2+} , Cr^{3+} , Mo^{3+} and Fe^{2+} in crevices showing that both the alloys underwent crevice corrosion [19].

2. EXPERIMENTAL

15 different commercial grade stainless steels, viz., 304L, 316L, 317L, 904L, 17-4PH, 254 SMO, 654SMO, HMO 1925, HMO 3127, 20Cb3, Remanit 4565, Remanit 4575, Monit 44635 and Duplex 2205 were used during the studies. [Table 1](#) lists the composition of the alloys.

Aqueous chloride solutions of varying chloride concentration, seawater (Arabian Gulf seawater) and chlorinated seawater were used during the experiments. The composition of the seawater is given in [Table 2](#). The chlorinated seawater was prepared by dosing with sodium hypochlorite and the residual chlorine was measured by HACH DREL/IC portable kit. For potentiodynamic polarization studies, circular specimens of ~15 mm diameter and 3-5 mm thickness were machined from the sheet and were abraded sequentially on 180, 320 and 600 grit SiC papers. Rectangular coupons of the size 10 x 20 x 3-5 mm were cut from the sheet and surface furnished at 0.12 μm rms were used for open circuit potential measurements.

Experimental details of crevice corrosion measurements and potentiodynamic polarization and cyclic polarization experiments carried out in this study are described in previous publications [2, 7, 10, 13].

Open Circuit Corrosion Potential (OCP) of alloys was measured in normal and chlorinated seawater. The residual chlorine was monitored everyday. A special cell was designed and fabricated in the laboratory. Two multiples chart records of 6 and 3 pens were electrically connected to the specimens. The change in voltage against SCE as reference was plotted vs time. Every day the data were transferred into the computer and combined graph was drawn to study the change in potential for each of the alloys.

2.1 Accelerated Tests

Salt spray tests were carried out in Salt Spray fog Chamber following ASTM B117 - 73. Test coupons of 12 cm^2 were cut from the sheet and abraded to 180 grit SiC paper. Accelerated testing for resistance to crevice corrosion initiation was also carried out.

The crevice corrosion assembly consisting of the specimen (rod or sheet form) attached with Teflon crevice former was mounted in epoxy former to provide a crevice free mount. The experimental details of salt spray and crevice corrosion accelerated tests are given in previous papers [7, 20].

3. RESULTS AND DISCUSSION

3.1 Accelerated Tests

The conventional (316 L and 904L) and high alloy stainless steels (SMO 254 and 654, hMo 1925 and 3127, 20 Cb3, Remanit 4565 and 4575, Monit 44635) were subject to salt-salt fog environment in a salt spray fog chamber for testing under accelerated conditions. Results of 3024 and 5000 hours exposure tests indicate very low weight losses corresponding to corrosion rates in the range of 0.001-0.005 mpy. This leads to a foregoing conclusion that conventional and high alloy stainless steels are resistant to general corrosion under severiest environments.

A study of the potentiodynamic polarization curves for the high alloy stainless steels in seawater indicate that little or no corrosion current was noticed on chloride additions showing thereby the outstanding resistance of these steels towards chloride. For getting measurable corrosion current, polarization experiments involving most aggressive conditions were carried out. In these experiments, such conditions were produced by bringing down the pH to low values (0-3) plus addition of NaCl solution at 50 °C. Critical corrosion current value representing as active peak height (APH) is taken as the measure of critical crevice solution (CCS). The CCS of the alloy is taken as the value corresponding to APH of $10 \mu\text{A cm}^{-2}$. Conventional alloys such as 304L and 316L and high alloy stainless steels such as 3127hMo and 654SMO have low CCS pH values of 0.481 and 0.50, respectively (Figure 1). These results indicate excellent crevice corrosion resistance of high alloy stainless steel under aggressive conditions. Plots of critical crevice index ($\text{CCI} = \% \text{Cr} + 4.1\% \text{Mo} + 27\% \text{N}$) and CCS pH of conventional and high alloy steels, show a liner relationship (Figure 2) indicating a strong but negative dependence of critical crevice solution aggressively on Cr, Mo and N content.

3.2 Effect of Surface Finish

The surface finish has a considerable influence on the localized corrosion behavior of stainless materials in seawater. Under surface finish conditions of wheel ground, as received, 180 grit SiC ground, 600 grit SiC ground, sand blasting and HNO₃ etching, except 304 L and 316L, none of the alloys corroded to measurable depth of attack at 25 °C thus indicating that crevices do not act as sites for corrosion initiation for high alloys stainless steels. Stainless steels 304L and 316 L provide small yet measurable crevice corrosion depth. At 50 °C, under aforementioned conditions, most of the high alloy steels either does not corrode or corrode surficially. The surficially corroded alloys showed very small crevice corrosion buildup. However, after crevice formers were removed and sample were cleaned, no perceptible depth of attack was found when examined microscopically. This has been attributed to high propagation resistance of the alloy due to the strong passivation of the protective passive film on the metal surface. Therefore, the crevice corrosion initiation of an alloy does not necessarily relate to its propagation rate. Solution immersion tests indicate that alloy SS 304 and 316L show mild attack at 25 °C, the attack is more pronounced at 50 °C, the former was attacked more severely.

3.3 Effect of Temperature

The temperature greatly influences the corrosion behavior of steels in seawater as has been indicated by the values of corrosion parameters from electrochemical studies. Pitting potential of the conventional and high alloy steels measured in the temperature range of 25-90 °C indicate a shift to more active values up to the temperature of 65 °C. Above 65 °C, Epit becomes constant. The constancy in the Epit values has been attributed to the decrease in dissolved oxygen level due to increase in temperature. This factor plays more prominent role at higher temperature (> 65 °C). A liner relationship (Arrhenius plot) exists between logarithm of corrosion rate and reciprocal of absolute temperature (Figure 3). The slop of line provides activation energy for the process in the temperature range of 25 °C to 90 °C. In general, with same exposure time, the severity of corrosion attack increases with increases in temperature.

3.4 *Effect of Chloride Concentration*

The effect of chloride concentration on corrosion rates of stainless at 50 °C as studied by electrochemical liner polarization resistance technique indicate that the corrosion rates do not follow a regular pattern but in majority of the alloys, the corrosion rate increase with increasing chloride content. Whilst the corrosion rates of conventional stainless steels such as 304L, 316L and 317L in seawater are higher than in aqueous chloride solutions containing up to 5000 ppm chloride, the high alloy steels in general appear to have slightly lower corrosion rates in seawater (Figure 4). The lower corrosion rates in seawater have been attributed to the formation of a stable biofilm, which acts as a barrier against corrosion.

The pitting potential, E_{pit} that is a measure of pitting tendency of a material under specific environment show a significant active shift with increasing chloride contents. Due to the formation of a strong and more resistance passive oxide film, the high alloy steels have much higher pitting potential than conventional stainless steels. This is further manifested by the strong dependence of E_{pit} on PRE_N , the pitting resistance equivalent. Alloys having greater PRE_N have lower tendency to pitting, requiring much higher potential (E_{pit}) to initiate pitting in the alloys. Two separate liner relationships exist for conventional and high alloy stainless steels.

3.5 *Effect of Chlorination*

Results from potentiodynamic cyclic polarization studies carried out on conventional and high alloys stainless steels under chlorinated and normal conditions indicate that the breakdown potential, E_b is lowered on chlorination (Table 3). The lower E_b values indicate more chances of breakdown of passive film easily and early start of pitting and crevice corrosion. Low decrease in E_b was observed for 3127 hMO, 1925 hMo, Remanit 4565 and 654 SMO. Therefore, these alloys have less chance of crevice and pitting corrosion in seawater and chlorinated seawater. SS 316L and 317L at 25 °C can suffer from general as well as crevice and pitting corrosion due to low E_b and high I_{max} values. Plots of E_b vs PRE_N for high alloy SS show that the alloys having PRE_N values of 30 or above are quite resistant to chlorinated seawater (Figure 5).

The open circuit potential of the alloys increases with increase in residual chlorine at 25°C. Whilst E_b values of superstainless steels at different levels of residual chlorine are much higher than conventional stainless steels, the open circuit potential values of superstainless steels are markedly lower than the conventional stainless steels.

3.6 Open Circuit Corrosion Potential (OCP) Measurement

Results from OCP measurements can be very well analyzed from corrosion potential vs time plots. These plots indicate 4 distinct stages:

- (i) Increase of potential in the noble direction resulting from thickening or healing of the passive film.
- (ii) Constancy in corrosion potential, although at time fluctuations in active direction characteristic of local breakdown of passivity may be observed.
- (iii) Steep or gradual fall in corrosion potential from the passive region representing pit initiation stage.
- (iv) Corrosion potential sustains low values during propagation stage.

The OCP vs time plots provide information about induction time for pit or crevice initiation, t_i , which is indicated by constancy in potential. Due to the presence of a strong passive film, high alloy stainless steels have much larger induction time than the conventional steels. This is demonstrated by the plots of PRE_N vs t_i (Figure 6) where two separate lines plots representing conventional and high alloy steels are obtained. In high alloy stainless steels induction time increases with increasing PRE_N whereas with conventional stainless steels an opposite effect is found. The latter behavior indicates that conventional steels are susceptible to pitting in much shorter time and pitting behavior is greatly influenced by low Cr + Mo contents. This behavior is also manifested by the similar linear plots of E_{pit} vs t_i for the two categories of alloys indicating strong dependence of Cr + Mo contents on the pitting behavior of the alloys.

4. CONCLUSIONS

- (i) The corrosion rates of conventional austenitic steels and high alloy stainless steels in seawater, under static conditions and at 25 °C and 50 °C, as

determined from immersion and salt spray tests, are extremely low (0.001 - 0.005 mpy).

- (ii) The corrosion rates as determined from electrochemical polarization technique are low (0.01 - 0.1 mpy) but are about one order of magnitude higher than from immersion tests. This has been attributed to the time lag for stabilization of protective oxide film.
- (iii) High alloy SS when creviced in seawater at 25 and 50 °C, show very small corrosion build up but no perceptible depth of attack indicating absence of propagation stage during crevice attack.
- (iv) In the temperature range of 25-65 °C, a linear relationship exists between logarithmic of corrosion rate and reciprocal of absolute temperature (Arrhenius plot).
- (v) Pitting potential, E_{pit} shows a significant active shift with active chloride contents. Due to the formation of strong and more resistance passive oxide film, the high alloy stainless steel has much higher E_{pit} than conventional stainless steels.
- (vi) For all the alloys, the breakdown potential, E_b is lowered on chlorination. However, much more decrease in E_b was observed for high alloy SS, therefore, these alloys have less chances of crevice and pitting corrosion in seawater.
- (vii) Pitting Resistance Equivalent, PRE_N appears to be a function of E_{pit} , t_i , E_b and CSPH. In general, two separate relationships exist for conventional (304, 316, 317, 904) and high alloy SS (254 and 654 SMO, hMO 1925 and 3127, Duplex 2205, etc.).
- (viii) For seawater applications, conventional and high alloy SS can be used without risk of localized corrosion in crevice and deposit free systems. However, for crevice forming system, only high alloy SS appear to be satisfactory materials for seawater applications including desalination plants.

Table 1. Composition of Stainless Steels

UNS No.	Alloys	Product	Fe	Cr	Mo	Ni	C	Cu	Mn	Others
S30403	304L	-	Balance	18	-	10	0.03	0.2	1	0.45P, 0.02S, 1.Osi
S31603	316L	-	Balance	16	3	11	0.02	0.2	1	0.045P, 0.02S, 1.OSI
S31703	317L	-	Balance	18	3	13	0.02	0.2	2	0.045P, 0.02S, 1.Osi
N08904	904L	AVESTA	Balance	20	5	24.5	0.02	1	1.5	0.045P, 0.02S
S31254	SMO 254	AVESTA	Balance	20	6	18	0.02	0.7	-	0.2N, 0.002Si
S32654	SMO 654	AVESTA	Balance	25	7	22	0.015	0.4	0.5	0.5N
N08925	hMO 1925	VDM	Balance	21	6	25	0.01	0.9	0.9	0.2N, 0.002Si
N0828	hMo 3127	VDM	Balance	27	6.5	32	0.02	1	2	0.003S, Nb, Pb
-	Remanit 4565	THYSSEN	Balance	22-25	4-6	16-18	0.02	0.1	5	0.5N, 0.003Si, 0.1Nb
S44635	Monit 44635	AVESTA	Balance	25	4	4	0.025	0.2	0.4	0.035N, Ti, Nb, Pb, Si
-	Remanit 4575	THYSSEN	Balance	27-29	2-3	3-4.5	0.01	-	0.1	0.025N, Ti, Pb, Si, Nb
S31803	Duplex 2205	AVESTA	Balance	22	3	6	0.02	0.2	1.5	0.15, 0.6 (Cb + Ta)
S41000	410	-	Balance	13	-	-	-	-	1	0.04P, 0.035S, 1Si
S17400	17-4PH	ARMCO	Balance	16	-	4.5	0.07	4	1	0.3Cb, 0.04P, 1Si
N08020	20Cb3	CARPENTER	Balance	19	2	33	0.02	3	0.4	0.4Si, 5Cb + Ta

Table 2. Gulf Seawater Composition, pH 8.2

Ions	Concentration mg/L
Calcium	Ca ⁺⁺ 508
Magnesium	Mg ⁺⁺ 1,618
Sodium	Na ⁺ 13,440
Potassium	K ⁺ 483
Strontium	Sr ⁺⁺ 17
Bicarbonate	HCO ₃ ⁻ 176
Chloride	Cl ⁻ 24,090
Sulphate	SO ₄ ⁻⁻ 3,384
Bromide	Br ⁻ 83
Fluoride	F ⁻ 1
Total Dissolved Solids	TDS 43,800

**Table 3. Breakdown Potential (E_b) of Stainless Steels
in Gulf Seawater at 25 °C**

S. No.	Alloys	E_b (mV) Normal Seawater	E_b (mV) Chlorinated (0.20-0.25 ppm)
1	316-L	228	197
2	317-L	524	300
3	904-L	1016	905
4	3127hMO	950	905
5	1925hMO	968	989
6	254SMO	918	911
7	Duplex-2205	1010	1003
8	Remanit 4565	1039	952
9	654 SMO	1001	948

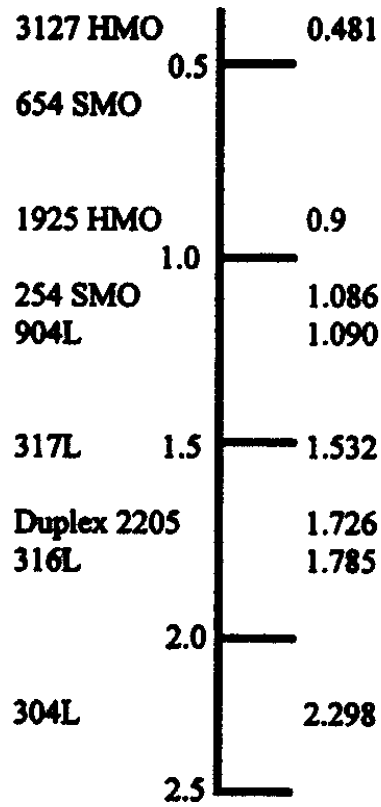


Figure 1. Predicted ranking of conventional and high alloy stainless steels

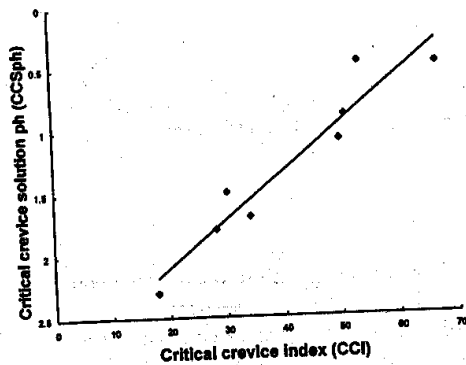


Figure 2. Plots of critical crevice index Vs. critical crevice corrosion pH

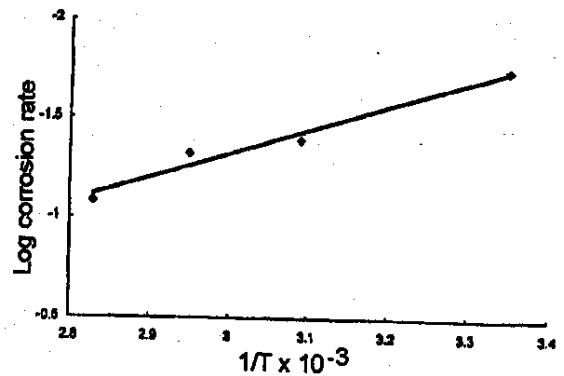


Figure 3. Effect of temperature on corrosion rate of SS 316L Arrhenius plot

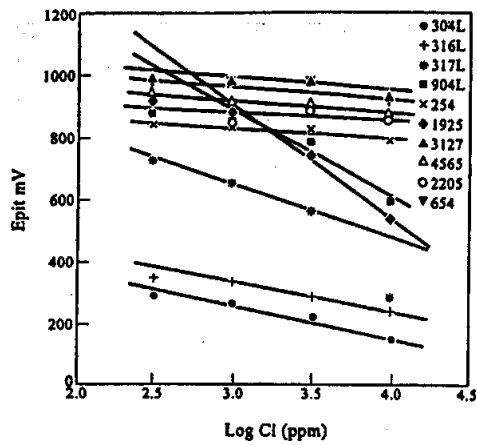


Figure 4. Plots of pitting potential, E_{pit} Vs. long $[Cl]$ for different steels in chloride containing aqueous solutions.

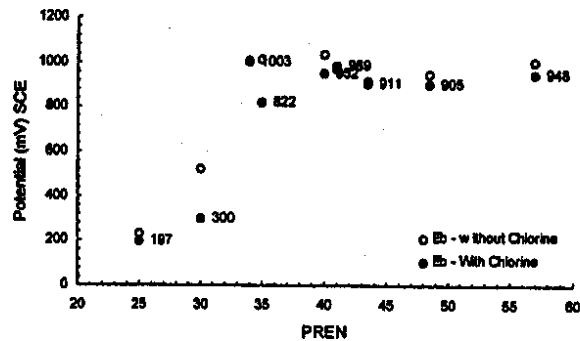


Figure 5. Variation in breakdown potential E_b with PRE_n values with and without chlorination (0.2 ppm) at 25 °C

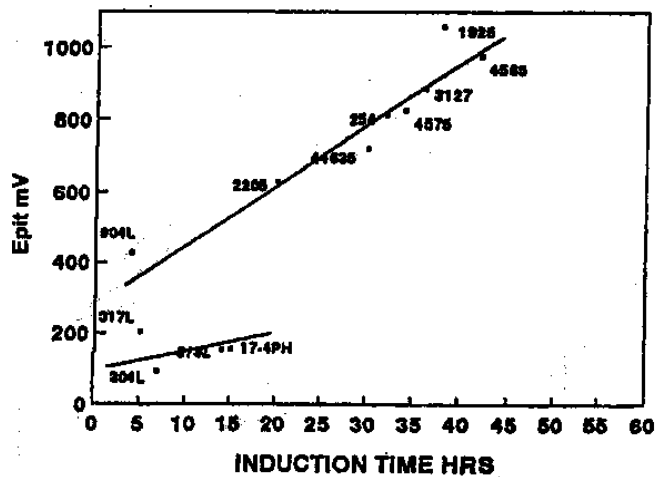


Figure 6. Induction time, t_i , and pitting potential, E_{pit} . Two separate linear plots represent conventional and high alloy stainless steels, respectively

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