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COUNTRY PAPER FROM KUWAIT

CORROSION PROBLEMS EXPERIENCED IN AMMONIA AND UREA PLANTS*

by

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80-30402

CORROSION IN AMMONIA PLANTS

Ammonia (NH_3) is the principal form in which fixed nitrogen is available for the manufacture of fertilizers in the world today. Our processes for manufacturing ammonia utilize atmospheric air as the source for nitrogen and natural gas for producing hydrogen. The process can be divided into the following stages:-

A. Sulphur removal.
B. Natural gas steam reforming.
C. CO conversion.
D. CO_2 removal and recovery.
E. Synthesis gas compression and Ammonia synthesis.
F. Cooling system.

Case of surface condensers of the ammonia compressors

1. Introduction

The function of these condensers is to cool the steam in shell side (Temperature 58.4° C. Pressure 0.19 Kg/cm^2) by sea cooling water in tube side (Temperature 32°C. and pressure 3 to 5 Kg/cm^2).

From initial start up of ammonia corrosion problems were experienced on all components of main condensers.

Condensers tubes are made of Aluminium Brass which is considered suitable for sea water service at low velocities. The recommended for design sea water velocities for using Aluminium Brass with resistance to impingement attack in sea water service is 2.1 - 2.25 m/Sec.

2. Visual inspection and microscopic examination

2.1. Appearance of external surface of the tube.

The whole area was covered with brown scale. Widely spread uneven corrosion was seen longitudinally and it was bitter (Photo 1).

2.2. Appearance of internal surface of the tube.

The whole area was covered with brownish black scale. After descaling leakage was found to take place longitudinally and no significant corrosion was observed in other areas. See Photo (2).

2.3. View of cross section and microscopic observation.

The view of cross section and microscopic observation of longitudinal and circumferential cross section at the leaked and corroded part are shown in Photo 3 & 4. The leakage is caused evidently by the corrosion of outside. However inside of tube, very slight corrosion is recognized as shown Photo (4-d).

2.4. Severe pitting at random usually noted on the inner surface of distribution chamber, return chamber, baffle plates, supporting rods and covers after peeling off epoxy.

3. Discussion and causes of failure

3.1. The Aluminium Brass tubes are considered not suitable a material in our condensers from design and actual operation point of view. As the sea water velocity is excessive enough to cause impingment attack to the tubes material from inside.

3.2. Corrosion of outside due to ammonia generated by decomposition of amines (morphaline) or ammonia which added for neutralization of boiler feed water.

The corrosion rate of Aluminium Brass exposed to steam condensate containing high concentrations of the neutralizing substances (i.e. in air cooling zone) is nearly five times greater than that observed in condensate containing no addition agent.

3.3. Peeling off the protective coating is the main cause of inner surface corrosion of channels. This peeling off coating is usually occur which cause the steel surface to be in contact with sea water and very deep pitting was developed.

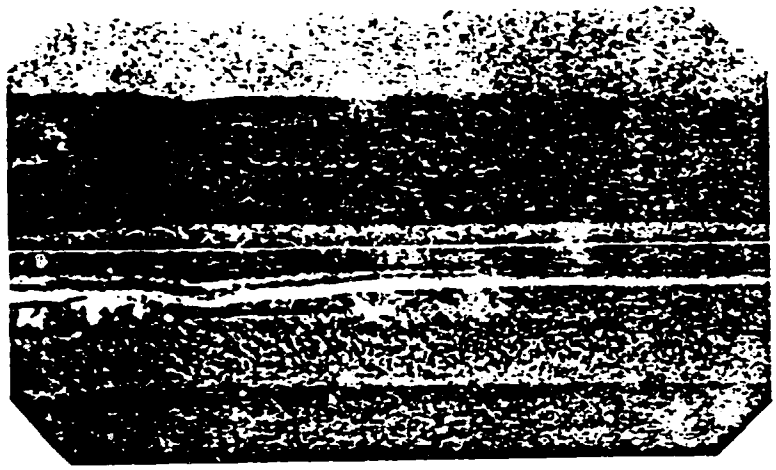
4. <u>Recommendation</u>

4.1. Modifying tubes material of the surface condensers. Both Cu/Ni 70/30 and Titanium were put under investigation as alternative materials.

4.2. It was recommended to replace the existing channels with rubber lining instead of Epoxy coating.

4.3. Screens at sea water pumps section should be of more narrow wire meshes to prevent large solids and marine growth to escape and plugging the tubes.

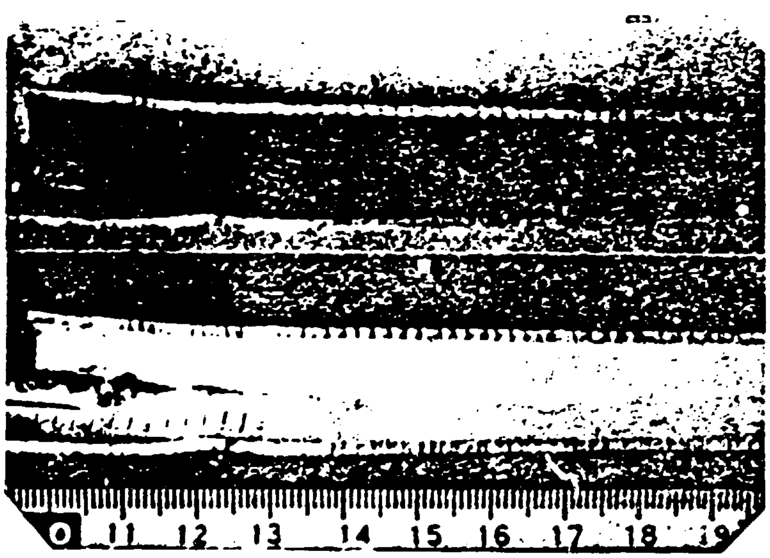
4.4. Proper sea water chlorination to prevent plugging of tubes by large marine growth.



Before descaling.

After descaling.

Photo 1 : View of external surface.



Before descaling.

After descaling.

Photo 2 : View of internal surface.

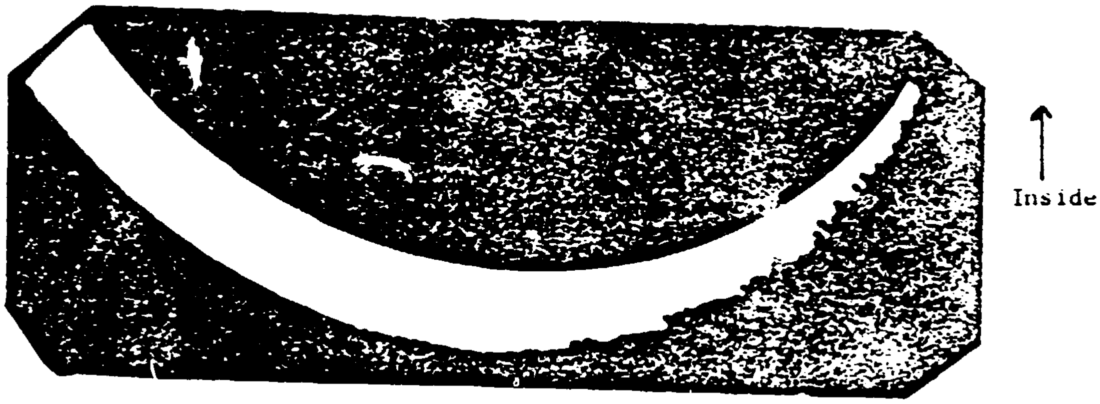


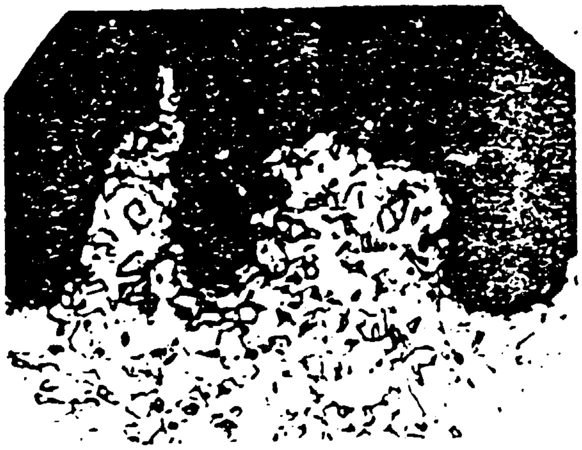
Photo 3 A: Leaked part circumferential.

Photo 3 B: Corroded part longitudinal.

Outside

Photo 4 A: End point of leaked part shown in Photo 1SA.

Photo 4 B: Corroded part shown in 18 B.



Outside

Photo 4 C: Corroded part shown in photo 18 B.

Photo 4 D: Slight corroded part of inside.

Case of Overhead Condenser

1. Introduction

Function of this condenser is to recover ammonia from purge gas by cooling with sea water. The following are design and operation conditions:-

	Shell side	Tube side
Material	Carbon steel	Bimetallic (Carbon steel ammonia side, Cu.Ni 70/30 Sea water side).
Fluid circulated	Ammonia	Sea water
Design pressure Kg/cm^2.	23	5
Operation pressure Kg/cm^2.	18	3
Design temperature $^{\circ}C$.	100	80
Operation temperature $^{\circ}C$.		
Inlet	49	35
Outlet	40	40

This condenser is of fixed tube sheet type made of carbon steel, cladded by 10 mm. thick Cu.Ni 70/30. Tube sheet layout standard for 4 passes.

The first overhead condenser put on line on August 1977 and replaced by a new one with the same specifications on June 1978 due to low cooling efficiency. The new one was opened after 10 days of operation for inspection.

2. Visual Inspection

2.1. Visual inspection of the first condenser.

2.1.1. Tube sheets were found covered by heavy salt deposits of white and blue colour. These salt deposits were heavier on west side tube sheet than that of the eastern one. (See Photos 1 & 2), after cleaning of tube sheets it was noted that a corroded groove around the tube end (1 - 6 mm. depth) and some of these tubes end were found completely eaten out - See Photoc 3, 4. The surrounding areas on the tube sheet s were subjected to corrosion of 5 m. m. maximum depth. Generally it was clear that corrosion is more severe in the west tube sheet that in the east one - See Photos No. 5, 6.

2.1.2. East Bonnet:

Partition plates edges were found severely corroded at their contact with the tube sheet as illustrated in Photo No. 7. A luster film of crystalline deposits green in colour were found adherent to the internal surface of bonnet bet ween its two partition plates i. e. in the 2nd and 3rd flow passes as illustrated in Photo No. 8.

2.1.3. West Bonnet:

Was found covered with heavy salts deposits and its partition plate edge was also found corroded at its contact with the tube sheet (See Photo No. 9).

2.1.4. The three Magnesium anodes fixed on the partition plates of the east Bonnet were found completely missed and the supporting bolts were corroded out. One of the bolts was found completely mis sed leaving a hole at its position. (See Photo No. 7).

2.1.5. Pressure test was carried out at 23 Kg/cm^2 using water detecting agent, water was found to seep from around 31 tubes on east side and 18 tubes on west side as shown in figures (1) and (2).

2.2. Chemical Analysis

Chemical analysis of the deposits collected from the surface of west tube sheet and east bonnet inner surface (2.1.2) showed the results as follows. Mainly composed from sea water salts and corrosion products.

	Sample (1) Tube sheet	Sample (2) Bonnet
Loss on Ignition Wt.%	39.96	35.44
Ca	19.41	1.52
Mg	19.8	6.57
Cu	0.16	0.45
Ni	0.08	0.012
Zn	0.12	0.24
Fe	0.56	1.13
Na	1.29	27.52
K	0.022	0.098
NH_3	0.007	0.052
Cl	1.13	1.16
SO_4	0.77	2.46
CO_3	8.24	7.31
SiO_2	1.25	0.67

2.3. Two tubes were pulled out from the condenser and thickness measurement carried out gave the reading in a range of 2.6 - 2.3 mm. which is within the design specification 2.77 mm.

2.4. Visual inspection of the 2nd overhead condenser E-1501 B.

The new condenser was opened after 10days of operation for visual inspection which showed the following:-

2.4.1. Tube Sheets:

Corrosion grooves (1.0 - 2.5 mm. depth) were noted on limited areas around the tube ends of 52 Nos. tubes also the surrounding areas of these tubes were subjected to corrosion of 4 mm. max. depth.

2.4.2. East Bonnet:

It was found in a good condition except slight corrosion on the edge of the partition plate.

2.4.3. West Bonnet:

It was found in satisfactory condition.

2.4.4. Magnesium Anodes:

2 Anodes were found eaten out 75% and the third one was completely missed. Inspection report had been issued for repairing the above remarks.

3. CAUSES OF FAILURE AND DISCUSSION

3.1. Improper sealing between tubes end and tube sheets

From the attached drawing No. (3) of tube end arrangement it is clear that the outer surface of the tube end inside the tube sheet consists of two metals carbon steel and Cu/Ni 70/30 of 20 mm. length to avoid contact of sea water with carbon steel. Ammonia may be leaked from a point of bad expanding till it became in contact with Cu/Ni material of outer tube end. Then severe corrosion took place on the Cupro Nickel outer tube surface and on the outer surface of the inner Cu/Ni tube causing ammonia leakage to sea water.

The sea water containing leaked ammonia attacked the Cu/Ni layer on the tube sheets at both condenser ends. This attack is remarkably increased in the order from the 1st to the 4th passes with the exception of the main sea water inlet and outlet at the east side. This is due to that at the inlet the sea water is free from ammonia while at the main outlet the ammonia contaminent in sea water has been consumed in the corrosion reactions with copper and precipitation of sea water salts. (See Fig. 4).

The chemical analysis of deposits which are concentrated on the west tube sheet showed that these deposits are mainly corrosion products of tubes end, tube sheets, Magnesium anodes and salts normally present in sea water.

3.2. Wrong choice of sacrificial anodes

Magnesium anodes are used economically and efficient only in media of high resistivity (sea water of low resistivity). They should generally not be used when the temperature is higher than approximately 45° C. in fresh water. In sea water their life is short. In sea water Magnesium anodes give high driving potential which caused peeling off of epoxy coating in some areas of the east bonnet internal surface and became highly cathodic which led to electrochemical decomposition of sea water salts. This is clear from the analysis of the lusture film of crystalline deposits which found on the internal surface of east bonnet (27.5% Sodium) see the attached chemical analysis report.

3.3. Galvanic corrosion

The potential difference exists between the partition plates made of carbon steel and the tube sheets of Cu/Ni on contact with each other after peeling off of coating and anodes consumption produced electron flow between them.

Thus corrosion start and continued on the less corrosion resistant metal (Carbon steel of the partition plate - anodic) caused it to be eaten out.

4. RECOMMENDATIONS

4.1. Magnesium anodes should be replaced by Zinc alloy anodes "C-sentry" which are the suitable and efficient anodes for cathodic protection in sea water medium. Bakelite or rubber washers should be fixed under the bolt heads and nuts to avoid galvanic corrosion of partition plates. However study and evaluation in hand to use Aluminium anodes which is better than Magnesium anodes in sea water service.

4.2. Pressure test with the application of water detecting agent should be carried out on any new condenser before putting on line to check that proper expanding has been done by the Manufacturer in case of rolled to tube sheet tubes arrangement.

4.3. All tubes ends were over expanded with special care to leaking ones which were plugged. The corroded grooves on tube sheet and corroded tubes ends to be filled by welding using Monel 67 filler wires and gas welding.

4.4. New design of tube end illustrated in Fig. (3) is to be revised for future arrangement.

Photo (1)

West Tube sheet Before cleaning.

Heavy corrosion products and sea water salts.

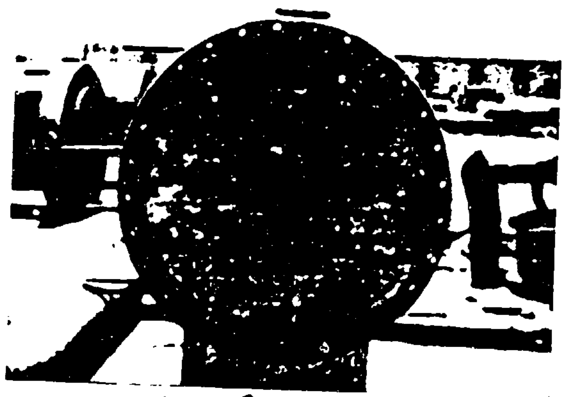


photo (2)

East Tube sheet before cleaning.

Notice the difference between the amount of salt deposits on East and West tube sheets.

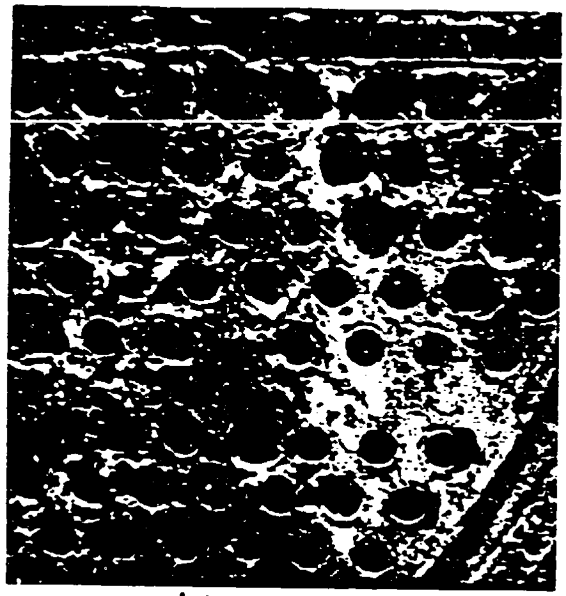


photo (3)

West Tube Sheet after cleaning.

Notice the corroded grooves around the tube ends, and the tube end which completely eaten out.

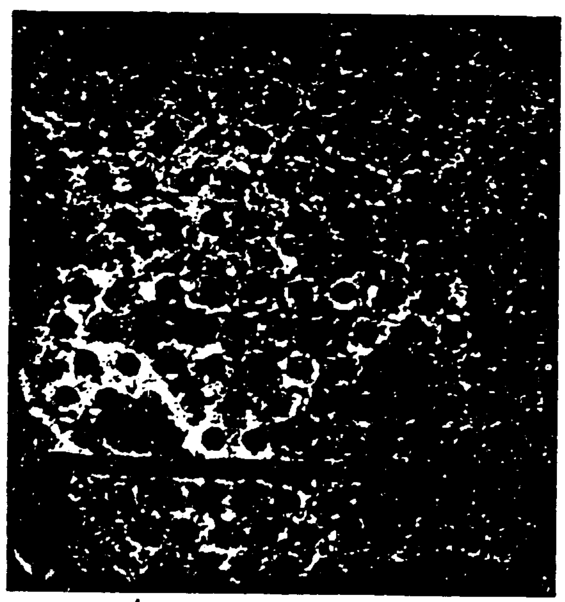


photo (4)

East Tube Sheet.

After cleaning.

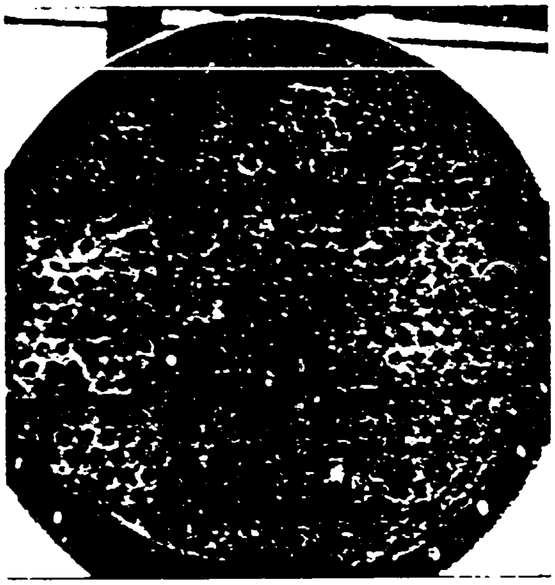


photo (5)

East Tube Sheet after cleaning:

Notice the absence of Corrosion in Main Inlet and outlet of Sea Cooling water.

photo (6)

West Tube sheet after cleaning.

All the tube sheet was subjected to corrosion due to Ammonia attack.

photo 7)

East Bonnet

Galvanic corrosion on the partition plates edges at their contact with the tube sheet after peeling of coating. Notice the hole at position of the supporting bolts of Magnesium anode.

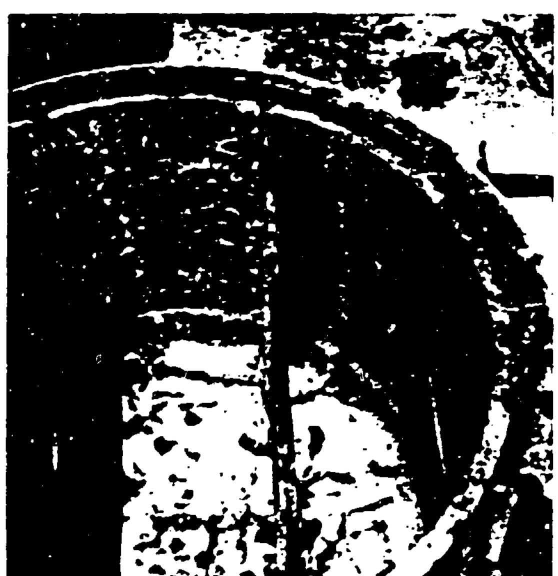


photo 8)

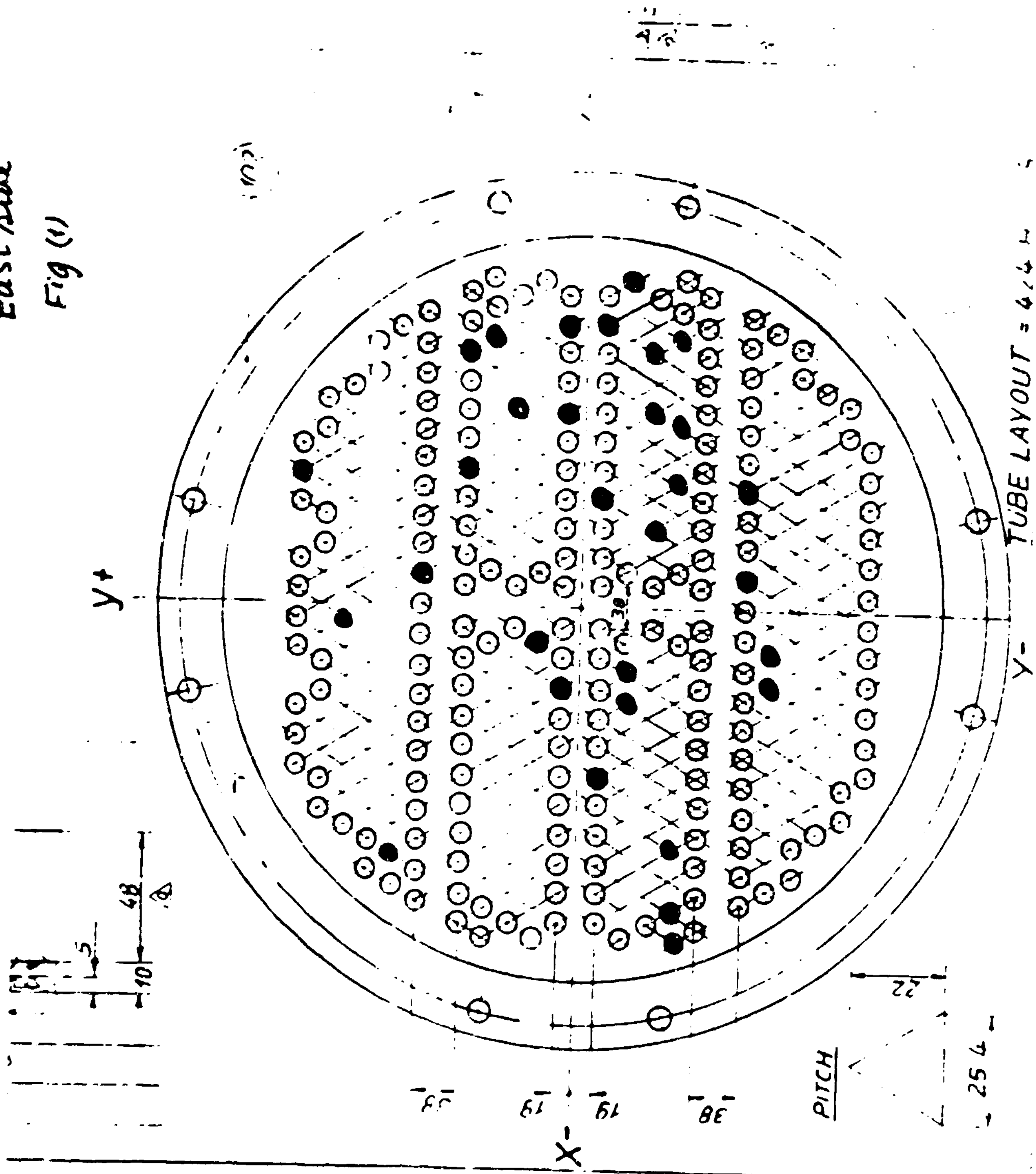
Lustre film of crystalline deposits due to electro chemical decomposition of sea water.

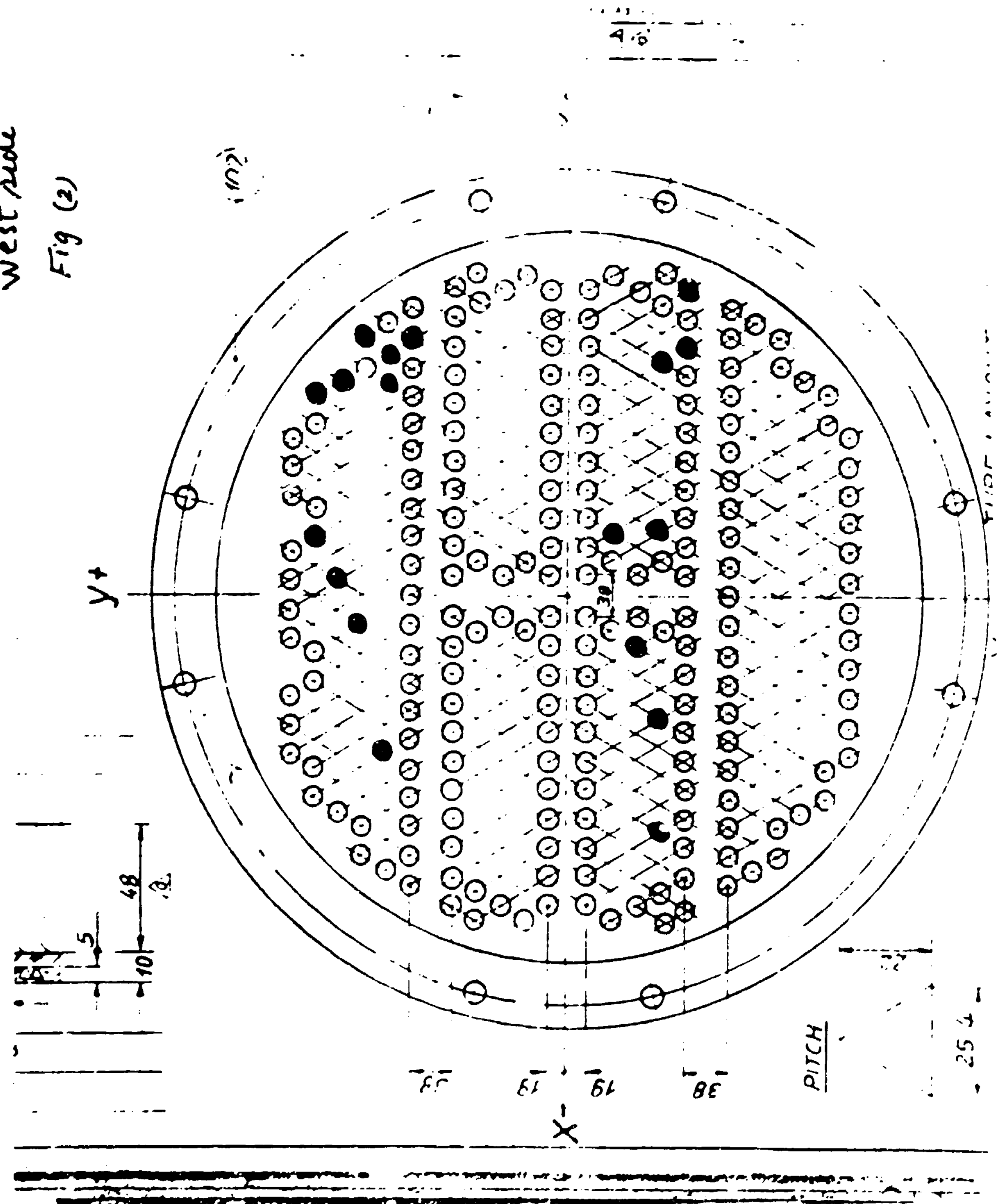
photo (9)

West Bonnet

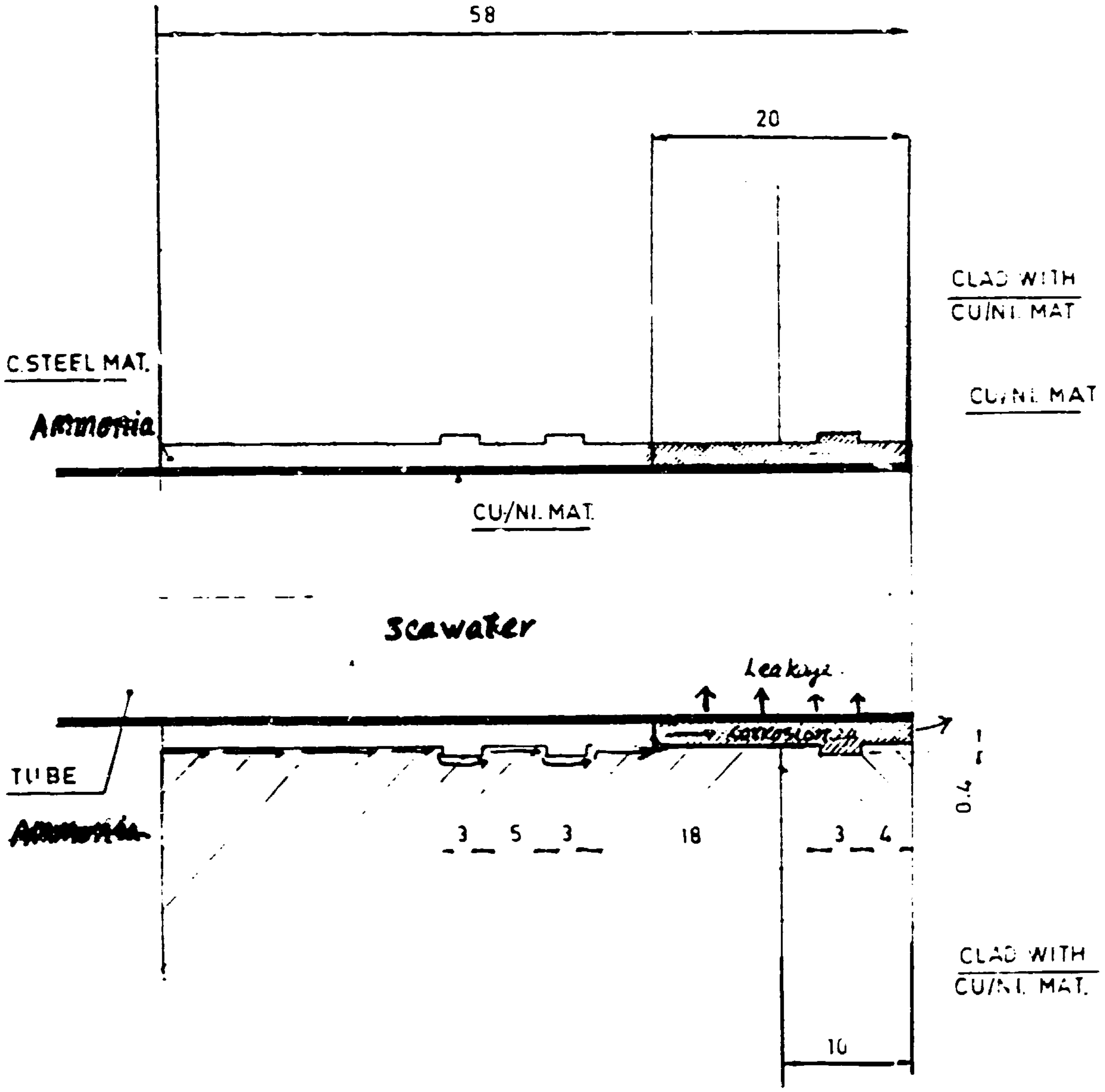
Heavy salt deposits of corrosion product and sea water salts. Notice the corroded edge of partition plate at its contact with Tube sheet.

East side
Fig (1)





west side
Fig (2)



PETROCHEMICAL INDUSTRIES COMPANY

Fig (3)

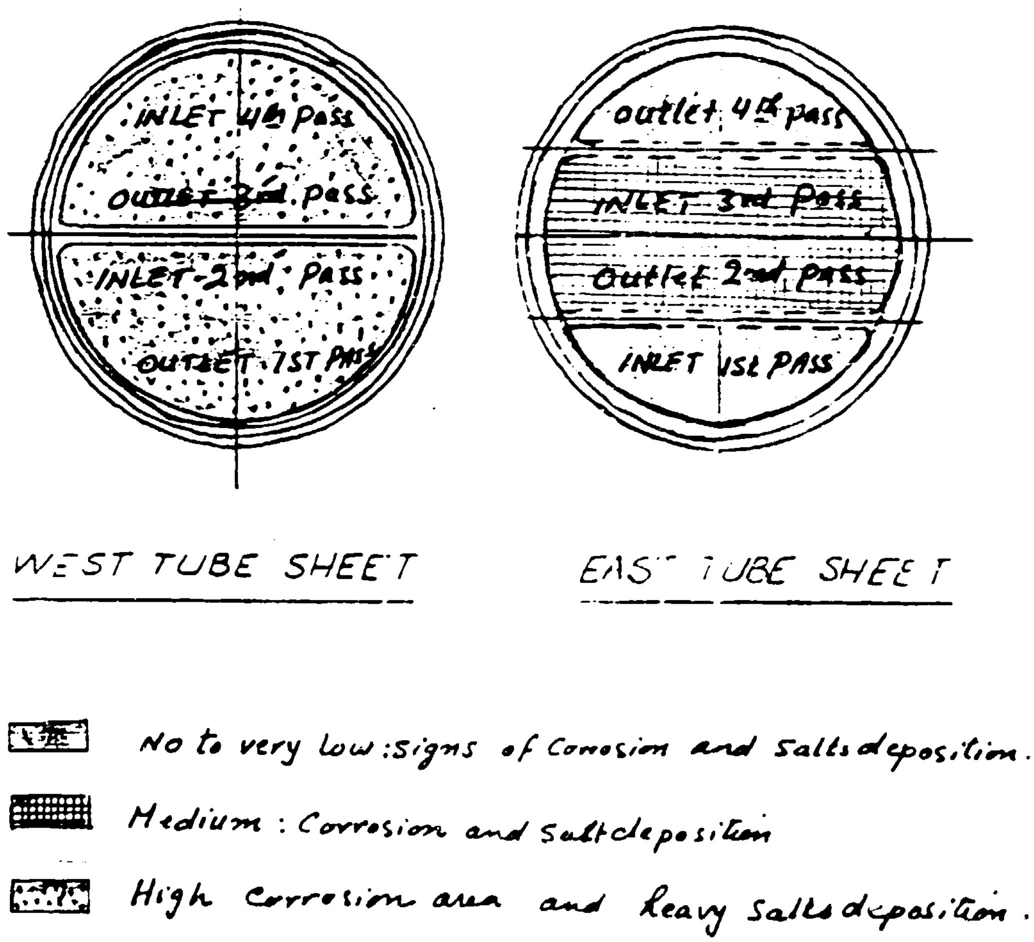
ABU BAKR

E-1501

TUBE END

18.7.1978

460864


INLET 4th Pass
OUTLET 3rd pass
INLET 2nd Pass
OUTLET 1ST PASS
outlet 4th pass
INLET 3rd Pass
Outlet 2nd PASS
INLET 1st PASS
WEST TUBE SHEET
EAST TUBE SHEET
No to very low: signs of Corrosion and Salts deposition.
Medium : Corrosion and salt deposition
High Corrosion area and heavy Salts deposition.

CORROSION IN UREA PLANTS

In recent Urea Plants, corrosion problems have been mostly, though not completely overcome. Generally speaking such inorganic corrosion resistant materials as glass lining cannot be used due to high pressure and such organic corrosion resistant material as polymers cannot be used due to high temperature and erosion susceptibility of these materials. Metal is the only suitable material in Urea Plant.

Corrosion problems in Urea Plant occur mainly in the reactor and let down valve, the high pressure decomposer and the carbamate pump.

General Process description

Urea is produced by the following two-step equations

$$2\,NH_3 + CO_2 \longrightarrow \underset{\text{Ammonium Carbamate}}{NH_4COONH_2} \longrightarrow \underset{\text{Urea}}{NH_2CONH_2} + \underset{\text{Water}}{H_2O}$$

The first reaction is assumed to go to completion but the second reaches equilibrium. Excess ammonia favours the Urea yield. Accordingly, the reaction product in the Urea synthesis reactor is a liquid mixture of unconverted ammonium carbamate excess ammonia, Urea and water. The ammonium carbamate is a highly corrosive intermediate. High temperature near 200° C encourage corrosion in the urea reactor. The reactor is generally of vertical cylindrical type, with internal baffle plates in certain instances.

The reaction product is usually heated in the next decomposition section, where unconverted ammonium carbamate is decomposed into ammonia and carbon dioxide gases. The urea solution thus formed is finally concentrated to 99.7% urea. The overhead gas from decomposers is condensed and recycled into the reactor by the recycle solution pump.

Case One Urea Plant Reactor

1. Introduction

In April 1978 the reactor lining was in several places repaired , patches were applied, partly in the form of straightened liner material partly in the form of new 316L material. Between April 1978 and February 1979 there have been 5 stops due to leakages, the leaks were the result of pin holes in repair welds and S.C.C. in the patch. Material the lining had been pressed inward in two places over lengths of 7 and 2 metres.

Reactor is consists of 75 mm carbon steel, clad with a 5 mm lining of A.I.S.I. 316L. The effective on stream time is approximately 12 years.

2. Visual Inspection

2.1. Compartment B1 - B8

The lining at the south side had been pressed inward over a width of about 110 c.m. and a length of about 710 c.m., this area comprised compartments B_2 through B_8. The lining was generally black and slightly roughened, there was no visually detectable difference between the dislocated lining and that which had remained in the original position.

At the northern side of the reactor there were small bulged areas in the lining of compartments B_4, B_5, B_6 and B_8.

The circumferential welds and the longitudinal welds showed selective attack and had been repaired in places.

2.2. Compartments B_9 - B_{14}

In compartments B_{11}, B_{12} and 13 the lining at the south side had been pressed inward; this area was about 1.8 m. long and 0.5 m. wide. The lining, the welds and the internals in compartments B_9 through B_{14} did not visually differ from the top section of the reactor as regards corrosion.

2.3. Compartments B_{15} - B_{22}

In compartment B_{21} six small bulges areas were found. The circumferential welds and the longitudinal welds showed selective attack and had been partly repaired.

2.4. Wall thickness measurements

Shell: - Carbon steel

The thickness varied :

From 76.6 to 80.2 mm. in B_{12} and

From 76.8 to 79.0 mm. in B_{13}

Lining:

According to the measurements, the wall thickness varied from 4.3 to 5.1 mm. with an average of 4.7 mm.

Assuming that the original wall thickness of the lining, prior to start-up was 5.1 mm. it can be concluded that the wall thickness decrease over a period of 11 years amounts to 0.4 mm. which corresponds with an annual corrosion rate of 0.04 mm.

3. Macroscopical examination

Two bridge strips taken from bulged and removed liner were welded (April 1978) on south east and south west boundaries of replaced liner section on this liner belt. Both strips leaked from cracks or pinholes on parent metal and caused two successive plant shutdowns.

3.1. South east - Bridge strip

Examination of the removed strip revealed a deep (mechanical) dent on the back surface of the strip (Macrograph No. 1). A series of branched cracks were found spread all over the back surface of the strip (Macrographs No. 2).

3.2. South west - Bridge strip

Leaked from two neighbouring pinholes developed on liner surface medium side.

3.3. Bridge strip on B_6 (South west boundary)

The strip was from bulged and removed liner and was removed as a preventive action. Back side of removed strip was found severely subjected to corrosion attack on local areas. A cross section midway one of corrosion pits is shown in Macrograph (3).

3.4. Bridge strip on liner belt B_{12}

This strip was carefully removed with the weld metal for examination and revealed the following:-

- Cracking immediately adjacent to weld beads See Macrograph No.(4).
- Corrosion attack across weld deposits was noted mostly at top start points of the weld. Macrograph No. (5).
- Cracking in the parent metal close to welds heat affected zones.
- Deep corroded holes and cuts in welds heat affected zones. Macrographs No. 6 - 9. Corrosion and surface blisters on parent metal of the strip were also noted. Macrographs No.10 & 11.

4. Microscopical Examination

4.1. Specimens from bridge strips on B_5 & B_6 - Original lining bulged and removed.

- General structure of the material was found good and free of abnormalities (Micrograph No.12)
- Numerous corrosion pits formed on local areas on back surface of the strips (Micrographs No. 13 - 17). and
- A pattern of several cracks radiated from each of the formed pits. Cracks propagated with extensive branching and displayed a transcrystalline mode of progression (Micrographs Nos. 13 - 22).

4.2. Specimens from bridge strip on B12 - New liner material.

- General structure of the material exhibit inhomeginity in austenite grain size (Macrographs Nos. 23 - 25).

- Corrosion and/or cracking of strip material developed mostly in vicinities close to weld joints as shown in Macrographs Nos. 26 - 28. Cracks were noted to penetrate through weld metal as Micrographs Nos.(29 - 31).

- Cracks displayed intercrystalline mode of progression as shown in Micrographs Nos. 32 - 34.

- Signs of grain boundary sensitization were noted in areas confined to heat affected zones of welds (Micrographs Nos. 35, 36). Dispersed precipitate was noted at austenite grain boundaries ahead of propagating cracks .

5. Discussion the causes of failure

5.1. Transgranular corrosion was detected with a result of branched cracks in austenitic stainless steels. This type of S. C. C. occured on strips taken from bulged-and-removed liner sections. The residual stresses induced in the material from bulging and subsequent straightening of bulged sections to re-use them. When stressed material come into contact with chloride ion cracking initiated. Chloride ions may be due to contamination of process liquid due to leaks at some condensers which use sea water and the sources of chloride ions on the back side of the liner may be due to steam injected through leak detection holes between shell and lining.

5.2. Intercrystalline (Intergranular corrosion).

This type of cracking can be occured when stainless steel contains more than 0.03% C. and not stabilized by Niboium or Titanium and that it has undergone thermal processing (Welding or heat treatment) in the so called sensitization range (500° C - 800° C).

Under this temperature the low carbon grades may subject to harmful effects. For eaample 316^{L} material may fail in the test for resistance to intergranular corrosion (Huey test) after heating for only one hour at 650^{o} C.

5.3. Bulge in reactor lining could be attributed to microcracks either at weld or pit liquid ammonium carbamate at lining. The liquid oozing through the crack once it reached to the gap between the liner and shell the liquid flashes since the pressure is essentially atmospheric releasing NH_3 and CO_2 and depositing solid carbamate. Accumulation of urea and corrosion products tend to plug the weep holes and permit a pressure build up behind the liner. Eventually the crack opens wider and larger amounts of liquid flow through until all the liquid cannot of flash away.

6. Recommendations

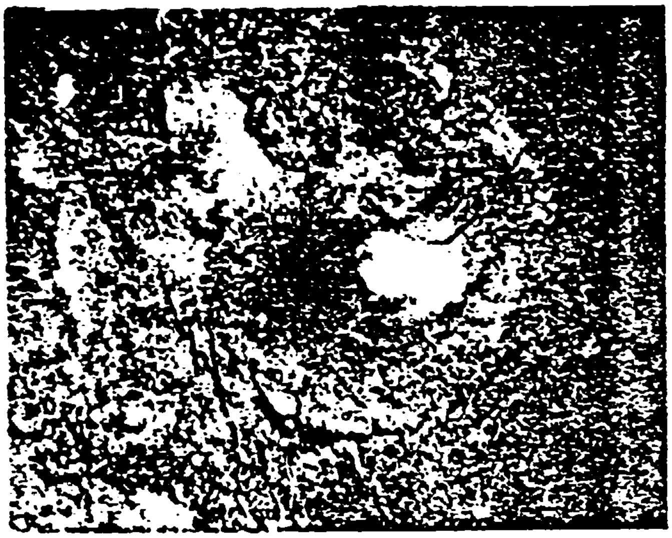
6.1. The new lining plates, thickness 6 mm. pressed down, spot welded and covered up with patches for all the welding work, Thermanit 191 SH electrodes was used.

6.2. Chloride content in the process stream and in steam must be strictly controlled.

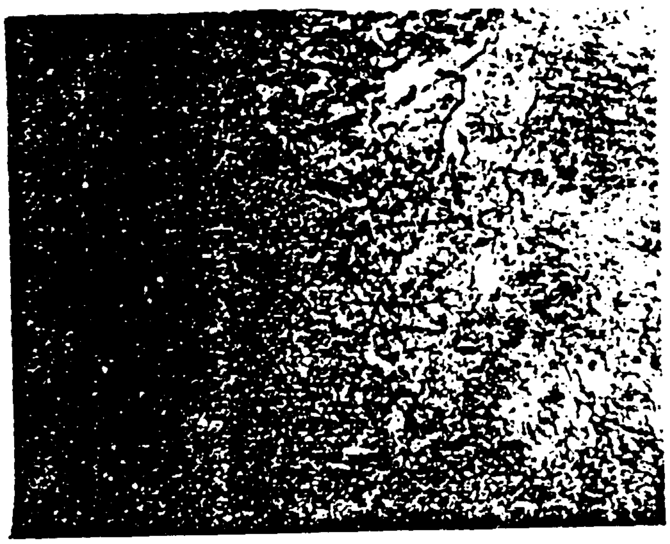
6.3. For future orders of lining material, suppliers will be asked to submit material test certificate and Huey test results. The remaining bridge strips that were not replaced during the last repair job have to replaced.

6.4. Additional 15 Nos. new weep holes been drilled directly adjacent to the backing strip, so that during operation each compartment is connected to at least one open weep hole.

6.5. Dissolved O_2 content is essentially in the actual process liquid therefore its determination in the liquid will be carried.



1- 5.25 X



2- 4.2 X

3- 13 X

4- 4.2 X

5- 5.25X

5.25 X

6-

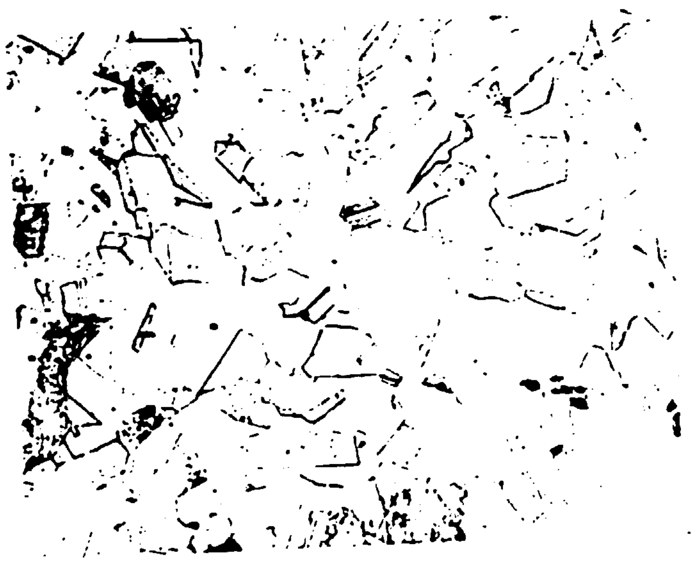
7- 26.25 X

8- 4.2 X

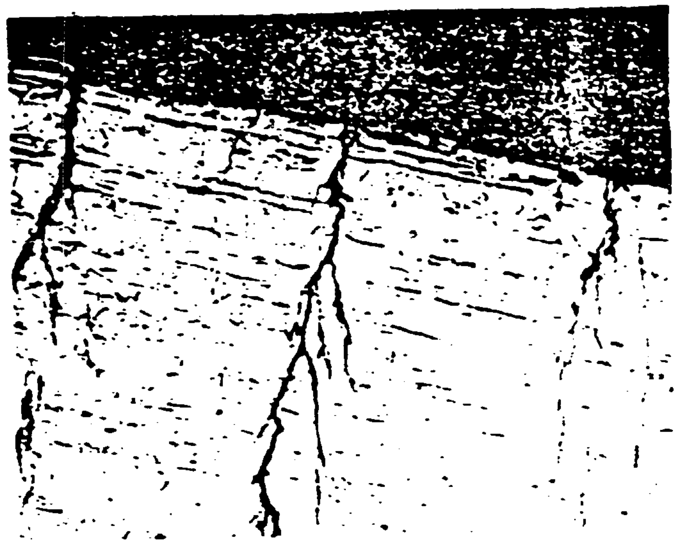
9- 10.5X

10- 4.2X

11 - 16.8X



12- 128X



13-

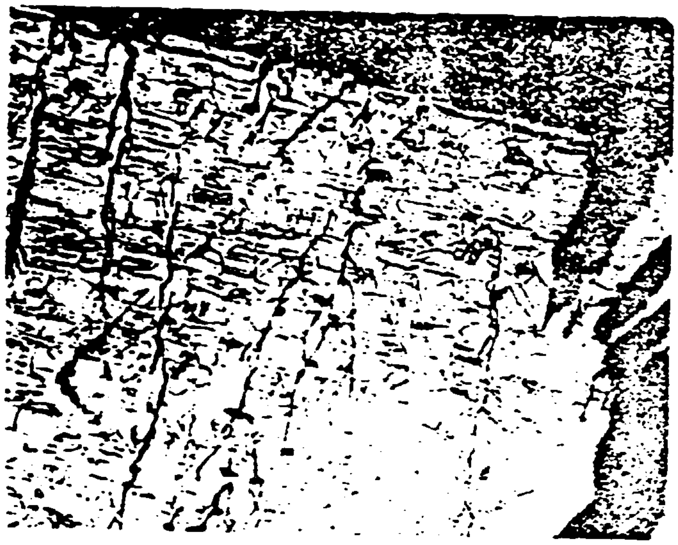
64X

14-

64X

15- 200 X

16- 100 X



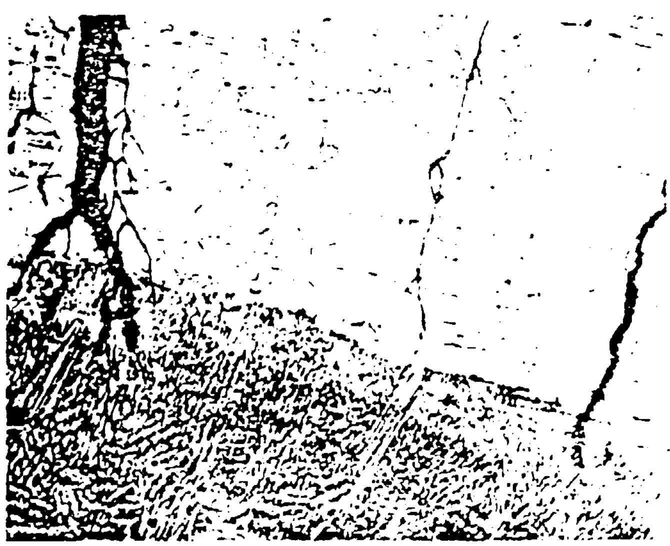
17- 64X

18- 100 X

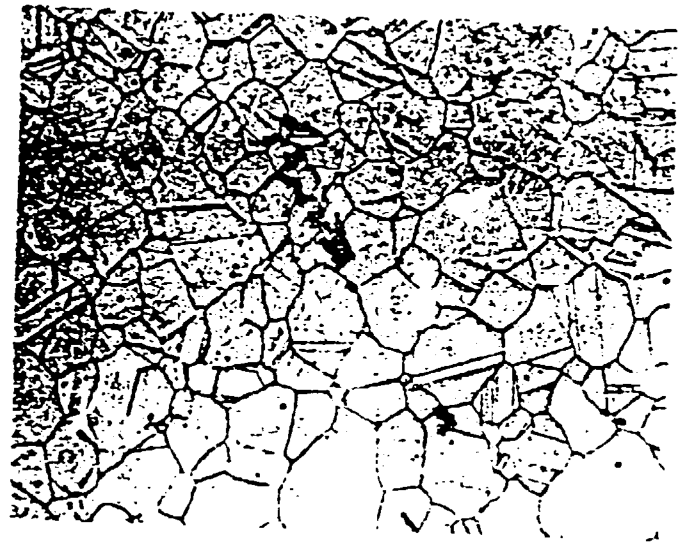
19- 100 X

20 - 100 X

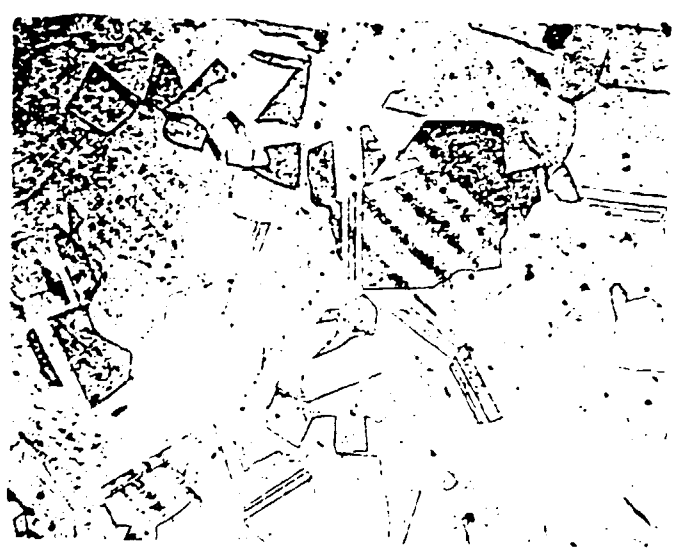
21- 256X



22- 64X



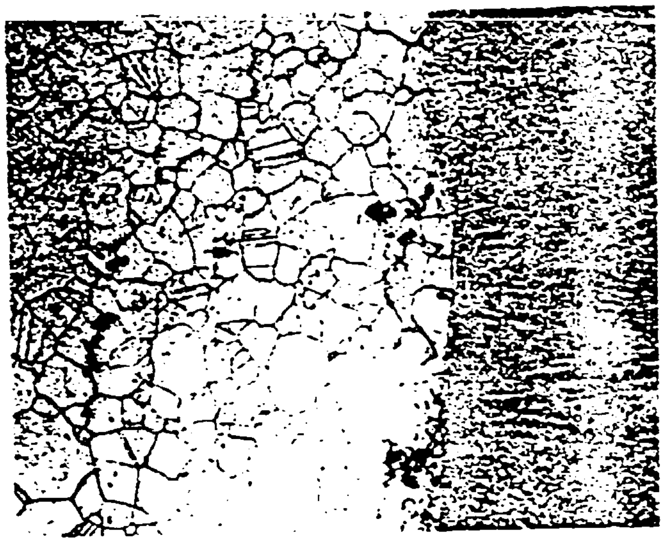
23- 100 X



24- 128 X

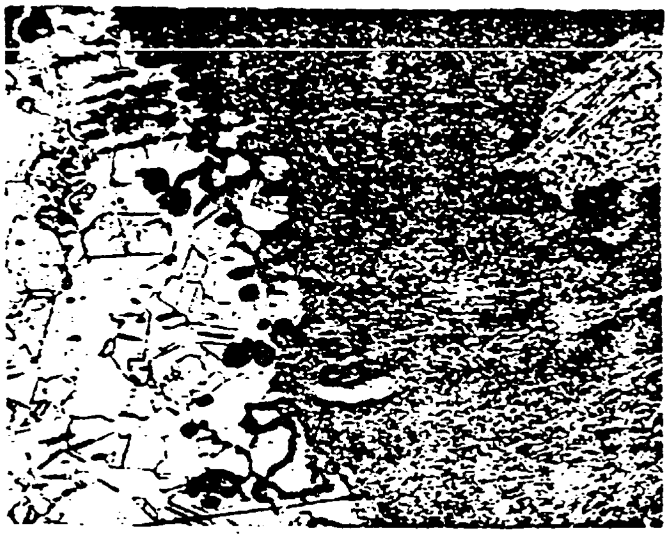
25- 128X

26- 64X



27—　　　64x

28-　　　64x

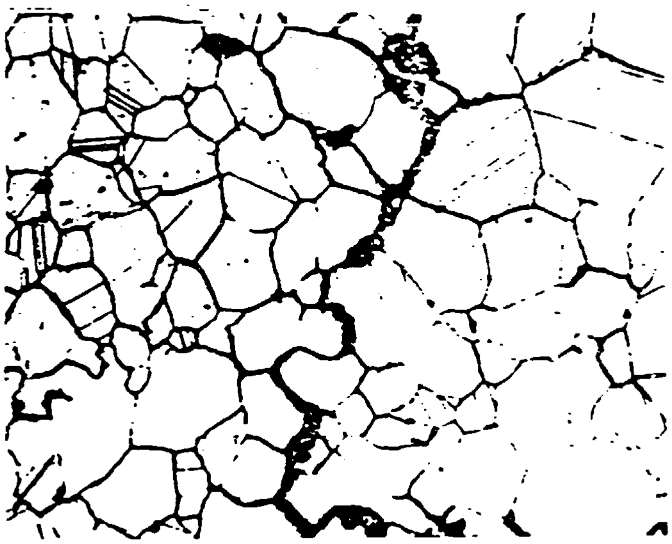


29- 64X

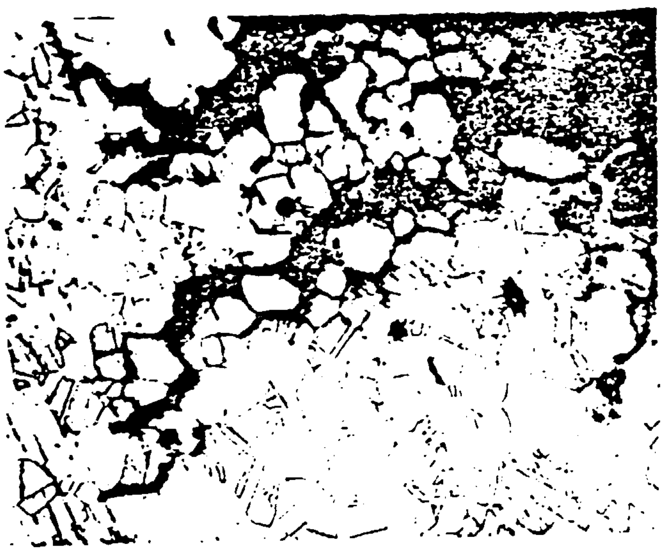
30 64X

31- 64X

32- 64X



33- 100 X



34- 64X

35- 1280 X

36- 640 X