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# The Evaluation of Corrosion Problems In Condensate Return Lines –South Refineries Company

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### Abstract

The corrosion problems in condensate return lines of "South Refineries Company-Basrah" were investigated . Frequent leakages leading to plant shut-down occurred in "Vacuum Distillation Unit" and "Propane De-asphalting unit" due to several punctures corrosion in the pipes interiors .The experimental work included : **a.** Evaluation of the corrosion damage, **b.** Metallurgical (microscopical) examination to identify the types and characteristics of the corrosion, **c.** Testing the chemical regime parameters during operation about any deviations from the standard limits. Furthermore, the chemical conditioning during the shut-down period were reviewed and **d.** Laboratory measurements of the corrosion rate for carbon steel pipe specimens in condensate water compared to that in raw water. The results of investigation indicated severe pitting corrosion resulted from gas attack which confirmed by metallurgical examination and chemical analyses. Methods for alleviating the attack of aggressive species with the necessary corrective measures were undertaken .Moreover, the practical means for corrosion control and monitoring were suggested.

# تقييم مشاكل التآكل في انابيب الماء المتكثف الراجع - شركة مصافي الجنوب

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*الخلاصة*

تم اجراء دراسة مشاكل التآكل الحاصل في انابيب الماء المتكثف الراجع- شركة مصافي الجنوب في البصرة.لوحظ تكرار التسرب الذي ادى الى توقف وحدتي التقطير الفراغي رقم 700 و ازالة الدهون بالبروبان رقم 800 وذلك بسبب حدوث عدة ثقوب داخل الانابيب.الجزء العملي تضمن الخطوات التالية:ا-تقييم التضرر بالتآكل ،ب_ الاختبارات الميتالورجية لمناطق التآكل لتشخيص التغيرات التركيبية في المعدن،ج-فحص متغيرات النظام الكيميائي خلال التشغيل لرصد أية انحرافات عن المواصفات القياسية اضافة الى ذلك تمت مراجعة طبيعة المعاملة الكيميائية (الحفظ الكيميائي) خلال فترة التوقف.د- اجراء قياسات التآكل مختبريا "للفولاذ في الماء المتكثف و كذلك في الماء الخام للمقارنة.بينت نتائج الدراسة حدوث تنقر شديد نتيجة الهجوم الغازي استنادا" الى التشخيص الميتالورجي ونتائج التحليل الكيميائي .تم اتخاذ الاجراءات ووسائل التصحيح لالغاء تأثير الفصائل الاكولة.كما تم اقتراح وسائل السيطرة ومراقبة التآكل.

## Introduction

The ''South Refineries Company'' has four central steam generating units working at a pressure of 33 kg/cm² .Three units 50 m³/h and one 150 m³/h capacity , were employed to provide steam for process utilities. The condensate is recycled and returned with a pressure of 3.5 kg/cm² at 150°C to the boiler plant for reuse as feed make-up water. The main headers of the return pipelines showed frequent leakages that led to plant shut-down. The number of failures during the period 1999-2002 are presented in Fig.(1). The maintenance work carried out solved the problem only temporarily.

It is well known that frequent shut-down results in significant expenditure for proper maintenance added to the loss of production during the outage period. The corrosion damage observed in the mild steel pipelines internal surfaces might be related to: metallurgical , electrochemical factors, environmental species and operational conditions (Fontana and Green 1978, Obuekwe 1981).

The condensate deduced from feed water usually subjected to chemical treatment by organic amine and oxygen scavenger to provide sufficient alkalinity and overcome the residual oxygen (Powell, 1974). A relatively high oxygen content in condensate may cause severe pitting of the metallic surfaces (Pollack1981). Furthermore, industrial pollution may introduce carbonic, organic acids and/or organic compounds which under the effects of high temperature and pressure are converted into acids (Booth et al 1985 ,Hochheimer 2000) .

Condensate with low concentration of dissolved gases and having small amount of dissolved solid possess high tendency to absorb atmospheric gases. Thus, their ingress into condensate through some connections would be possible .Hence, very pure water afforded no protection to metallic surfaces (Shim et al 1988).

In general the factors that promoted pitting corrosion in addition to dissolved gases are: the presence of salts especially the chlorides and the low pH value (below 7). The Pitting corrosion usually associated with metals having the tendency to form passive film (Dortwegt 2003,Grossbaltt 2001). Severe pitting may proceeded during prolonged shut-down more than that experienced during operation.

However ,the aim of the present investigation is to recognize the factors that promoted corrosion damage in the condensate returns and to find suitable means and corrective measures to control such kind of troubles.

## *Experimental Procedure*

### Evaluation of the corrosion damage

#### local observations

Inspection of the condensate returns main header 75 mm diameter, 60 m length and 5 mm thickness showed heavy leakages which received the condensate from 10 branches of different diameters tubes. The header is located horizontally between unit No.700 and 800. A partial replacement for the failed regions were undertaken. Unfortunately, the leakage appeared after one month of maintenance. The frequency of the failures occurred during 1999-2002 were indicated in Fig. (1).

Due to reoccurrence of failure in the same header , a complete replacement for the whole header were carried out. But , this did not solve the problem, once again ,other leakages appeared.

**Visual Examination**

One meter segment was taken from the damaged part of the horizontal header pipe. Small specimens of 10 cm length were cut and divided into two longitudinal sections. Visual Inspection revealed that severe pitting corrosion proceeded in the internal surfaces of the pipe . The pitting were concentrated and aligned at the lower part of the pipe section. It was found that the pit density 7-9 pit / $cm^2$, max. pit depth 4 mm , max. pit mouth or width 3 mm. In addition, the pitting was scattered and spread unevenly over all the internal surface. Some of the pits incorporated a pin hole inside with an apparent deep penetration through the pipe wall. Evidently , some of these pits have ended up into punctures. The characteristics of the observed pitting can be classified according to their morphology into three types: first/small regular pits deeply penetrate the pipe wall, second/irregular wide mouth pits and third/irregular wide mouth incorporated a very tiny pin hole inside.

Notably ,the whole corroded surface of the pipe interiors were found covered with black magnetite film. This has shown the effect of oxygen scavenger in the formation of protective film(obuekwe et al 1981) i.e. as hydrazine dosage was usually practiced in the refinery.

All observations had revealed that the characteristics of pitting corrosion exist in the pipe might be related to some deficiencies in the chemical regime .It is likely that dissolved oxygen associated with $CO_2$ attack might be responsible for the damage. Moreover, the mechanism of pitting by "differential aeration" is more likely to be operative during the shutdown period and / or under un-preserved chemical conditioning.

## Metallurgical examination

### Specimen preparation for microscopic examination

Four groups of specimens were prepared :

1.Two from the internal surface of the corroded area, 2. Two from the internal surface of the intact un-pitted area, 3. Two from the corroded cross sectional area, and 4. Two from the intact cross sectional area, 1x1 cm ,5 mm thickness each .

All specimens were polished by silicon carbide paper then by alumina powder to ~1 micron.

### Specimen Etching

The specimens were etched by nital according to the standard method given by ASTM-74 a ( 1984).

### Microscopic Examination

An Optical microscope (Olympus,Japan,1989 ) was used to examine the microstructure of the mild steel(106B) pipe specimens (Corrosion Program Manual 1989).The microscope equipped with a Pentium III computer. The assigned features of the metal specimens were photographed by means of a ''Video Camera'' which transfer these photographs directly to the printer through Windows 1998. The observed features were presented in Plates 1-4.

## Chemical parametric operational conditions

### Testing of the chemical regime

The chemical treatment of the boiler feed water was carried out according to the standard methods stated in the "Operating Instructions". The average chemical analysis results of the boiler feed and condensate compared to the standard limits (Pp. and Maind. Inst. 2002 ) were listed in Table (1).

The demineralized water DMW in the refinery was prepared from water treatment plant which included: pretreatment., reverse osmosis and demineralization. The characteristics of the DMW is shown in Table (1). It can be seen that the TDS $\leq 1$, $SiO_2 < 20$ ppb, pH = 6.5 – 7.0 . The boiler feed chemical treatment involved the alkaline dosage using morpholine as neutralizer and hydrazine as oxygen scavenger.

It was anticipated that there might be some deviations occurred arbitrarily beyond the standard limits. For instance, the un programmed shut-down and emergency stoppage.

It was noticed that deficient deaeration increases the oxygen and $CO_2$ levels. Also , deficient chemical dosage would not eliminate totally the presence of residual $O_2$ and $CO_2$ (Taher 1999).

Furthermore , pitting corrosion if it is initiated , it can be propagated at an ever increasing rate and accelerated by the presence of dissolved oxygen and/or $CO_2$ especially when there was in- sufficient chemical dosage during running or during preservation.

**Dissolved oxygen testing**

The chemical analysis of dissolved oxygen in the condensate and feed water were carried out by using the analytical method of Indigo carmine . The sampling points were provided with new coolers to ~20 °C, as the existing coolers were not working. (Op. and Maint. Inst. 2002). The results of dissolved oxygen analysis are shown in Table 1.

**Corrosion rate measurements**

Two specimens (mild steel 106B) (1 cm²) were cut out from the intact area of the pipe and subjected to mechanical pressing in order to be flattened, then annealed at 600 °C for 1 hour . The specimens then polished to ~1 micron and etched by nital. The microstructure of the alloy was inspected by means of optical microscope (Olympus , Japan 1989) to check the recovery of the microstructure after annealing. The corrosion rate measurements were carried out for the annealed specimens after polishing to

600 micron (ASTM-G71,1980) by using corrosion rate measurement system model 350A (USA 1989). The corrosion potentials were measured relative to SCE for condensate water (TDS 20 mg/l) and raw water(TDS ~ 3500 mg/l). The results of corrosion rate measurements were presented in Fig. 3 and 4 respectively. The amounts of $O_2$ and $CO_2$ dissolved in condensate and raw water were found within their equilibrium concentration at the working pressure 3.5 kg/cm$^2$ and 1 atm respectively.

### *Results and Discussion*

**Plant operating conditions:** practically, it was found that the normal operating conditions are frequently subjected to a large number of variables concerning the deaeration process. The complete removal of oxygen and carbon dioxide could be achieved under-well controlled pressure and temperature(Taher,1999). Proper deaeration and well controlled chemical dosage are essential in eliminating the presence of dissolved gases(Shim et al 1988, Dortwegt 2003). There is also a possibility of $O_2$ ingress to the feed water that increases it's level to more than the tolerated value of 10 μg/l.

However, the $CO_2$ ingress from the atmosphere to the condensate is greatly possible, as it is highly soluble.The Shallow pits of corrugated mouth observed in the pipe interior are the characteristics of $CO_2$ attack as observed by the optical microscope.

There are two important situation have to be considered: a.The starting of the unit provided a high oxygen content, which needs considerably high levels of chemical dosage. Therefore, it is necessary that during starting, high $O_2$ and $CO_2$ contents have to be carefully controlled and continuously monitored until complete removal will be assured and b. The shut-down and the period of standing which was considered very important in determining the welfare of the unit. Thus, a precise decision have to be undertaken to manage the process of chemical conditioning. If the standing period is extended to more than 72 hours, a chemical preservation has to be carried out by using oxygen scavenger and alkaline solution i.e. pH 9-9.5. (Haleem *et al.* 1984). If the plant is left without preservation, then pitting corrosion can proceed under such circumstances when there is a great possibility of gas ingress into the condensate or feed water. Now , it is well-known that the corrosion proceeded during the outage more severely than that experienced during operation. Moreover, the corrosion products formed during the outage under the effect of low temperature in the presence of moisture or droplets of water were found loose. This was considered to be the characteristics of corrosion products of the standing period. These can be easily removed during start up and passed into solution thereby increasing the iron content as suspended particles.

Hence, the iron content in water can be used as a measure for the corrosion rate of mild steel (Shim et al 1988) . In such cases, wall-thinning occurred leading to a decrease in the thickness of about 70%. During stagnation, the liberated air bubbles attached themselves to the metal surfaces , thereby initiating anodic attack under the effect of electrochemical concentration cell (Grossbaltt 2001).

***Microscopic examination:*** The results of microscopic examination of the corroded area (specimen1) showed that pits are varying from single pit holes to a wide spread attack approaching uneven localized pitting corrosion (see plate 1).The intact area adjacent to the corroded area (specimen 2) showed a distortion of the micro structure to the extent that the ferrite incorporate very low percentage of pearlite . Plate 2 indicate clearly the phase change of steel micro structure ( Pollack 1981).

The cross sectional area (specimen 3) visually showed pit penetration to more than 70% of the wall thickness. Some of the pits emerged together to form wide mouth pit as appeared in Plate 3.The corrugation of the pit mouth is the characteristics of carbon dioxide attack. Plate 4 showed the normal microstructure of steel with no distortion .

The intact cross sectional area ( specimen 4 ) showed that there was no evidence of microstructural changes as evidently appeared in Plate 4(a & b).

***Corrosion rate measurements:*** from the results obtained from the polarization of the pipe specimens on an electrochemical cell , it was indicated that condensate showed relatively low corrosion rate (2.7 mpy) compared to that observed with raw water (6.5 mpy), refer to Fig. 3 & 4 . However , although the condensate in reality showed low corrosivity to the metallic surfaces in the short term experiment. But, practically it did not confer sufficient protection against corrosive agents such as $H^+$,$O_2$,$CO_2$ in the long term exposure (Hochheimer 2000).

Therefore, pure condensate is very weak and causes metal break-down unless chemical conditioning by oxygen scavenger plus neutralizer were carried out.

## *Suggestions*

To avoid pitting corrosion in the main condensate return lines, the following points have to be fulfilled :

1. Proper deaeration through verification of the specified temperature and pressure, according to the specifications.
2. Proper chemical dosage according the desirable levels which should be increased during start up and before stoppage .
3. Periodical oxygen checking in feed water and condensate in the returns should be related to the chemical dosage immediately
4. Facilitate complete drainage of horizontal headers during stoppage. Alternatively, complete filling of the pipe line with alkaline hydrazine solution (pH 9.5) will provide good protection.
5. Plant shut down timing record should be kept to indicate the necessary actions of dry or wet preservation .
6. Spool installation parallel to main condensate line would provide pre-information about pit initiation prior to pit propagation .
7. On line installation of oxygen recorder and pH meter are necessary.
8. The use of a vapor phase inhibitor during shut-down. (Iso 9001-14000 bulletin 2000).

### *Conclusion*

On the basis of all observations and testing results , the following conclusions can be drawn:

i. Serious pitting attack concentrated in the return lines was found in the unit subjected to frequent shut down. The main cause was the presence of dissolved gases. Proper deaeration is essential.

ii. The whole lines either completely filled or drained during the stand still condition to combat the gases attack.

iii. Deficient chemical preservation during shut down, without using oxygen scavenger promoted serious pitting corrosion.

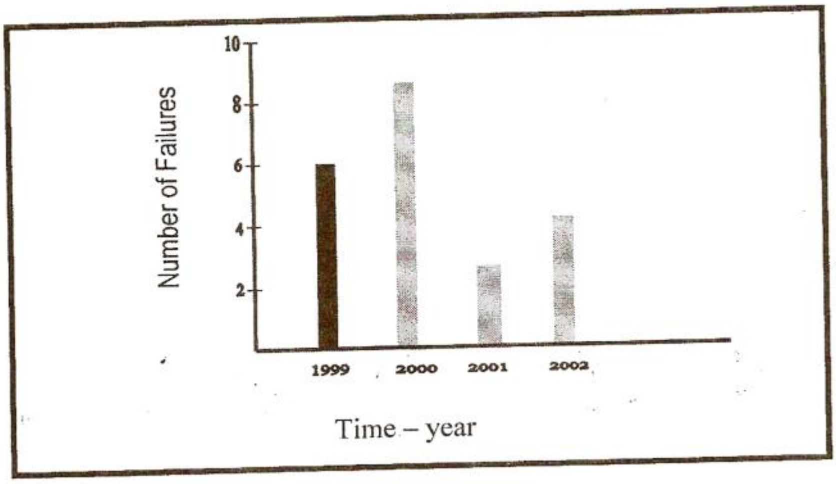



**Fig. (1) -Represent the number of failures during the period 1999-2002**

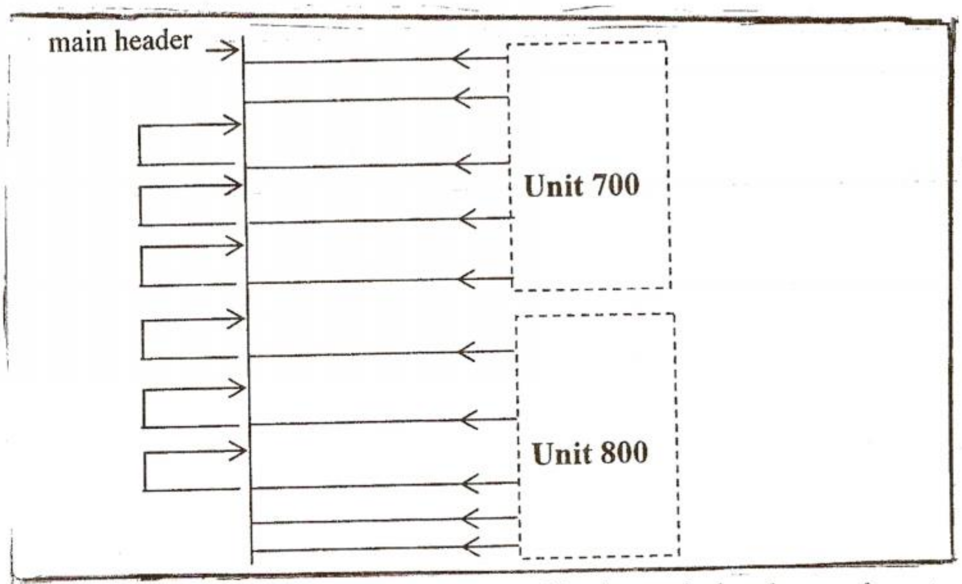



Fig. (2) – Location of the failure occurred in the main header condensate return lines-South Refinery Company.

**Table (1): Average chemical analysis results of condensate , feed and raw water compared to the standard limits-South Refineries Company**

| Characteristics | Average Chemical Analysis Results | | | Standard limits | | |
|---|---|---|---|---|---|---|
| | Feed | Condensate | *RW | Feed | Condensate | *RW |
| pH | 8.5-9.5 | 7.0-8.5 | 7.6-8.3 | 8.8-9.6 | 8.3-9.2 | 8-8.5 |
| Conductivity µs/cm | 5-15 | 1-6 | 3000-6000 | Max. 10 | Max. 20 | - |
| * S.S. mg/l | Nil | Nil | 10-45 | Nil | Nil | 10-40 |
| * T.D.S. mg/l | 4-7 | 1-4 | 2000-3500 | Max. 4 | Max. 9 | - |
| M-Alkalinity mg/l | 4-8 | 3-6 | 120-190 | - | - | - |
| * $DO_2$ mg/l | 0.01-0.04 | 0.02-0.04 | 7-9 | 0.01 | - | >5 |

*SS - Suspended Solids. *RW- raw water.
*TDS - Total Dissolved Solids.
*$DO_2$ - Dissolved Oxygen.

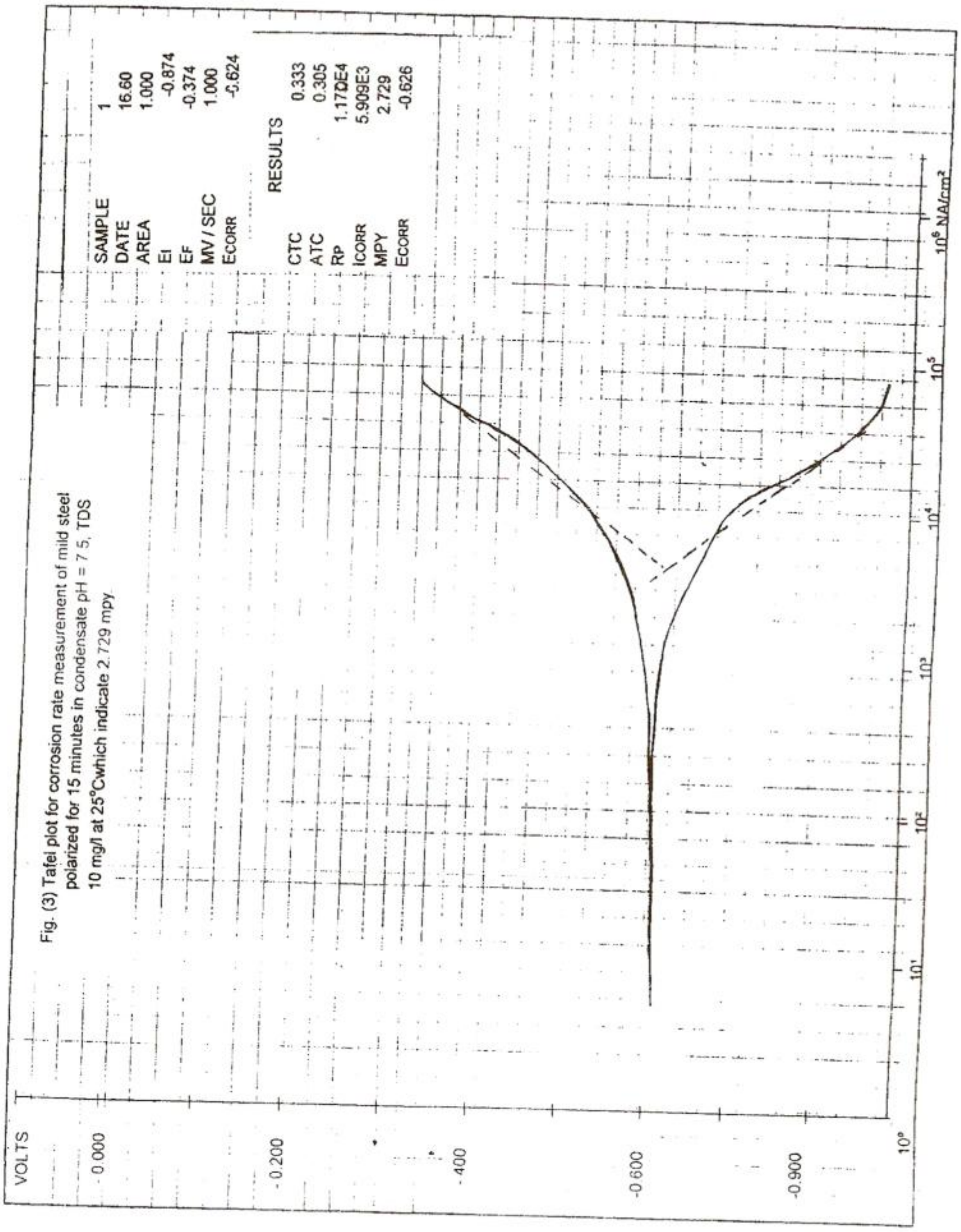



Fig. (3) Tafel plot for corrosion rate measurement of mild steel polarized for 15 minutes in condensate pH = 7.5, TDS 10 mg/l at 25°C which indicate 2.729 mpy

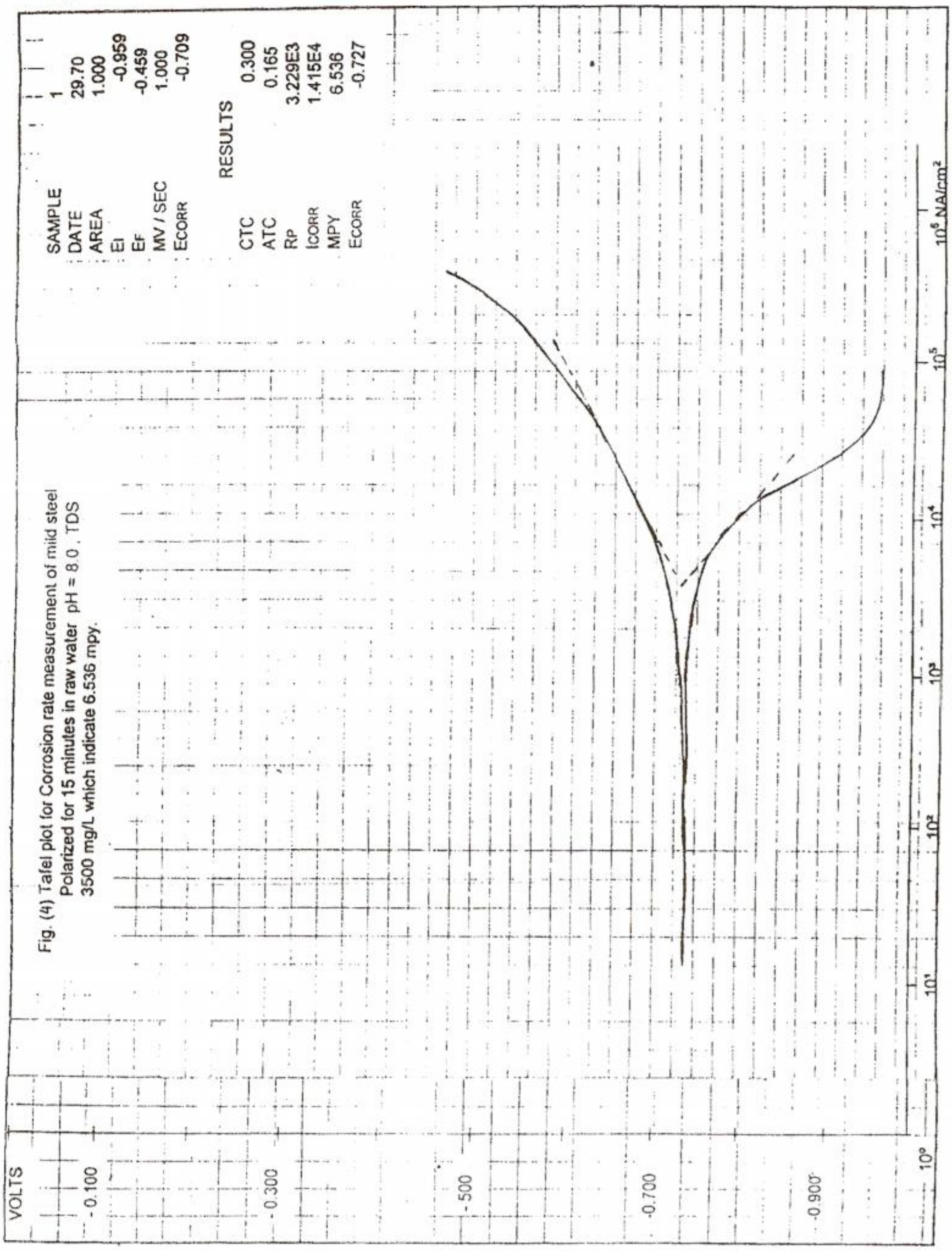
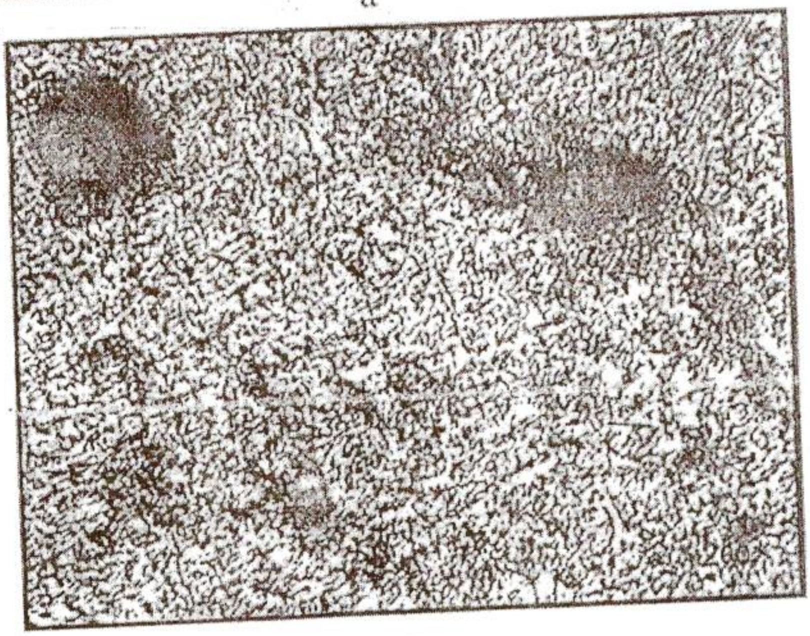



Fig. (4) Tafel plot for Corrosion rate measurement of mild steel Polarized for 15 minutes in raw water pH = 8.0 , TDS 3500 mg/L which indicate 6.536 mpy.


a



b

Plate 1- Localized pitting corrosion in the mild steel (106B) pipe interior , specimen 1, a-100x and b-200x .

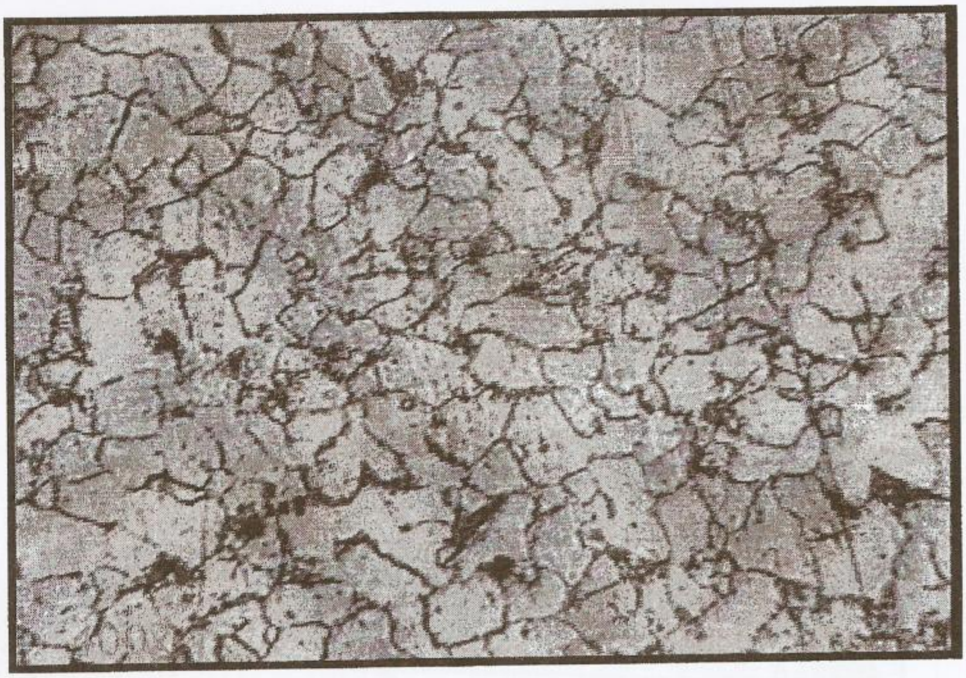
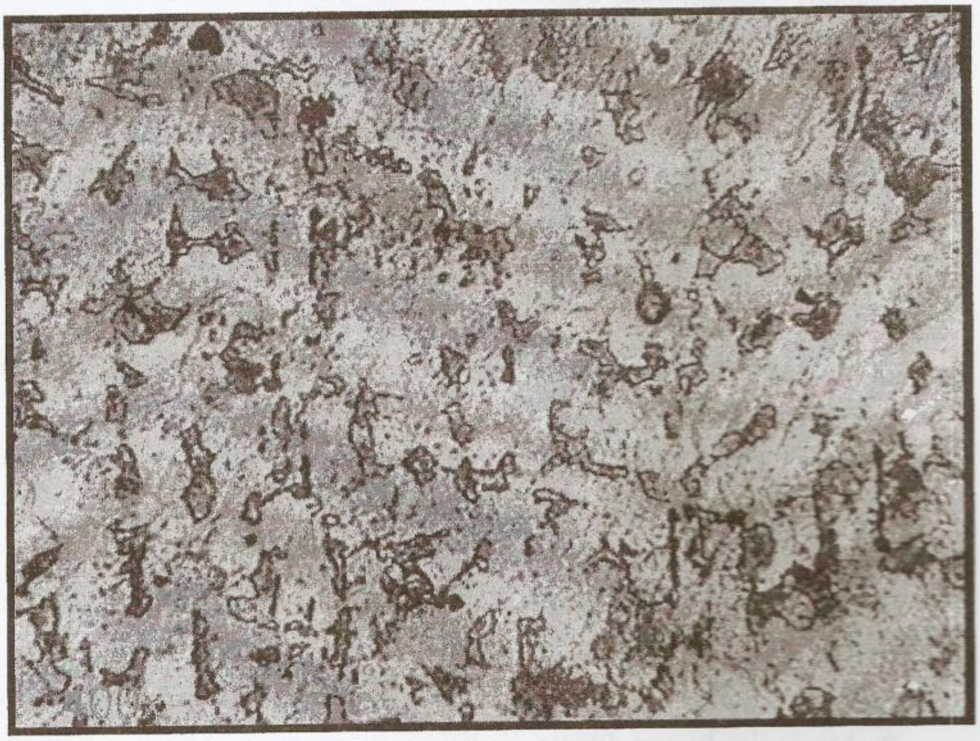


**Plate 2- Distored microstructure of mild steel (106B ) showing the phase change ,specimen(2) ,etched by nital,400x.**


**Plate 3- Surface feature of mild steel (106B) pipe interior showing the pitted areas, specimen (3) ,etched by nital,400x.**

a



b

**Plate 4(a&b) - Microstructure of mild steel (106B ) showing the normal structure of the two phases of steel, specimen(4), etched by nital ,400x .**

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