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ANALYSIS OF PITTING AND CREVICE CORROSION ON INCOLOY 825-CLADDED CARBON STEEL PIPELINE IN AERATED STAGNANT WATER

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Abstract:

Corrosion failure and behavior of Incoloy 825 clad carbon steel pipe welded with Inconel 625 in stagnant formation water was investigated by using failure analysis tools and procedures. A pipe section suffering from perforation and pitting is received with clear water line marks along the bottom sides, and perforation and leakage had mainly occurred near and away from the HAZ of circumferential weld. Stagnant formation water analysis had shown a high degree of salinity and positive scaling tendency. Anodic sites were formed under water scale which led to the creation of pits, and subsequent crevice corrosion attack under clad-base metal interface, then followed by general corrosion to outer surface. The laboratory Potentiodynamic polarization test has been used to evaluate the effect of Cl^- concentration on pitting corrosion potential for both clad and weld metals. Temperature and chloride concentration was found to have great effect on Incoloy 825 pitting potential. High Mo filler Inconel 625 overcomes the weld metal corrosion. This paper outlines the corrosion resistant clad and filler alloy characteristics in highly saline stagnant water, and the precautions to be taken in the running and commissioning of lines.

Keywords: chloride, cladding, Inconel, Failure, Incoloy, NDT, Pipeline, Pitting.

Introduction:

separate Corrosion failure is one of major obstacle facing petrochemical, oil, and gas industries, each of them trying to develop, and select high quality corrosion resistant alloys. The potential for saving, is greatly recognized by utilizing available and economic practices to improve corrosion prevention, control, and considering the initial cost of materials. The corrosion behaviors of corrosion resistant alloys have been investigated extensively [1-4]. Nickel-based alloys exhibit exceptional corrosion resistance because of the presence of passive films, which can effectively the matrix of these alloys from corrosion environments [5-7]. Clad alloys are the foremost candidate material for such required quality. Cladding as an economical alternative to expensive high-alloy solid plates or pipes, which can combine the base material mechanical properties and corrosion resistance of the surface materials. Surface layers of nickel alloys or stainless steel on a carbon steel substrate can be produced by solid state welding, such as hot mechanical pressing [8] or rolling [9], and also hydraulically or thermo hydraulically expanding for pipes. In mild environments, the high alloy content of alloy 625 enables it to withstand a wide variety of severe corrosive environments, Cr provides resistance to oxidizing chemicals, whereas high Ni and Mo contents make the alloy resistant to non-oxidizing environments. The high Mo content also makes this alloy very resistant to pitting and crevice corrosion, while the added niobium (Nb 3-4%) acts to stabilize the alloy against sensitization during welding. Alloy 825 is a titanium stabilized austenitic Ni-Fe-Cr alloy with additions of Mo and Cu improves resistance to reducing acids and localized corrosion in chlorides. This alloy is characterized by good resistance to stress-corrosion cracking due to its Ni content (38.0% to 46.0%) and satisfactory resistance to pitting and crevice corrosion. Alloy 825 has shown good corrosion resistance in oil and gas production environments containing H_2S, CO_2, and chlorides. Under certain conditions, this alloy is susceptible to localized pitting and crevice corrosion in chloride containing, and buildup of ions environments. The breakdown of passivity is attributed to localized corrosion which develops in conjunction with changes in the adjacent aqueous environment which support rapid dissolution, and realized as a common type of failure in passive nickel-based alloy [10]. At the air-water inner face in water tanks or pipelines as in a stagnant water condition, fully aerated cathodic areas with higher O_2 concentration drive the corrosion of air-deprived areas, resulting concentrating cells and favors cathodic reaction which tends to increase the rate of pit propagation after initial pitting at the inner surface sites providing that, the water level stays constant [11]. The dissolution of metal increases the number of cations, and therefore anions, which mean chlorides migrate into the pit to uphold the electroneutrality of the pit. Equation (1) and figure 1, shows the hydrolysis of the cations which occurs within the pit, where M represents the different metals, which are Cr, Mo, Ni [12].

$$2M^{2n+} + 4\,H_2O \rightarrow 2M\,(OH)_2 + 4\,H^{n+} \quad \text{.. Eq. 1}$$

Many authors [13, 14, & 15] have shown through different polarization measurements the pitting potential has a linear function of the logarithm of the chloride concentration. An increasing chloride concentration therefore gives an increasing susceptibility to pitting corrosion, particularly in the real environment where both crevice and pitting corrosion are normally present. Electrochemical tests [16] reports that, with an increase in temperature the pitting potential (E_{pit}) decreases and the damage caused by corrosion increases.

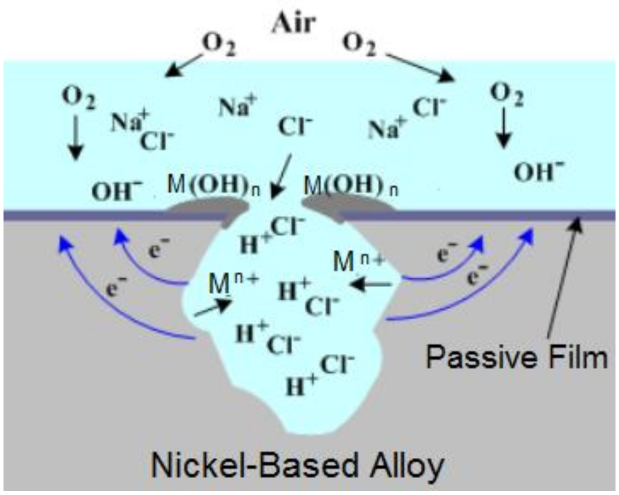

Figure 1.Sketch of a pit from in passive alloys.

The increasing temperature causes higher current transients and promotes the conversion of metastable pits into stable growing pits. While in a chloride environment the growth of pits increases. [15] found that E_{pit} is a linear function of temperature in a chloride solution. Deoxygenating occurs when no oxidizing agent is left in the pit, or depletion of oxygen. This is caused by slow oxygen diffusion into the crevice and therefore a concentration gradient builds up between the crevice and the outer passive surface of the material. Hydroxide forms in the crevice in alkaline seawater, causing a rise in the pH [17]. That leads to hydrolysis-acidification which is directly induced by the deoxygenating. The depletion of oxygen causes the cathode reaction to move to the outer passive surface, where oxygen is more easily accessible, while the oxidation of the components of the alloy Cr, Fe, Mo and Ni continues in the crevice. S. Missori et al [18] have studied the microstructural changes near the interface in a carbon steel cladded by hot rolling with an AISI 304L stainless steel, such process gives rise to the inter diffusion of carbon towards the austenitic side. A narrow band (cladding line) is observed parallel to the original interface, that follows the ferritic grain profiles and separates the base steel from the austenitic layer. In present paper the versatility of Nickel-based alloys 825 and 625 as a useful material in various corrosive environments is investigated, when an Incoloy 825 clad steel pipes experience a corrosion failure. The paper is divided into two sections: (1) applying NDT tests for Failure analysis, and (2) conducting laboratory pitting potential tests to affirm the analysis.

Experimental Work:

Component and working conditions:

A nominal length of 6.5 m, and 254 mm internal diameter Incoloy 825clad steel pipes as furnished, is selected to construct a 12 km butt welded pipeline intended for offshore formation water disposal. For filling metal, Inconel 625 used as circumferential weld metal (CWM), and API X52 as a base metal (BM), figure 2, shows the clad alloy cross section. With a moderate pressure to pump the formation water through the line, the maximum designed pressure of 3 bars is considered to result a Hoop stress on the pipe wall 10 times below the calculated yield strength. The seamless clad Incoloy pipes are expected to be produced by inserting the clad meta (CM) Incoloy 825 pipe through the steel pipe ,and then hydraulically or thermo hydraulically circumferentially expanding to (CM) which both mechanically adherent .

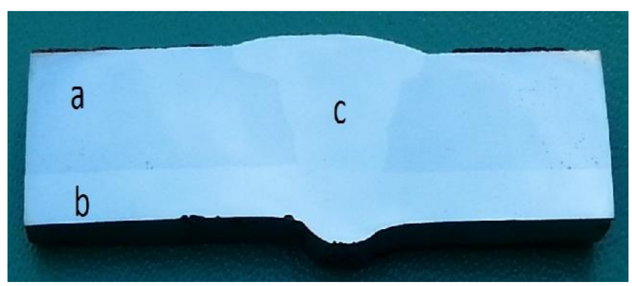

Figure. 2- **a**- BM 8mm, **b**- CM 3mm, & **c**- CWM

The received material:

A portion of perforated Incoloy 825 clad carbon steel pipe welded with Inconel 625 as welding consumables was received from a failed 254 mm Diameter water disposal line. The line had been used on a discontinuous basis for disposal of highly saline formation water. After construction the line was never commissioned because of the presence of sludge. However, this pipeline has left filled to certain level of water under stagnant conditions for a time period over six months where the chance of corrosion was highly increased specially on those susceptible locations such as heat affected zone (HAZ), and at any welding defects such as welding spatters or surface inclusions if present. The received section was visually inspected and all observations, remarks, and the required tests are reported and considered for further work and analysis. Figure 3 shows the internal surface of the pipe and the perforated location and, pitting corrosion nucleation and growth next to the weld line root.

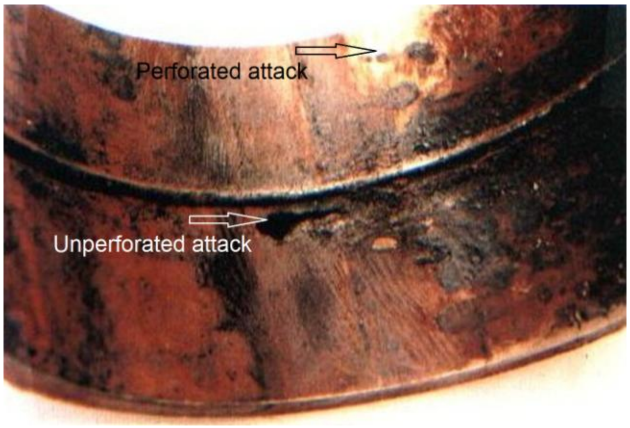

Figure 3. as received portion of the failed pipe.

Non-Distractive Testing NDT:

To fulfill the requirement of the failure analysis process, NDT survey on failed pipe represented by the received portion is essential, by using ultrasonic (UT) and x-ray radiography (RT) both tests are carried out. NDT test data is important to be available in present study to define pitting corrosion sites and sizes with respect to the weld line and heat affected zone. The valuable data of NDT survey was but in hand to be employed and discussed to give support to further analysis.

Chemical analysis:

Both clad metal (CM) and circumferential weld metal (CWM) were chemically analyzed using vacuum spectrophotometer analyzer. Also the formation water chemical analysis has been done to specify its degree of salinity and presence of any corrosive media.

Macro-Microstructure examination:

The structure of received samples were metallographicaly examined after being mounted, wet ground to 1000 grit finish, and then fine polished. After 2% nital etching optical microscopy examination was done with a range of magnifications 50x, 200x.

Pitting corrosion test:

Based on the obtained information of the visual inspected, tests are designed to evaluate the pitting potential (E_{pit}) of small samples of (CM), and (CWM), mainly to aid in further analysis. The potentiodynamic polarization measurement technique is employed, the E_{pit} measured is corresponded to the nucleation and growth of pits. The working electrodes used are cold mounted prepared specimens with $1cm^2$ as an exposed surface area. Reference electrodes being saturated calomel electrode Ag/AgCl. The potential of calomel electrode was checked to ensure the accuracy of the electrode. A platinum auxiliary electrode was used as counter electrode. All specimens were except the exposed surface area of $1cm^2$ at the center of the mount. Three different concentrations of NaCl in distilled water solutions used as an electrolyte for pitting corrosion (20000, 100000, & 150000 ppm as Cl^- ion). All pitting corrosion tests were carried out at Room temperature 25°C, and Relatively high temperature of 50°C.

Results:

Component material compositions:

From the chemical analysis shown in table 1. it is clear that the (CWM) is alloyed with relatively high amount of Mo to enhancing pitting corrosion resistance, and 1.2 % Ti as stabilizer against any chromium carbides formation (sensitization), the (CWM) is a typical Inconel 625 with high Ti, and Mo contents. (CM) Alloy is a Ti-stabilized austenitic Ni-Fe-Cr alloy with additions of Mo, and Cu. The chemical composition of the alloy is also listed in Table 1. The alloy is characterized by good resistance to stress corrosion cracking due to its Ni content (38.0% to 46.0%), with satisfactory resistance to pitting and crevice corrosion. (CM) Alloy has characterized as a good corrosion resistance in oil and gas production environments containing hydrogen sulfide, carbon dioxide and chlorides. The metal substrate is low carbon Steel type API 5L-grade B.

Table 1. Chemical Analysis of both 825 (CM) & 625 (WM).

Elements %	Ni	Cr	Fe	Mo	Nb
Incoloy 825	40.90	21.21	27.85	3.26	0.17
Incone 625	55.23	20.22	12.19	6.23	2.16
Elements %	Cu	Sn	Ti	V	C
Incoloy 825	1.40	4.20	0.86	0.09	0.03
Incone 625	1.30	1.19	1.2	0.28	0.03

The Formation water chemical analysis results is shown in table 2. It is clear from these results that, the amount of chloride (1,68,500 mg/lit) which is much higher than its value for sea water which is about (32,000 mg/lit), and considered to be very severely corrosive. Also the total dissolved solids (TDS) are very high (2,64,500 mg/lit) as compared to TDS of 40,000 mg/lit for sea water, and the scaling tendency is positive*. As the below parameters value presented, the corrosion resistant alloys (CRA) were recommended and selected in order to resist the severely working conditions.

Table (2) Formation water chemical analysis.

PH	6.1
Salinity of NaCl mg/lit	269,000
Sodium, mg/lit	78,000
Calcium, mg/lit	20,000
Magnesium, mg/lit	2650
Barium, mg/lit	0
Chloride, mg/lit	1,63,500
Sulphate mg/lit	250
Bi, Carbonate mg/lit	200
TDS mg/lit	2,64,500
Scaling tendency	Positive*

*Saturation Index (S.I) = $pH_{measured}$ - pH_s >1 i.e. Scale tendency is Positive and scale was accumulated on the pipe inside wall.

Visual Observations:

The visual inspection to the received section led to the following observations:

1- The failed section of the pipe had a clear mark of water accumulation at the bottom of the line (between the 4 and 8 o'clock positions) as in Figure4.

2- The perforation and leak occurred within the water marked area. The leak was in area close to HAZ of the circumferential weld as shown in Figures 3 and 5**.**

3- The pipeline was seamless made of carbon steel as the base material, and cladded with Incoloy 825 and welded with Inconel 625, all pipe joints are butt welded.

4- The pipeline was suffering from accumulation of stagnant water for a time perid more than six months.

5- Dimension measurements indicated that thickness of cladding is 3 mm and the base metal thickness is 8 mm, i.e, the total pipe thickness is 11 mm.

Ultrasonic Testing Results (UT)

The inspected points and defects found at different pipe joints using (UT) were noted as in table 3, where WXX indicates the classification of different selected locations of weld joints along the pipeline as it used in this work. These results strongly indicate that corrosion had occurred on both adjacent to welding zone and away at parent metal as in table 3. Some of these spots were suffering very severe corrosion.

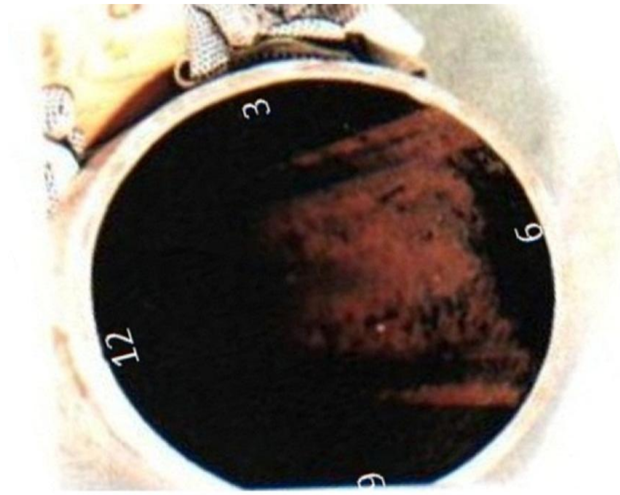

Figure 4. Indication of watermark on the internal surface

Figure 5. Perforation as appeared on external surface of pipe.

Table (3). WXX for different selected locations.

code	CBW	RWT	CA	CR
W59	107mm	2 mm	L S	V S
W69	90mm	3.05mm	L S	V S
W78	30mm	2 mm	L S	V S
W60	AWM	HWC	L S	-
W64	AWM	HWC	L S	-
W65	AWM	HWC	L S	-
W66	AWM	HWC	L S	-

CBW= Corrosion from Butt Weld, RWT= Remaining Wall Thickness, CA= Corrosion Attack, L S= Localized Spots, CR= Corrosion Rate, VS= Very Severe, AWM= Adjacent to Weld Metal, HWC= Hidden by Weld Cap

X-Ray Radiography Testing Results:

Presence of seven radiographic "hot spots" that were identified as areas of intense localized corrosion. Four of these "Spots" were located adjacent to welds but three were located in the parent cladding material away from the welds. The three spots in the parent cladding material away from the welds were located within 100 mm of the welds centerline and from HAZ. Usually HAZ is about 2.5 – 3 mm from the weld centers.

Metallography:

Figures 6 (a,b,c, &d) shows the microstructure of BM (carbon steel) with ferritic and pearlitic structure. The macrostructure of both the CM & CWM shows a clear yellow reddish Ti carbides spreads in the matrix of the clad metal alloy, and also black spots which expected to represent the formation of Cr carbides during weld cooling. From fig.s a & c. It is very obvious that, at interface between carbon steel and CM the narrow band has formed during cladding process at the contact surface of CM, while a sold interface line between weld metal and base metal is clearly found as in Figs c & d.

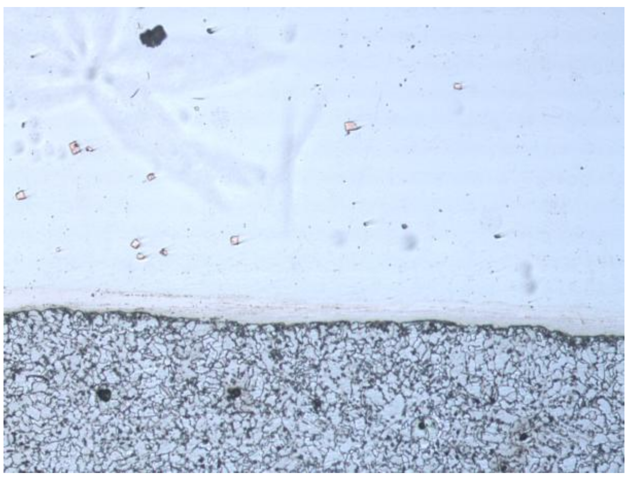

Fig.6-a, CM with TiC, narrow band & base metal

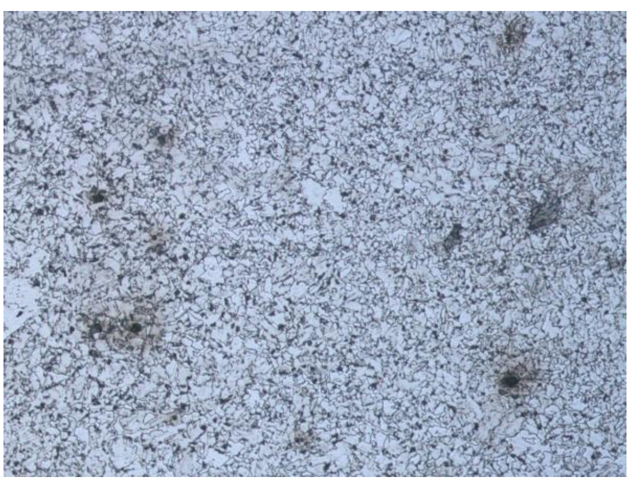

Fig.6-b, hypoutectoed structure of base metal

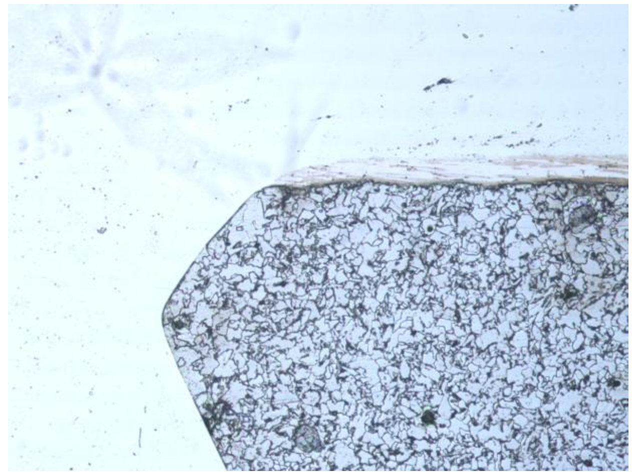

Fig.6-c, the interface lines between base metal-CWM, & base metal-CM

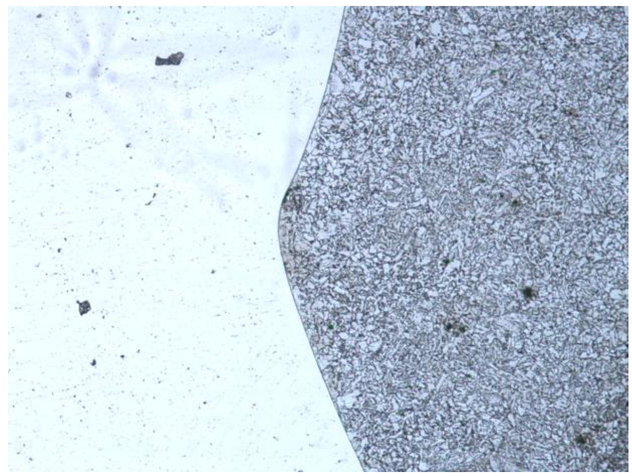

Fig.6-d, solid line interface base metal- CWM

Pitting Corrosion Potential:

The effect of test temperature on pitting potential of both CM, and CWM is obvious especially for CWM, after being tested in various concentrations of chloride ions. It can be observed that, the increase of test temperature form RT to 50°C caused a marked reduction in E_{pit} for CM, Which found to be more depend on the concentration of chlorine ions (Cl^-). In other hand, CWM shows a gradual decrease in E_{pit} as concentration of chlorine ions (Cl^-) with considerable effect of test temperature. All that effect is clearly shown in table 4, and at the comparing figures (7 a & b).

Table (4).Pitting Potential of CM & CWM at Different Cl^- ppm.

Concentration Of Cl^- ppm	20,000 mV	100,000 mV	150,000 mV
CM 25 ºC	72	-20	-50

CM 25ºC	40	-50	-80
CWM 50 ºC	940	910	860
CWM 50 ºC	310	260	100

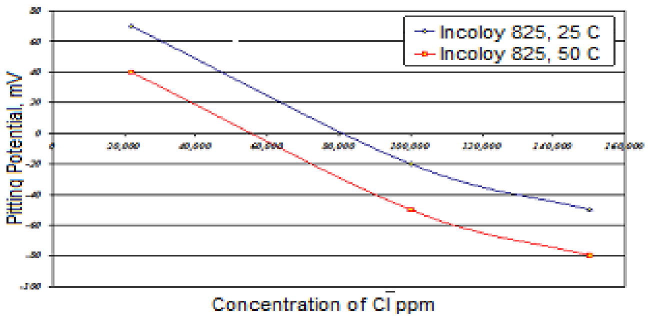

Fig.7-a Effect of Cl^- concentration &Tep. on E_{pit} of CM.

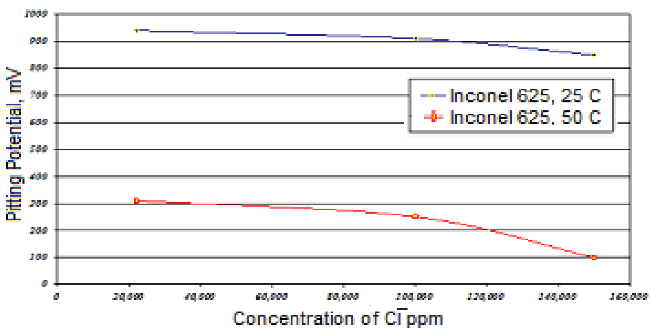

Fig.7-b Effect of Cl^- concentration &Tep. on E_{pit} of CWM

Discussion:

As can be observed after 2% Nital etching (figs. 6a & c), the cladding line follows the profile of the Ferritic and pearlitic grains of BM, a narrow band parallel to the original interface has been formed in the wake of hot cladding process. This band separates the base steel from the single austenitic (fcc γ) phase of CM. metallurgical bonding gives inter diffusion of elements such as carbon to diffuse in the austenitic clad metal, that leads to metallic carbide precipitation. Regarding to the high Ni and Cr contents, the solubility of carbon is low and abundant Cr carbide precipitation takes place mainly on twins and grain boundaries. The Presence of corrosion spots in forms of reduction in wall thickness all over the CM can be attributed to galvanic action between the parent CM incoloy 825 (Anode) and the CWM Inconel 625 (Cathode) after exposure to the highly saline formation water. The pitting defects present at CM surface away from the HAZ is more likely to be occurred underneath the water scale buildup in which the formation water inside the pipe has a positive high scaling tendency, specially under the water stagnant condition of high chloride contents, where the scale can play a role of cathode with respect to the CM which acts as an anode. The radiographic results clearly indicates the defects shown are not within the HAZ, with possibilities of other weld related problems such as weld spatters or contaminations should not be excluded. Presence of such discontinuities besides the aerated stagnant formation water accumulated in the line might lead to the creation of galvanic sites for pitting corrosion. Once the attack penetrates through CM surface, intense localized crevice corrosion along the narrow band parallel to the original interface of carbon steel is occurred Cl^- and OH^- diffuse into the crevice to maintain a minimum potential energy and metal chloride then formed, the hydrolysis of metal chloride lowers pH as: $MCl_n + n\ H_2O \rightarrow M(OH)_n + n\ HCl$. More Mn^+ ions attack more Cl^- leads to metal dissolution acceleration and more M^{n+} ions will be produced which lowers pH. The attack reaching to final stage, when a general galvanic corrosion took place to complete perforation of the pipe wall then leaking of stagnant water that had been accumulated in the line in the surrounding environment. The results obtained from potentiodynamic polarization measurement shown more pronounced effect on the susceptibility of Incoloy 825 to pitting corrosion than weld metal Inconel 625. This trend was shown for both temperatures used at RT and 50°C which represent the actual working temperatures of pipeline as well as the three different Cl^- concentrations, since the highest value of Cl^- containing in the formation water reaches to 163,000 ppm. These results represent a standard laboratory condition, specimen preparation as a uniform surface free of contamination and discontinuities, while in the real application the pipeline is welded in service site with many discontinuities such as weld spatters and contaminations may presence besides the aerated stagnant formation water. Such discontinuities could reduce the pitting potential and creation of galvanic sites. This finding explain the formation of pits quite away from the HAZ**.** However, the alloy under use contains an addition of Ti, which during an appropriate heat treatment stabilizes the alloy against such sensitization, as a result of exposure to temperatures of 650º - 760º during welding. Since Cr carbide phase was shown to some extent in both CM matrix macrostructure, therefore structural sensitization as a result of gradual cooling taking place between (650 ºC and 760 ºC) should not be excluded. If this happens, then the metal will be weakened specially at the HAZ, which leads to pitting corrosion. Perforation is mainly attributed to crevice corrosion along the narrow band between clad-base metal interface, then followed by an accelerated galvanic action till Perforation as a result of carbon steel (base metal) exposure to saline water.

Conclusion:

1-- Perforation of the examined section of leaking water disposal pipe has been caused by intense localized corrosion of Incoloy 825 lining material by the act of stagnant water formation water with both high saline, and scaling tendency that has been lying in the bottom of this pipeline for long enough time.

2-- The received radiography survey of accessible parts of the pipeline has revealed the presence of areas of severe localized corrosion of the lining material, both adjacent to and relatively away from the cladding welds. Also the obtained results of UT give a good indication to the remaining wall thickness of the attacked sites.

3-- Under deposit, the pit formation starts the pitting corrosion, caused by the accumulated sludge inside the unoperated aerated pipeline. Perforation is mainly attributed to crevice corrosion under clad-base metal interface, then followed by general corrosion to outer surface.

4-- Increase in test temperature and chloride concentration was found to have great effect on Incoloy 825 lining material pitting potential. The use of high – Mo filler metals Alloys 625 overcomes the weld metal corrosion.

5- In such condition, the line should be immediately drained of formation water and flushed out with inhibited fresh water to prevent further corrosion or deterioration of the lining material. Also a strict quality requirements, and auditing should be imposed.

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