



THE EFFECT OF CHANGING FROM MSF TO RO WATER ON THE INTERNAL CORROSION OF LINE 3

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ABSTRACT

Carbon steel, electroless nickel (ENP-1018), 304 SS, 410 SS, 420 SS and 431 SS which constitute the main materials of construction of the components of Line 3 were chosen to study their behavior in two types of RO water: lower limit water (LLW) and upper limit water (ULW) containing 250 ppm and 350 ppm chloride, respectively. Corrosion resistance under operating and shut down conditions and effect of phosphate dosing were the tasks included in the testing program. The corrosion rate studies under operating condition revealed that carbon steel had the highest corrosion rate when compared to other materials. Addition of 2 ppm phosphate reduced the corrosion rate considerably by off setting localized corrosion. The 410 SS was susceptible to corrosion only next to carbon steel. The corrosion rate under shut down condition revealed pitting and crevice attack on carbon steel and ENP-1018 in LLW and ULW with and without 2 ppm phosphate additions as inhibitor. The least susceptible was 304 SS. The issues concerning the application of phosphate dosing and material upgradation are addressed task-wise from the material component point of view in the light of increasing chloride content and temperature of RO water.

Keywords: RO water, MSF water, Corrosion resistance, Jet impingement, Potentiodynamic Polarization, Crevice Corrosion, Phosphate dosing.

المخلص

431SS 420SS 410SS 304SS

ENP-1018

1. BACKGROUND

Al-Jubail – Riyadh pipe line (Line 3) has a pipe length of 375 km and a diameter of 1524 mm. It has 6 reservoirs and 4 pumping stations. The pipeline is internally cement lined. The pipeline was initially tailored for pumping MSF water but towards the end of 1993, SWCC decided to use it for transporting RO water instead of MSF water. A change over from MSF to RO water may not affect the cement lining but it can affect pumps, valves and instrumentations constructed of carbon steel, cast steel materials, low alloy steels and stainless steels due to high chloride contents of RO water. Keeping in view the possibility of corrosion in steel components of Line 3 as a result of flowing RO water, SWCC asked R&D to carry out a study on the assessment of the effect of the change in water analysis from MSF to RO on the internal corrosion of Line 3.

2. INTRODUCTION

The Line 3, an internally cement lined steel pipeline, was installed in 1989 but is yet to be commissioned. Towards the end of 1990, SWCC made the decision to change the water quality from MSF to RO. The pipeline has already been constructed and the auxiliary hardware such as valve, pump, instrument etc. were installed. The possibility of corrosion of materials could not be ignored due to relatively aggressive nature of RO water (high chloride and TDS) which could be aggravated further in case water remains stagnant during pipeline maintenance / shutdown. However, there should be no problem in protecting the inner cement concrete coating from aggressive RO water as long as this water has a pH of 8.5 and a positive Langlier Index (L.I) of 0.3 which provides a fine CaCO_3 coating on the inner surface of the pipe. A survey of literature indicates that no information is available regarding the corrosion behavior of carbon steel, alloy steel and stainless steel in RO water. In order to avoid prohibitive cost involved in replacing the existing hardware by better corrosion resistant, it was a logical approach to determine the corrosion behavior of existing materials in new water (RO). The results of such a study should be helpful in taking a decision regarding the future course of action before the line 3 comes into operation.

3. OBJECTIVES

The studies were conducted taking into consideration the following objectives:

- (1) To establish the electrical potential required to provide cathodic protection (CP) to components in water transmission system in particular valves which are made of ferritic stainless steels.
- (2) To carry out jet impingement tests in order to obtain data regarding the corrosion behavior of materials relevant to operating condition in pipeline.
- (3) To carry out corrosion testing of materials under stagnant water condition, a situation which raises during shut down of the pipe line.
- (4) To study the effect of phosphate dosing in water on corrosion protection of material under pipeline operating condition.

4. SCOPE OF WORK

The following tests were carried out to meet the objectives of this project.

Task-1 Cathodic Protection:

Laboratory tests were carried out in RO water to establish the electrical potential required to protect components in the water transmission system particularly the valves.

Task-2 Corrosion Resistance under Operating Condition:

To simulate flow conditions in the pipeline, jet impingement tests were carried out in RO waters at 40 °C. The results interpreted to provide performance of the existing material that had helped selection of alternate materials.

Task 3 Corrosion Resistance under Shut Down Conditions:

A series of electrochemical tests were carried out coupled with short term crevice corrosion testing in stagnant RO water which was similar to shut down condition in pipeline. The results provided information about the corrosion behavior of materials and rate of attack under stagnant conditions.

Task 4 Effect of Phosphate Dosing:

To evaluate the effect of phosphate dosing required to determine whether intermittent dosing, e.g., once a month will be sufficient to maintain improved corrosion resistance. The testing will be carried out in a dynamic loop.

5. EXPERIMENTAL

5.1 Material

Alloy materials were consisted of carbon steel 1018, 410 SS, 420 SS, 431SS, 304 SS and electroless nickel plate (ENP). The composition of the materials is given in Table 1.

5.2 Specimens

The dimension of the specimens used for different studies was as follows. All specimens were prepared in duplicate:

- (i) *Electrochemical*: circular specimens of 14 mm diam. 3 mm thick, finished on 600 grit.
- (ii) *Jet Impingement* : 40 x 80 x 3 mm finished on 400 grit.
- (iii) *Multiple Crevice Assembly* : 30 mm OD and 20 mm ID producing a 5 mm annular crevice site. Torqued to 10 N/mm² force.
- (iv) *Dynamic Test Loop* : 100 x 50 x 3.5 mm finished on 120 grit.

5.3 Test Media

Following types of water were used during the studies:

- (i) ULW represents upper limit of dissolved solids in RO water.
- (ii) LLW represents lower limit of dissolved solids in RO water.
- (iii) ULW and/or LLW containing phosphate.

The composition of ULW and LLW is given in Table 2.

5.4 Techniques

Following techniques were used during the studies

- (i) *Electrochemical* : EG &G model 342-2 soft Corr. Measurement system consisting of 273 EG & G potentiostat, model 342 software and a computer with saturated calomel and graphite as reference and counter electrodes, respectively.
- (ii) *Jet Impingement (JIT)*: Cortest jet impingement test apparatus with 2 plenum chambers made of titanium metal. Each plenum chamber consists of 12 nozzle

ports with 1 mm diameter orifice, thus allowing 24 number of samples to be tested in each experiment.

- (iii) Multiple Crevice Assembly (MCA) used had washers containing a number of bore holes which enable environment access to the ID creating a crevice depth. The assembly was torqued between crevice former assembly and sample.
- (iv) A close circuit recirculation dynamic test loop (DTL) fabricated at R&D Center. The test loop had a facility to monitor inlet/outlet pressure, temperature and flow rate on continuous basis.

6. RESULTS AND DISCUSSION

6.1 Corrosion Resistance under Operating Conditions (JIT)

To generate data relevant to corrosion resistance under operating conditions, Jet Impingement Test (JIT) was carried out. The test method was based upon ASTM G73-82 (Reapproved 1987) for liquid impingement erosion testing using Cortest Jet Impingement Apparatus. In the JIT, a flow induced localized corrosion would occur when metals and alloys are subjected to water jets of specified velocity. Velocity has a major role in inducing corrosion. During JIT, the corrosion process is accelerated by the removal of protective corrosion products layer on the metal surface by the action of shear stress and turbulence of fluid flow. This would result in direct exposure of base metal to environmental agent and accelerates the metal dissolution. Tests were carried out at two temperatures namely, 50°C and 35 °C in ULW water at a velocity of 10 m/sec which represents velocity of flow normally encountered at the immediate vicinity of pump outlets of Line 3. The tests were of 14 days and 28 days durations.

The Corrosion Rate (CR) data calculated from weight loss using standard formula, namely,

$$CR = \frac{534 \times Wt. Loss (mg)}{D \times A \times T}$$

where, D = Density (gm/cm³), A = Area (in inch²) and T = Time (in hours).

The radius of impingement (RI) and Depth of Impingement (DI) are measured after the test using calibrated microscope. The JIT test results are summarized in Table 3. Figure 1 shows photographs of the alloy specimens after jet impingement tests before and after cleaning.

The following facts were emerged from the analysis of test data.

In ULW at 50°C the corrosion rates of carbon steel- 1018 and ENP 1018 in 14 days test were higher than that of 28 days test. In 410SS and 420SS, there is an increase of 1.5 mpy and

1.1 mpy in average corrosion rates, respectively during 28 days test while compared to 14 days test. Alloys 304SS and 431SS were free from corrosion in 14 days and 28 days tests.

Effect of velocity was analyzed in terms of extent of corrosion by the measurement of depth of impingement attack (DI) as a function of Impingement diameter (RI). The results indicate that only carbon steel was susceptible for impingement corrosion.

In ULW at 35°C, the corrosion rates of 304SS, 410 SS, 420 SS and 431 SS were found higher in 14 days test than in 28 days test. Extent of corrosion due to impingement in carbon steel was lower than at 50°C. The impingement corrosion was not noticed in the rest of the materials.

In ULW containing 2 ppm phosphate at 35°C, the effect of addition of phosphate on the corrosion rates was found more pronounced in the carbon steel and 410SS samples (Table 3). Corrosion rates were significantly reduced to 25% of its value of that without phosphate. Phosphate, as expected, acted as an effective corrosion inhibitors for carbon steel and 410SS. Alloys 304 and 431SS were free from corrosion in 14 or 28 days tests.

6.2 Corrosion Resistance under Shutdown Condition

Electrochemical polarization and crevice corrosion tests were carried out to study the corrosion resistance under shutdown condition.

6.2.1 Electrochemical Polarization Tests

Electrochemical polarization studies were carried out on deaerated solution following the procedures as per ASTM G 61 – 86 at 45°C. Mounted samples were placed in the solution and corrosion potential, E_{corr} mV measured until it reaches a stable value. Typical potentiodynamic cyclic polarization curves obtained in the electrochemical tests on the materials were recorded and are shown in Figures 2 and 3. The results of the test are summarized in Table 4.

Potentiodynamic cyclic polarization tests have been successfully used to determine the materials pitting susceptibility on the basis of pitting potential, E_{pit} . A noble value of pitting potential is taken to indicate a high resistance of material to pitting.

It is noted that 1018 ENP, had shown pitting in LLW and ULW without phosphate (Table 4). However, Phosphate had provided inhibitive effect by showing improved pitting resistance in LLW.

The pitting susceptibility has generally been observed for rest of the materials. The most resistant material was found to be 304 SS in all test media (Table 4). Out of the three martensitic chromium steels (namely, 410SS, 420SS and 431SS), 431 SS had shown highest resistance to pitting followed by 420SS and 410SS in water containing no phosphate.

For 431SS, the inhibitive effect of phosphate is seen only in ULW, whereas, such inhibitive effect of phosphate was noticed only in LLW for 420 SS.

6.2.2 Crevice Corrosion Tests

The crevice corrosion tests were performed following the procedures as per ASTM G 78-89. The results obtained from crevice corrosion tests are summarized in Table 5. Figures 4 and 5 show some typical crevice attacked samples. In ULW, corrosion rate was high for carbon steel, negligibly small for 431 SS and nil for 304SS materials. The number of pits observed was highest for 420SS and no pits were observed for 1018 ENP and 304SS. The maximum depth of pit was found for 420SS. In LLW, the results from Table 5 indicate that carbon steel 1018, ENP1018 and 304SS were free from crevice attack. However, materials 410SS, 420SS and 431SS were attacked and the depth of attack and number of pits were found greatest for 420SS. The result obtained from test with ULW containing 2 ppm phosphate indicate that the presence of phosphate, in general, has considerably reduced the overall corrosion rate and the maximum depth of attack when compared to the test without phosphate addition. The carbon steel - 1018, was particularly free from any crevice attack. The results from test with LLW containing 2ppm phosphate indicate that it is almost identical to that of test conducted with ULW water containing 2ppm phosphate. Apart from carbon steel 1018, 304SS, 431SS and 1018-ENP were free from crevice attack.

In this study, it can be seen that 304SS was free from crevice in all the four tests. The maximum depth of attack was experienced by 420SS followed by 410SS when compared to other samples. Addition of phosphate resulted in pronounced inhibitive effect by total elimination of crevice attack in carbon steel 1018 and 431SS.

6.3 Effect of Phosphate Dosing (Dynamic Test Loop)

The test was carried out as per ASTM G 31-72 (reapproved 1990) for weight loss method in the dynamic test loop. The corrosion rate was calculated using standard formula. The corrosion rates calculated for all the experiments are given in Table 6.

Figure 6 shows picture of coupons removed after 14 days exposure in ULW at 40°C and at a velocity of 4 m/Sec. A loose thick brown oxide layer was found on the CS coupons. The oxide layer over the samples were easily cleaned (mechanically), dried and weighed. All the samples of 410 SS alloy showed large number of pits over the edges. Addition of phosphate decreases the corrosion rates of alloys significantly (Fig. 7). A sharp drop in corrosion rate of CS by 70% was observed with the addition of 2 ppm phosphate after 14 days of exposure. However 15 ppm ZHMP addition decreased the corrosion rate of CS by 50%. The maximum corrosion rate of 410 SS was in the acceptable range (3.5 mpy) without phosphate addition.

7. CONCLUSIONS

7.1 Under Operating Condition

- (1) Corrosion rate of carbon steel material was found to be the highest when compared to other materials but it is not found significant.
- (2) For carbon steel, addition of 2ppm of phosphate to the testing media although reduced the corrosion rate considerably by off setting the effect of localized corrosion.
- (3) 304SS and 431SS materials show no or very little corrosion from impingement in all conditions of test.
- (4) Next to carbon steel 410 SS is the most susceptible material to impingement corrosion.

7.2 Under Shutdown Conditions

7.2.1 Potentiodynamic Studies

- (1) The electroless nickel plated carbon steel, ENP -1018 had shown pitting susceptibility in LLW and ULW waters. The pitting tendency was highest in ULW. The phosphate inhibitive effect was found in LLW.
- (2) The 304 SS shown least susceptibility to pitting in LLW and ULW with and without phosphate.
- (3) In 431 SS pitting tendency was found superior to that of 421 SS and 410 SS materials in waters containing no phosphate.
- (4) The inhibitive effect of phosphate was found for 431 SS in only ULW.

7.2.2 Crevice Corrosion Studies

- (1) Test results confirm that 304SS materials was free from crevice corrosion for all the waters under shut down condition.
- (2) Materials 410SS, 420SS and 431 were susceptible to crevice attack in all waters. However, crevice attack was considerably less when phosphate is present.
- (3) The maximum depth of attack was observed in 420SS in all waters.

7.2.3 Effect of Phosphate Dosing

- (1) Corrosion rate of Carbon steel in ULW was found high when test medium did not contain any inhibitor.
- (2) Addition of phosphate reduces the corrosion rate significantly for all the alloys tested except 420 SS, which shows no change in corrosion rates on inhibitor addition. Addition of 2 ppm ZHMP resulted in the reduction of corrosion rate approximately 70% while with 15 ppm the reduction is around 50% for carbon steel 1018.

8. GENERAL RECOMMENDATIONS

- (1) Corrosion rates of carbon steel under all test conditions were found to be high. On the basis of technoeconomics and technical feasibility all the components made up of carbon steel which are in contact with RO waters should either be cathodically protected or phosphate dosing be considered. Alternatively, upgrading of material to 316 SS may also be considered.
- (2) Phosphate dosing (2 ppm Zinc Hexametaphosphate) was found beneficial to carbon steel 1018. Hence, optimization dosing studies may be taken separately keeping in view the economic viability and acceptable limits of phosphate as per the WHO guidelines. Alternatively, the viability of any food grade phosphate compounds, e.g., sodium phosphate, are to be investigated to avoid any side effects related to human or equipment malfunction.
- (3) The electroless nickel plated carbon steel material exhibited crevice attack under shutdown test condition. It is, therefore, essential either to apply CP or up-gradation of material to 304 SS in order to protect the valves.
- (4) Components made up of 304 SS and 431 SS could be used safely under operating and shutdown condition in proposed Upper Limit Water (ULW) of 350 ppm Cl⁻ and Lower Limit Water (LLW) of 250 ppm Cl⁻.
- (5) Materials used in pumps such as 410 SS and 420 SS were found susceptible to crevice and pitting corrosion in some of the tests in shut down condition. It is, therefore, recommended strongly not to expose these alloys to RO waters. Materials such as 1.4462 duplex stainless steel (for shaft application in pumps) and 316 SS (for other components of pumps and valves) should be considered as replacement material. Alternatively, if feasible, cathodic protection may be considered.
- (6) Provision of reduced chloride water at each pump location is to be considered for flushing during extended shutdowns.

Table 1 : Chemical Composition of the Alloys used in Testing Program

Sr.#.	Alloy	AISI Type	UNS No.	% C	% Cr	% Ni	Other Elements
1	Carbon Steel	1018	J2503	0.25 max.	0.5 max.	0.5 max.	Cu 0.3 max. Si 0.6 max.
2	Electroless Nickel Plated Carbon Steel*	1018 ENP	-	-	-	-	-
3	Austenitic Stainless steel	304SS	S30400	0.08 max.	18-20	8-12	-
4	Martensitic Chromium Stainless Steel	410SS	S41000	0.15 max.	11.5-13.5	-	-
5	Martensitic Chromium Stainless Steel	420SS	S42000	0.35-0.45 max.	12-14	0.5 max.	-
6	Martensitic Chromium Stainless Steel	431SS	S43100	0.2 max.	15-17	1.25-2.5	-

- *30 μm thick plating of Nickel metal on carbon steel.*

Table 2 : Composition of RO Waters used in Testing Program

Concentration	LLW	ULW
Sodium (ppm)	160	225
Chloride (ppm)	250	350
Sulfate (ppm)	14	20
pH	8.5	8.5

Table 3. JIT Test Results
 Velocity : 10 mm/sec, Duration : 28 days

S. No.	Medium	Parameters	Alloy					
			1018	ENP	304L	410	420	431
1	ULW (35 °C)	Weight loss mg	3099	125	0.5	528	121	3.0
2	ULW (35 °C)	Corrosion rate mpy	28	1.1	0.0	4.8	1.1	00
3	ULW+2 ppm phosphate (35 °C)	Weight loss mg	688	105	00	43.5	16	6.5
4	ULW+2 ppm phosphate (35 °C)	Corrosion rate mpy	6.2	1.0	00	0.4	0.1	0.1
5	ULW (50 °C)	Weight loss mg	3219	00	00	634	192.5	00
6	ULW (50 °C)	Corrosion rate mpy	29	00	00	5.7	1.75	00

Table 4. Results obtained from Cyclic Polarization Test Under Shutdown Conditions.
 Test Solution pH=8.5, at 45°C in deaerated LLW and ULW with and without 2.0 ppm ZHMP.

Alloys	LLW, 45°C				LLW, 45°C +ZHMP				ULW, 45°C				ULW, 45°C + ZHMP			
	E _{Corr}	E _{Pit}	E _{Prot}	E _{Pit} -E _{Prot}	E _{Corr}	E _{Pit}	E _{Prot}	E _{Pit} -E _{Prot}	E _{Corr}	E _{Pit}	E _{Prot}	E _{Pit} -E _{Prot}	E _{Corr}	E _{Pit}	E _{Prot}	E _{Pit} -E _{Prot}
410-SS	-783	-12	-590	578	-771	-60	-594	534	-793	-36	-619	583	-791	-36	-625	589
420-SS	-802	185	-582	767	-790	203	-600	803	-799	60	-533	593	-809	-61	-600	539
431-SS	-748	390	-531	921	-738	352	-532	884	-762	263	-456	719	-764	425	-447	872
304-SS	-765	465	-315	780	-753	433	-331	764	-788	388	-242	580	-780	344	-326	670
1018-ENP	-485	-20	-195	175	-448	153	-334	662	-440	-12	-	-	-325	259	-	-

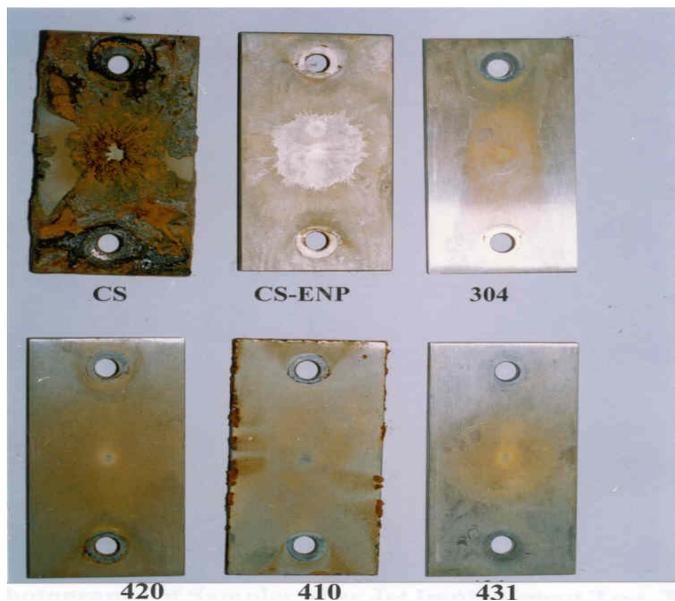
Table 5. Crevice Corrosion Test Results

S. No.	Condition	Alloy	Corrosion Rate mpy	Max pit depth mm
1	ULW at 45°C	C.S 1018	25.5	0.16
		ENP 1018	3.15	-
		SS 304L	0	-
		SS 410	2.05	1.20
		SS 420	1.25	1.40
		SS 431	0	0.30
2	ULW + 2 ppm phosphate at 45°C	C.S 1018	5.0	-
		ENP 1018	1.0	0.2
		SS 304L	0.0	-
		SS 410	0.8	-
		SS 420	0.5	1.2
		SS 431	0.0	-
3	LLW at 45°C	C.S 1018	17.2	-
		ENP 1018	2.3	-
		SS 304L	0	-
		SS 410	2.0	0.45
		SS 420	0.35	1.4
		SS 431	0.5	0.6
4	LLW + 2 ppm phosphate at 45°C	C.S 1018	4.2	-
		ENP 1018	0.5	-
		SS 304L	0.0	-
		SS 410	0.49	0.1
		SS 420	0.8	1.2
		SS 431	0.0	-

Table 6. Corrosion Rate (mpy) calculated by weight loss method from Dynamic Loop Tests.

ZHMP (ppm)	Materials					
	Carbon Steel		410 SS		420 SS	
	14 Days	28 Days	14 Days	28 Days	14 Days	28 Days
0	168.7	114.1	3.37	3.4	0.1	0.0
2	49.7	37.9	2.31	2.6	0.0	0.0
15	34.3	22.2	2.18	2.6	0.0	0.0

TEST 1: JET IMPINGEMENT TEST
(AFTER 24 DAYS – BEFORE CLEANING)



TEST 1: JET IMPINGEMENT TEST
(AFTER 24 DAYS – AFTER CLEANING)

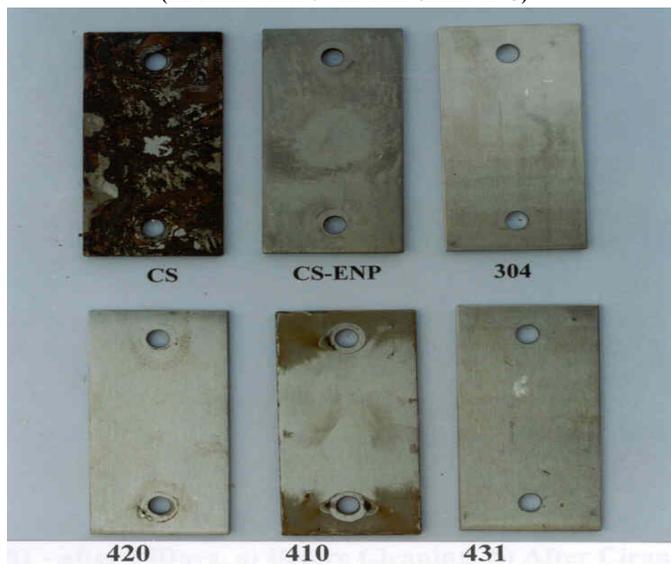


Figure 1. Photographs of samples after Jet Impingement Test. Test – 01 – after 28 Days. (a) Before cleaning (b) After cleaning

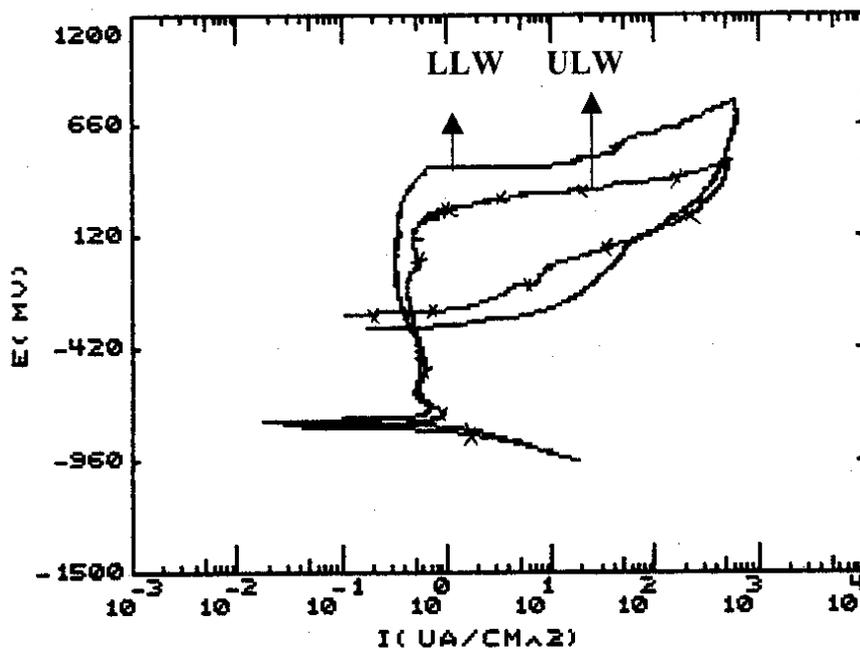


Figure 2. Cyclic polarization curves of 304 SS in deaerated LLW and ULW solution at 45° C

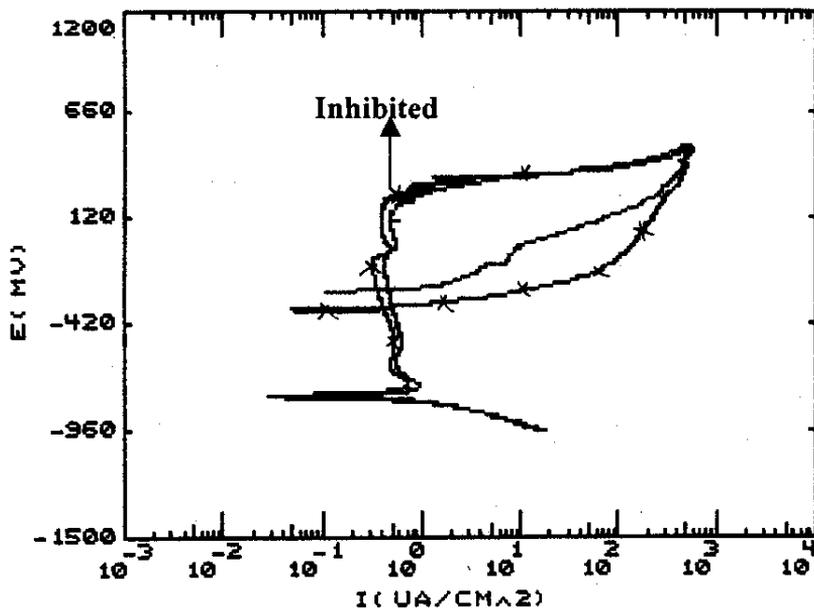


Figure 3. Cyclic polarization curves of 304 SS in deaerated ULW solution with and without inhibitor at 45° C

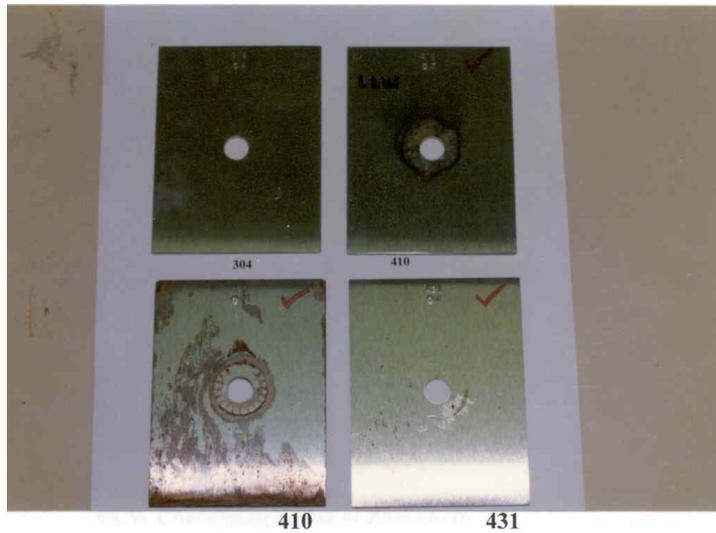
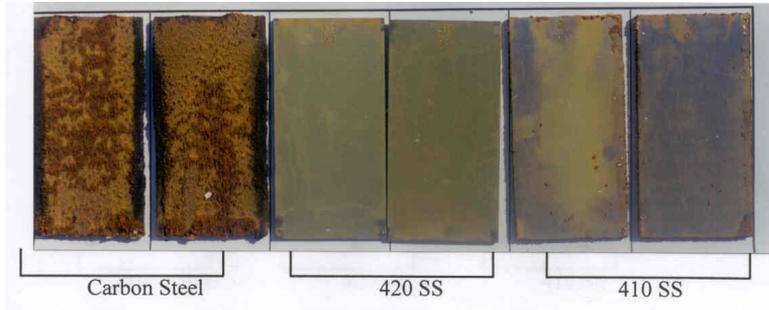


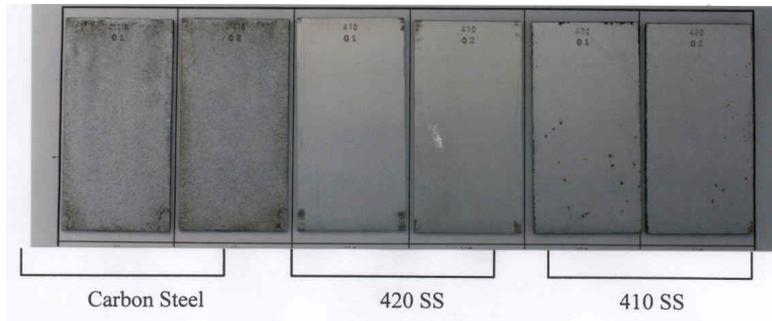
Figure 4. Photograph of crevice tested samples of 304 SS, 410 SS and 431 SS in LLW



Figure 5. Close-up view of crevice attack on 410 SS in LLW



[a]



[b]

Figure 6. Photographs showing the coupons exposed for 14 days in ULW [a] before and [a] after cleaning

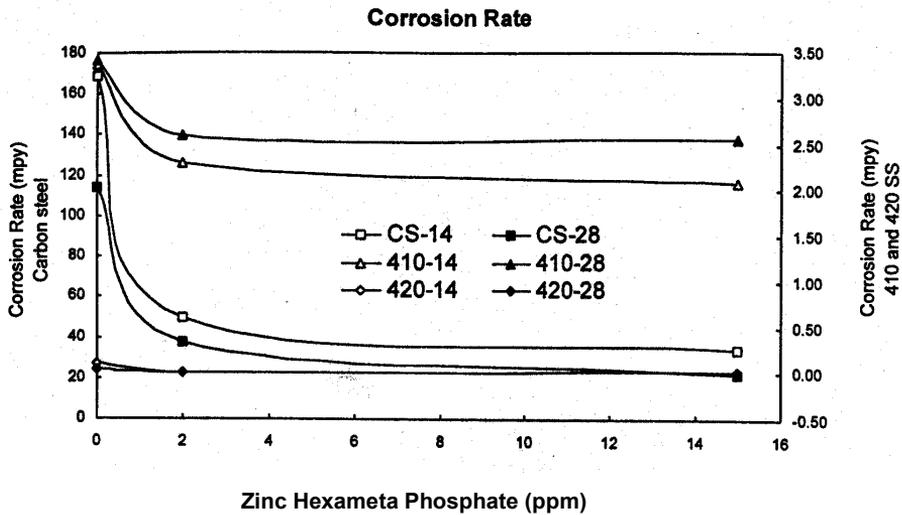


Figure 7. Graphs showing the variation of corrosion rates of CS, 410 SS and 420 SS