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JUBAIL CORROSION & MATERIALS ENGINEERING FORUM
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CHALLENGES & SOLUTIONS

بتروكيميا
petrokemya

UNEXPECTED SILENT KILLER IN HIGH-GRADE MATERIAL

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OUTLINE

- Introduction
- T/A Observation
- Background
- Process Description
- Analysis of Damage Mechanism
- Discussion of Laboratory Results
- Root Cause
- Conclusion
- Recommendation

INTRODUCTION AND BACKGROUND

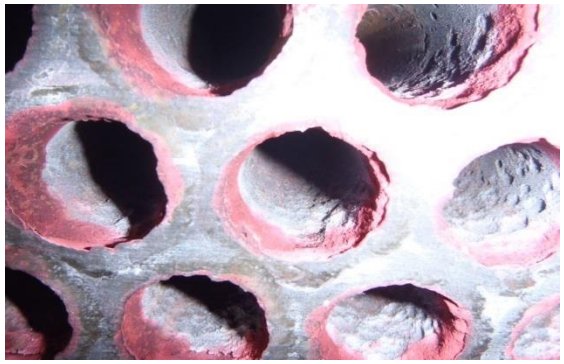
INTRODUCTION

During scheduled turnaround of VCM plant in the month of Oct-Nov-2014, Heads Column Condenser was inspected as a part of preventive maintenance.it was suppose to be normal clearing job. However , after opening the exchanger many observations and damages found in separate locations. Severe pitting on tube ID and localized corrosion found in the hot side i.e. tube inlet side. The tube-to-tube sheet area had pitting around 2mm deep. Pitting and loss of thickness beyond the acceptable limit founds in 350 tubes. Many tube-to-tube sheet joint found severely damaged.

On the other hand, there was no any significant damage either in tube or in tube sheet at the tube outlet.

The tube material of this exchanger is duplex stainless steel Alloy-2205, the tube sheet is carbon steel cladded with Inconel 625. the target was to extend the life to 10 years but it fail after 18 month only.

The original material was carbon steel an It worked up to 10 years , then it been upgraded to SS after 10 year and it worked up to 2 years only. After the SS failure it been upgraded to DSS.



BACKGROUND

- The condenser inlet temperature remains in the range of 78-85 degree °C and out let from 44 - 55 degree °C.
- The pH in the reflux remains an average 6.5 with lower side (EDC side) average of 5 years.
- The channel head of the hot end it is Alloy-2205 material also have similar pitting.
- The column overhead line is carbon steel, where no much thickness reduction observed.
- The condenser outlet lines and decanter are of Alloy-2205, with no much significant defects.
- During turn around, in the heads column which is before the condenser it was observed that 19 trays (alloy-2205) collapsed, broken, fallen down, detached and thinned out due to excessive corrosion and thinning, out of 70 trays.

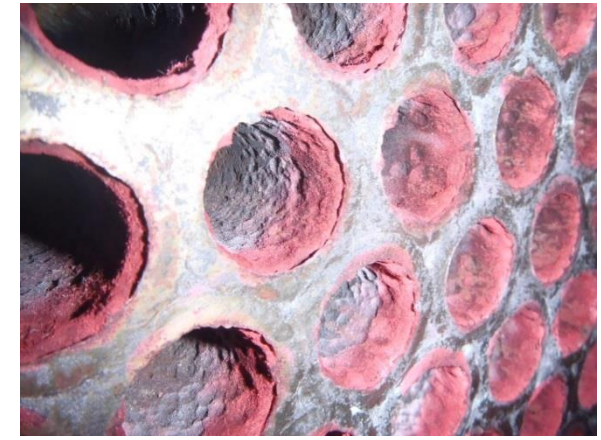
TURNAROUND OBSERVATION

Visual inspection:

1. Corrosion pitting (About0.5 mm to 2.5 mm deep) at Internal surface.
2. Pinholes & corrosion pitting was observed 36 tubes to tube sheet seal weld.
3. Deep pitting were observed over 60mm length inside the tube surface for entire tubes.
4. Thinning observed on all tube-to-tube sheet seal welds at both north & south

Hydro test:

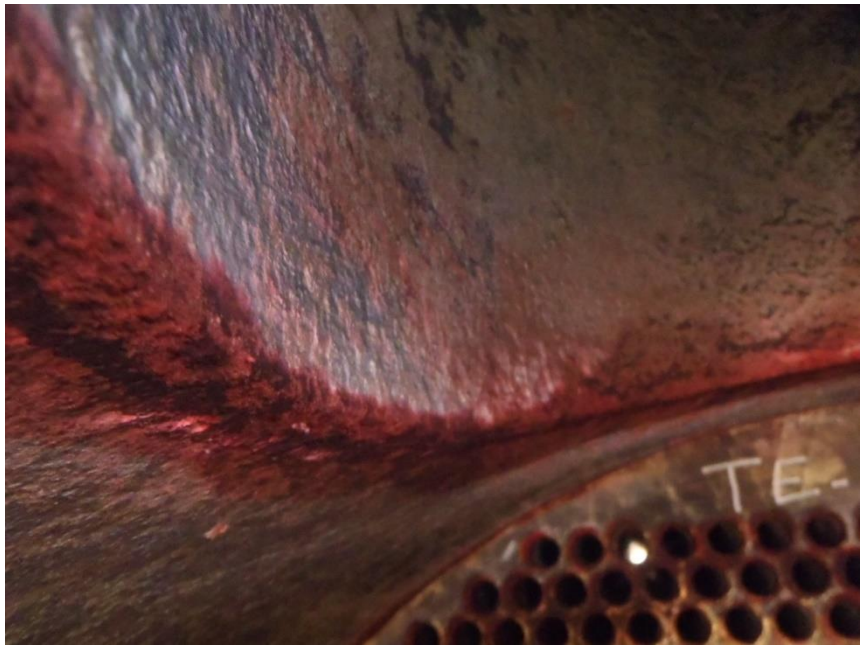
Many tubes were found leaking which could not be quantified during shell side hydro test.



Tube scanning (MFL):

Out of 1301-Nos. 70-Nos. with wall loss from 40 % to 100 %

TURNAROUND OBSERVATION



Inlet shell found heavily corroded

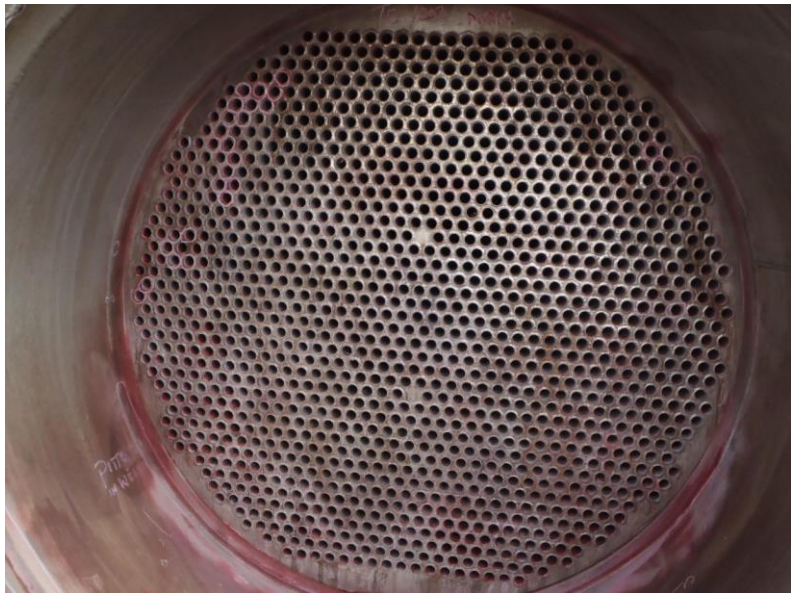
Inlet shell found heavily corroded

TURNAROUND OBSERVATION

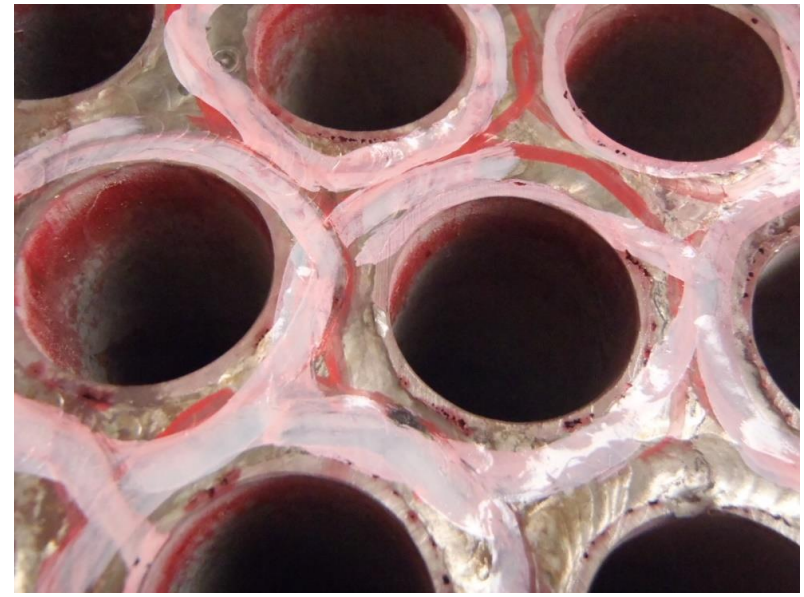
Severe Corrosion at tube Inlet side tube sheet

Deep pitting at tube inlet

TURNAROUND OBSERVATION



No corrosion found at tube outlet



Outlet tubes are very clean

OTHER VISUAL FINDINGS

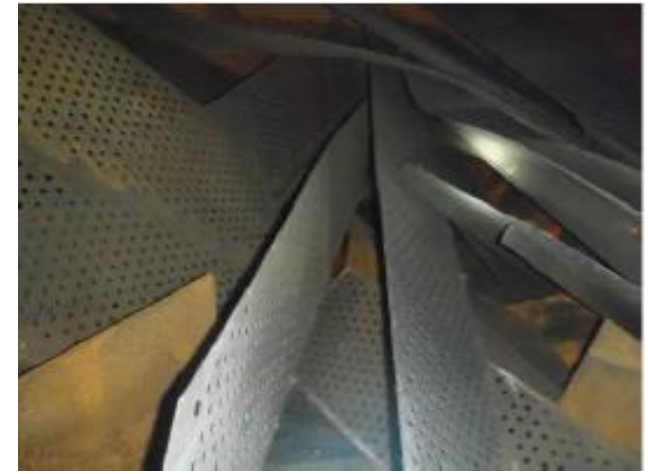
During 2014 turnaround Head column and EDC tank was inspected and there are many finding :

1. Collapsed, broken, fallen down, detached and thinned out trays.
2. EDC leaking was observed in the lower portion of the 5th shell course south-west side of the tank.

OTHER VISUAL FINDINGS

Head column:

Collapsed, broken, fallen down, detached and thinned out trays.

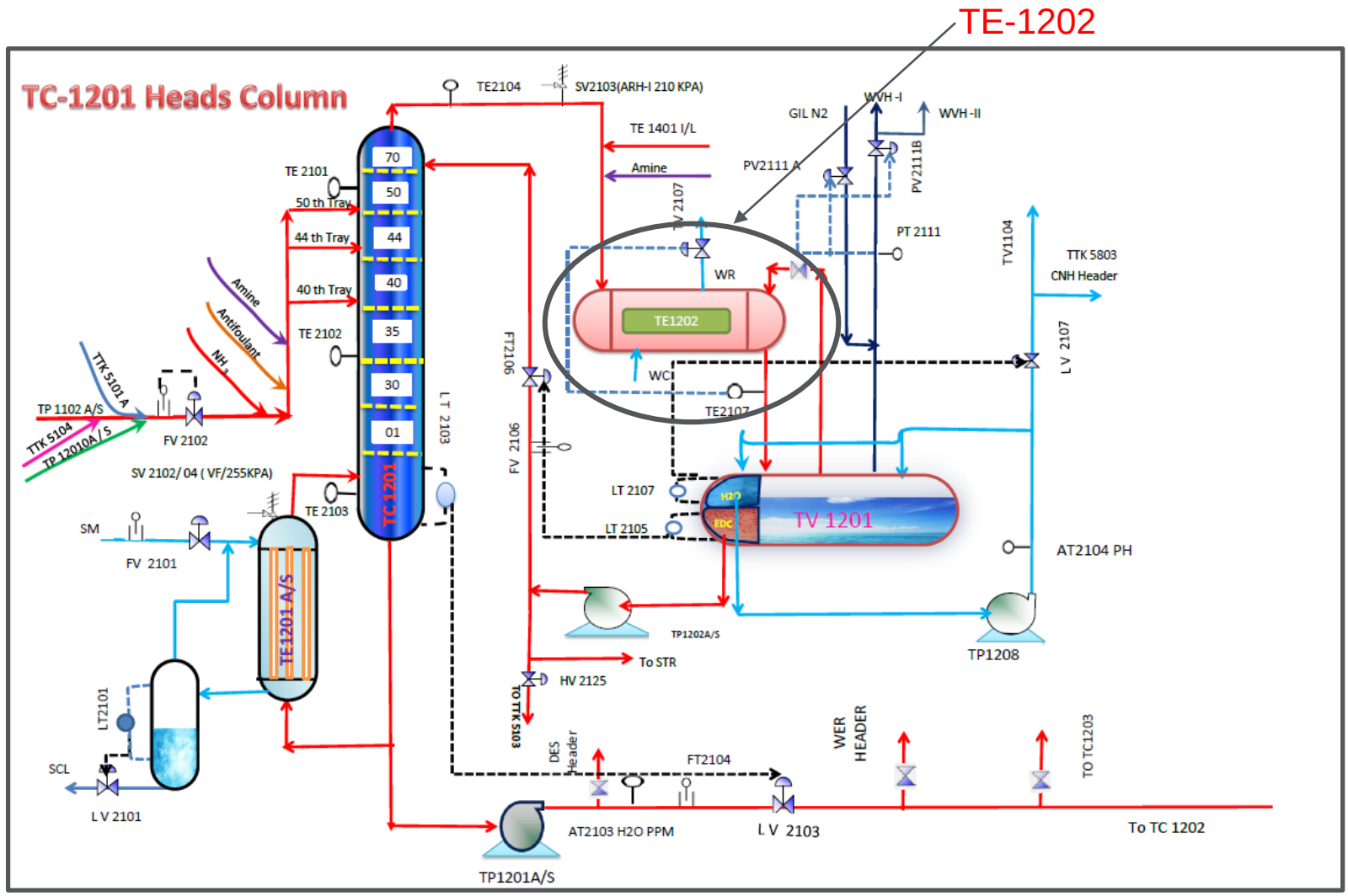


PROCESS DESCRIPTION

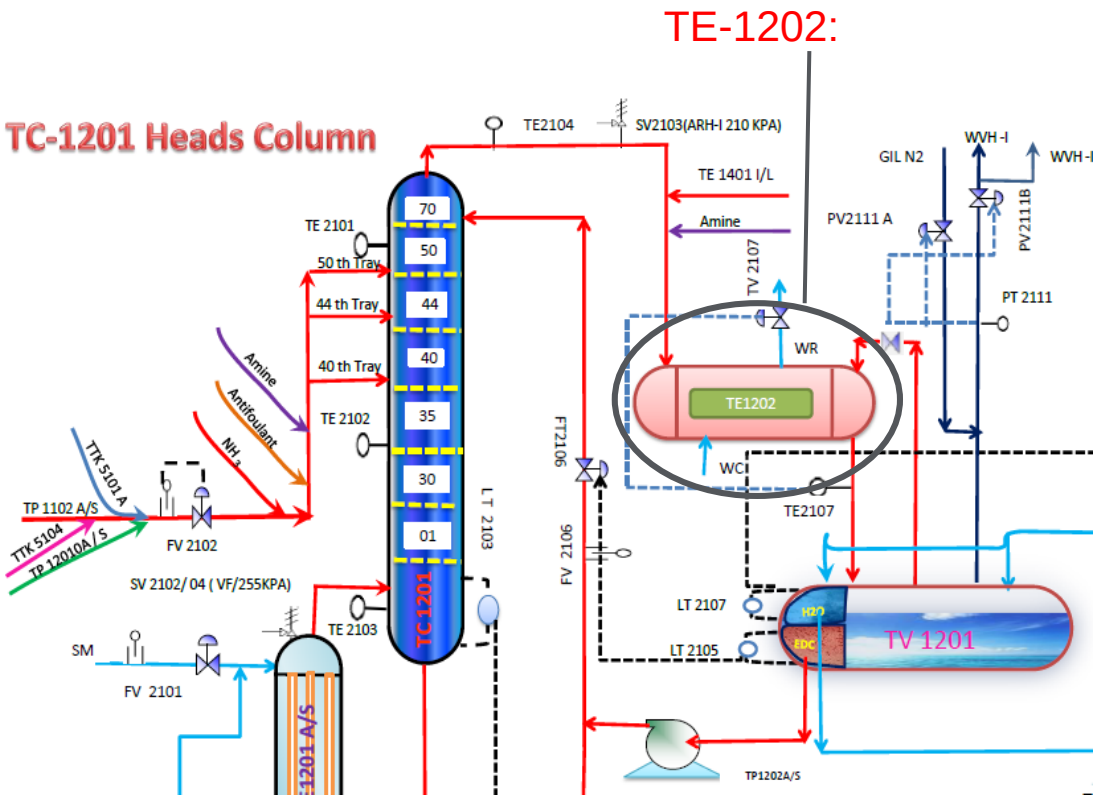
FUNCTION OF THE HEADS COLUMN CONDENSER

- The heads column over head vapor is fed to this condenser at around 80 C˚
- This vapors is condensed in the condenser by cooling water to 49 C˚.
- To control the process out let temperature, a temperature control valve is installed on the cooling water side which controls the cooling water flow to control the process side temperature.

PROCESS DESCRIPTION



PROCESS DESCRIPTION



Parameter	Shell side	Tube side
Design Pressure	690 Kpa	210 Kpa
Fluid Circulated	Fresh cool water	Chlorinated H.C.S
Design Temp.	177˚C	180/150˚C

INVESTIGATION PROCESS

ANALYSIS OF DAMAGE MECHANISM

Tubes samples was pulled out from the exchanger. Different examination was performed as following :

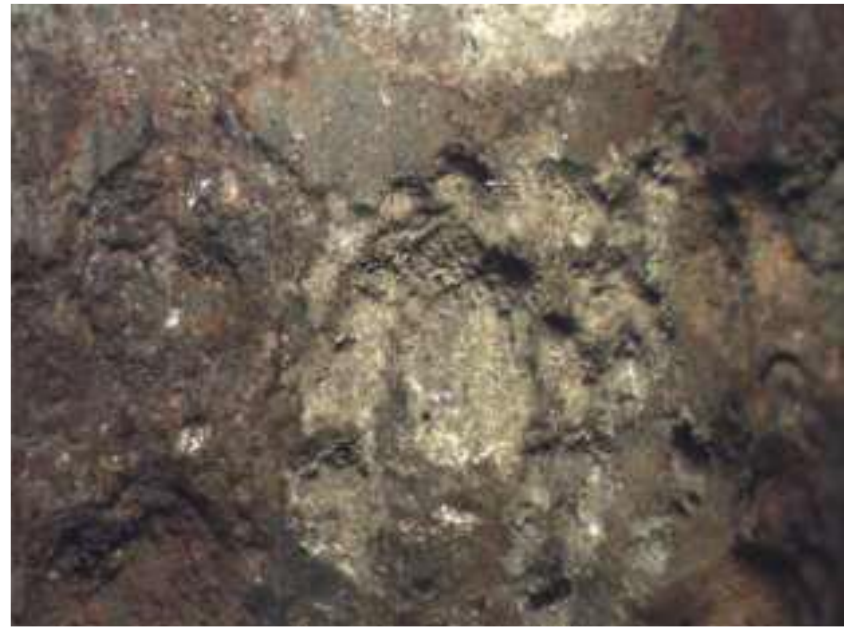
1 Visual Examination

Shows inner surface view of tube at inlet portion. Scattered pitting as well as corrosion marks seen in longitudinal direction.

Shows inner surface near outlet end. The surface is free from any pitting corrosion damage.

ANALYSIS OF DAMAGE MECHANISM

2 Low Magnification Examination:



Inner surface low magnification views. Pitting corrosion is noticed which is surrounded by uneven but adherent scale on the surface.

ANALYSIS OF DAMAGE MECHANISM

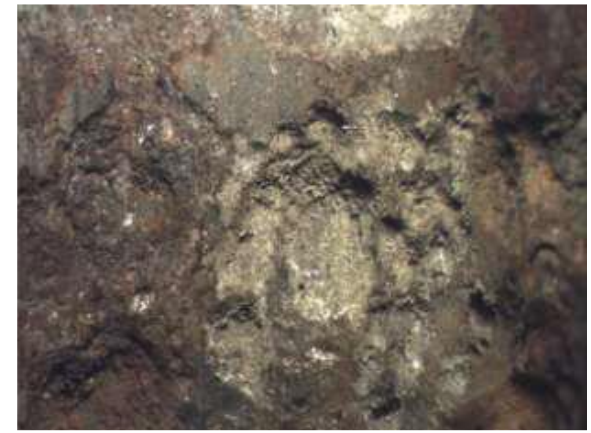
1 Visual Examination :

Inlet

Outlet

- Liquid drops.

2 Low Magnification Examination:



Inner surface low magnification views

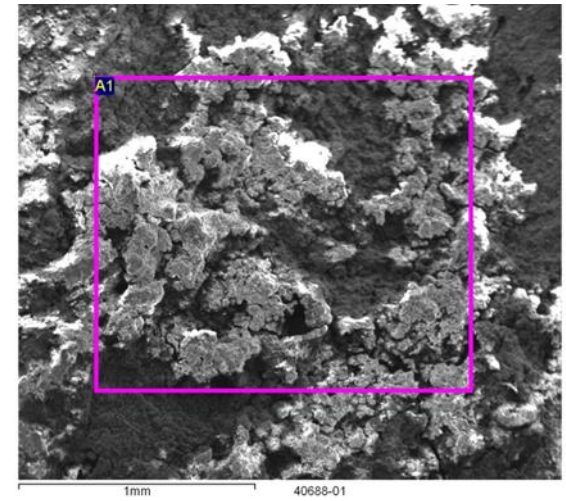
- Stagnant.

ANALYSIS OF DAMAGE MECHANISM

3

XRF Analysis:

Results reveal the material to be a Standard Duplex Stainless Steel.



4

Analysis of deposit material by SEM- EDS :

Confirmed the presence of Chloride. The tube side fluid contains chlorinated hydrocarbon. The source of Chlorine is from these chlorinated hydrocarbons. This causes the localized accelerated dissolution of metals resulting into Pitting corrosion.

PRESENCE OF HIGH PERCENTAGE OF CHLORIDE

Processing option : All elements analysed (Normalised)

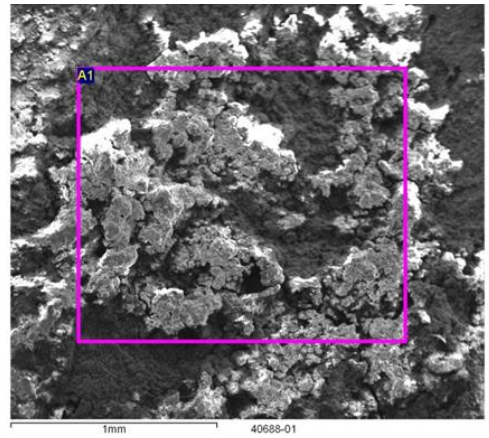
All results in weight%

Spectrum	C	O	Mg	Al	Si	S	Cl	Ca	Cr	Fe	Zn	Total
A1	11.70	38.58	0.24	0.85	0.81	0.25	3.42	0.48	1.77	41.90	0.00	100.00

Spectrum	C	O	Si	S	Cl	Ca	Cr	Fe	Total
A1	16.15	35.31	0.26	0.15	5.96	0.24	0.95	40.98	100.00

ANALYSIS OF DAMAGE MECHANISM

3 **XRF Analysis:**



- Material conformed

4 **Analysis of deposit material by SEM- EDS** :

- Low pH feed.

PRESENCE OF HIGH PERCENTAGE OF CHLORIDE

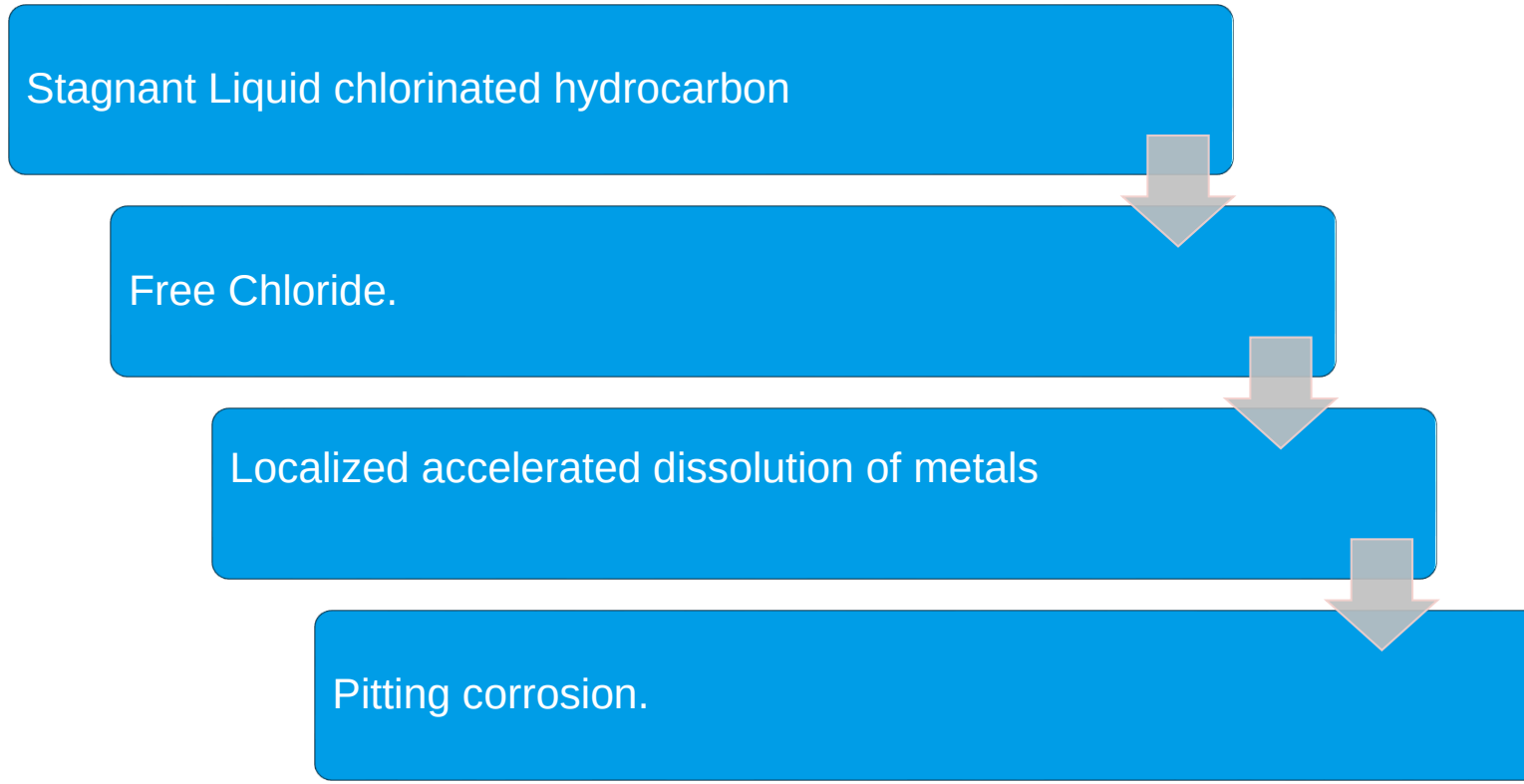
Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	C	O	Mg	Al	Si	S	Cl	Ca	Cr	Fe	Zn	Total
A1	11.70	38.58	0.24	0.85	0.81	0.25	3.42	0.48	1.77	41.90	0.00	100.00

Spectrum	C	O	Si	S	Cl	Ca	Cr	Fe	Total
A1	16.15	35.31	0.26	0.15	5.96	0.24	0.95	40.98	100.00

DISCUSSION OF LAB RESULT



DISCUSSION OF FINDINGS

Pitting corrosion.

Because of

Localized accelerated dissolution of metals

Because of

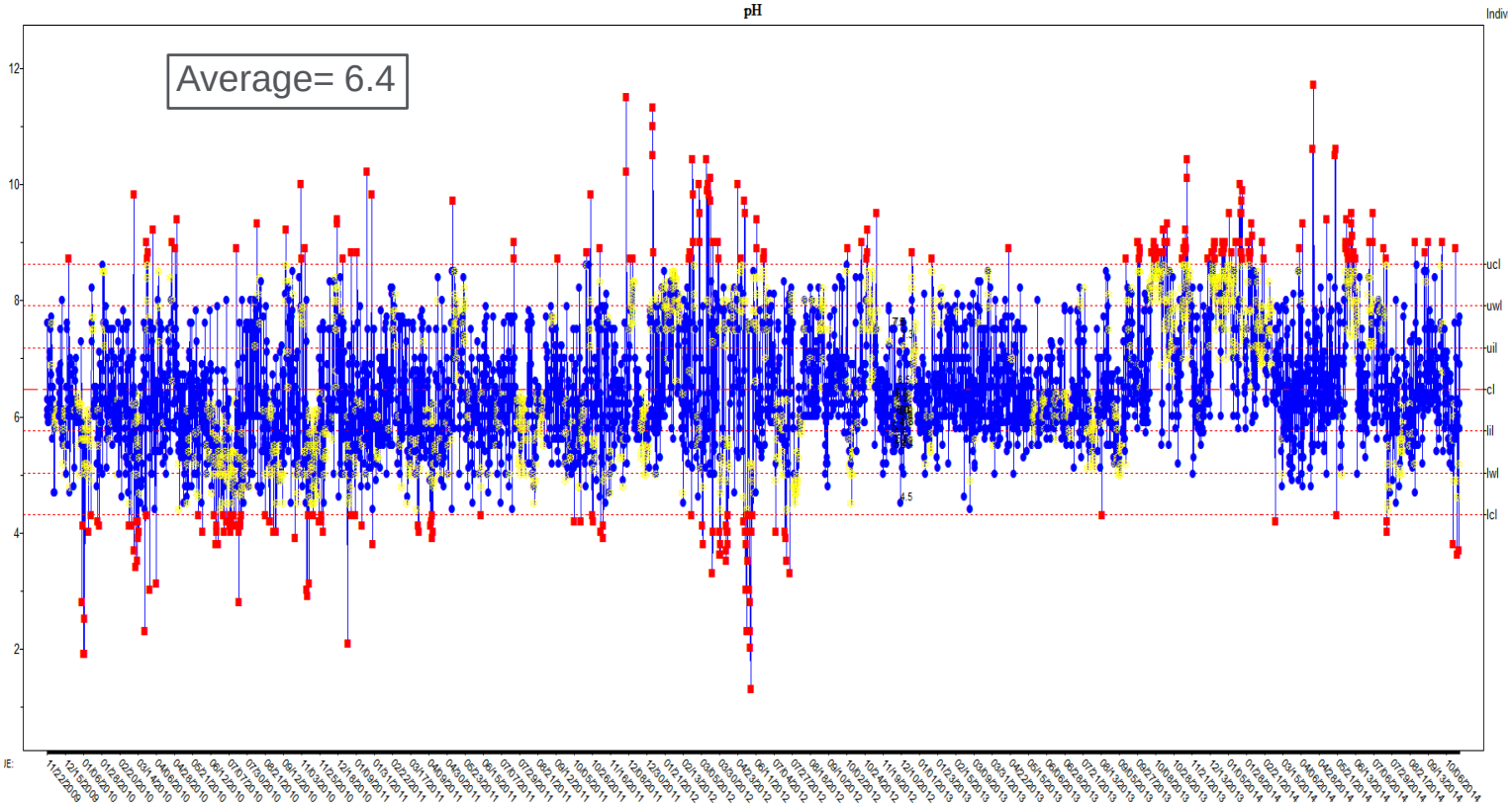
Stagnant liquid chlorinated hydrocarbon feed with low pH.

This happened because of

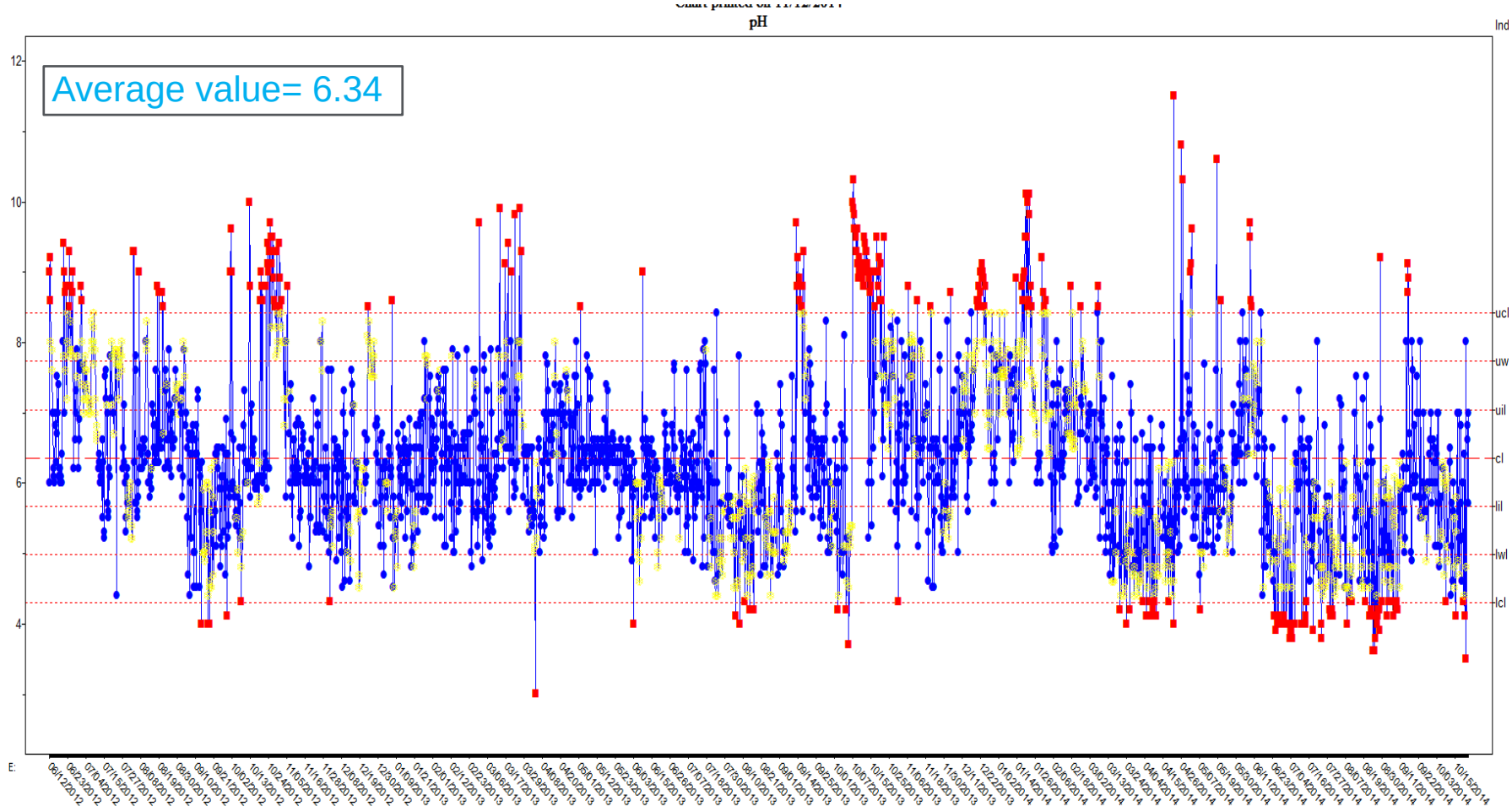
Liquid feed carry over from head column → Head column trays not functioning well → Trays felled down due to corrosion → Corrosion caused by low pH feed

STATUS OF HEADS COLUMN

PH range since 2009 (Feed of head column)

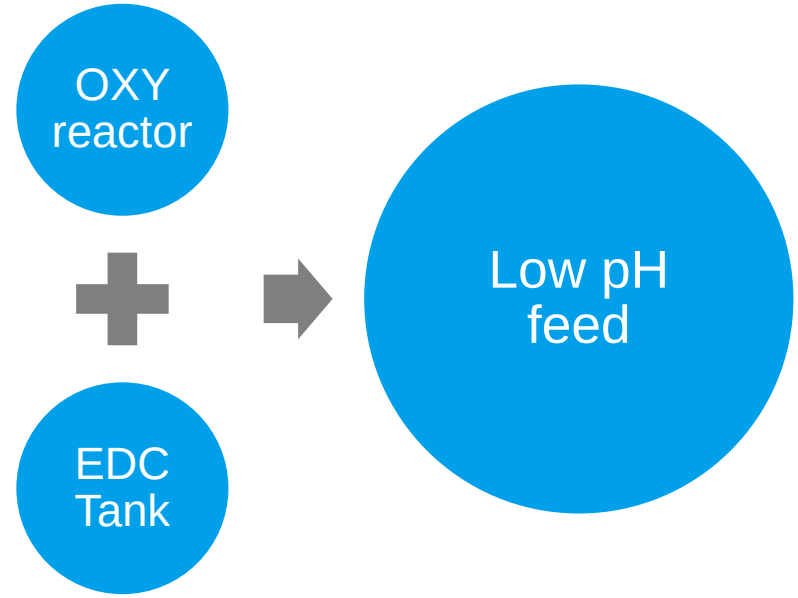


REFLUX PH VALUES (JUN 2102 – NOV 2014)



SOURCE OF LOW PH FEED

What can cause low pH feed to the column??



WHAT HAPPENED ?

During year of 2013 , there was issues in unit 55 (plugging of the header to the incinerator . etc.) a continues diversion of dry vent header (DVH) and wet vent header (WVH) to wet EDC tank which caused existing of low pH and high acidity feed in the tanks and accordingly this feed will be sent to head column and had direct effect on the trays.

ROOT AND CONTRIBUTOR CAUSES

Explanation for condenser pitting and corrosion:

Condenser is horizontal exchanger and vapor flow rate is very important to prevent stagnant condensed liquid. Physical observation of Condenser inlet tube sheet and tubes (50-60 cm from inlet), indicates pitting corrosion which is a highly localized. The exchanger is big and drop wise condensation is possible (which has more HCL dissolved) In case of low vapor feed, it cannot push the condensed drops, and low vapor feed is an indication of weeping case in distillation column. In heads column, weeping case is possible because of tray falling (20 tray found fallen) which led to less vapor flow. These trays' showing very high corrosion and it is due to chemicals, mainly HCl. The tray falling may be gradual phenomena, which resulted column frequent disturbances. Secondly, total reflux may keep a blind eye for trouble shooting. After travelling 50-60 cm of distance in the tubes, the concentration of HCl will come down in bulk quantity of liquid. Hence, there will not be any corrosion.

Root Cause:

Presence of free chloride in the EDC (tube side) that caused localized accelerated dissolution of metals resulting into pitting corrosion.

Contributory Cause:

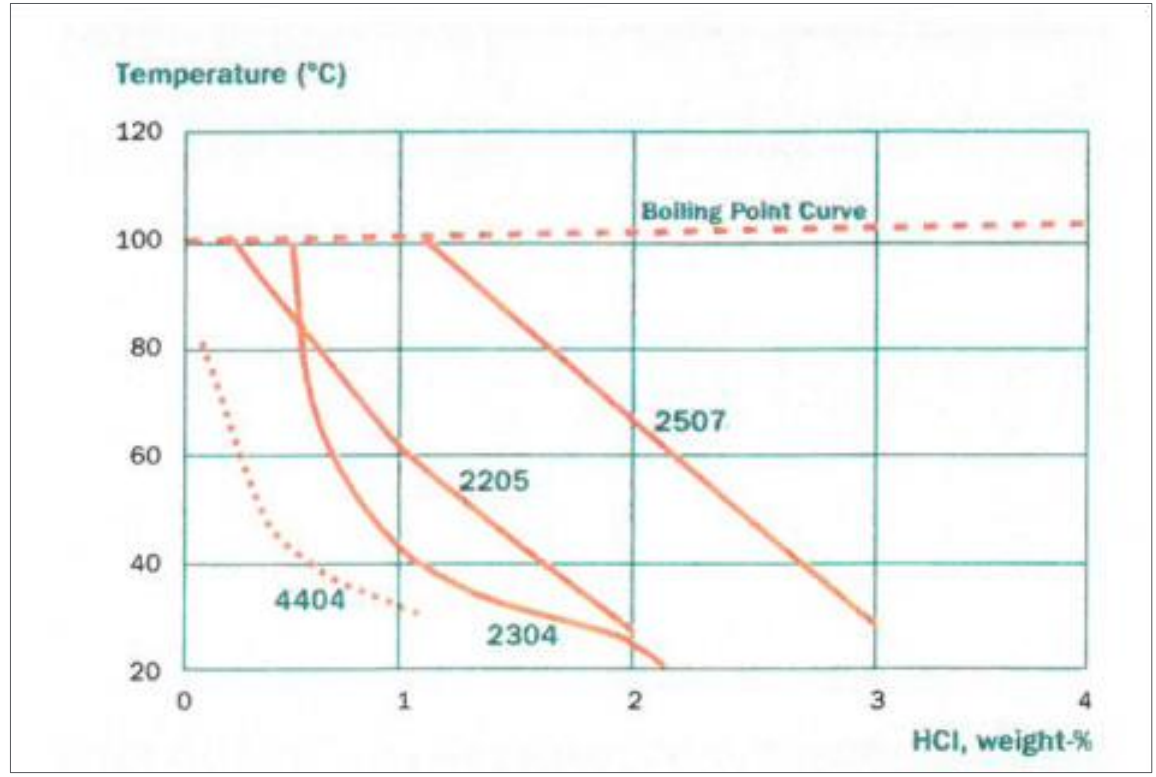
1. Low PH.
2. The EDC coming in partially in liquid phase to the cooler instead of coming as vapor only.
3. Poor quality of manufacturing.

CONCLUSION:

XRF analysis of the sample confirmed the material to be a standard 2205 duplex steel. Highly localized corrosion as deep rounded pits on the tubes inner surfaces at the inlet areas (Figures 3 A & B) was found recently after being in service two years. Some of them developed through whole thickness. SEM/EDS analysis revealed presence of chloride (3% on top and 6% in pit bottom) content in the deposits (corrosion product) inside the pits (Figures 3). Cross section examinations revealed the presence of selectively attacked ferrite on depth of 200 to 300 µm on the bottom of pits (Figures 5B). Tube inlet side fluid (vapor): 35% chloroform, 15% EDC, 40% carbon tetrachloride, non condensable, water with max. amount of steam. The source of Chloride is from these chlorinated hydrocarbons. This causes the localized accelerated dissolution of metals resulting into Pitting corrosion. No any damage found on the tube outlet.

CONCLUSION:

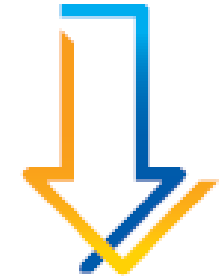
Severe pitting corrosion of alloy 2205 at about 81°C indicates that concentration of hydrochloric acid was about 1% on the tube surfaces at inlet areas, as per the below iso corrosion curves 0.1mm/year, in Hydrochloric acid.



ROOT CAUSE

WHY?	Tube damaged at inlet
WHY?	Pitting corrosion
WHY?	Free chloride
WHY?	Liquid carry over to the cooler
WHY?	Trays fall down in the column
WHY?	High acidity feed to heads column

WHY?	low pH feed from storage tanks 5104/5101A
WHY?	Procedure for controlling the pH not been followed.

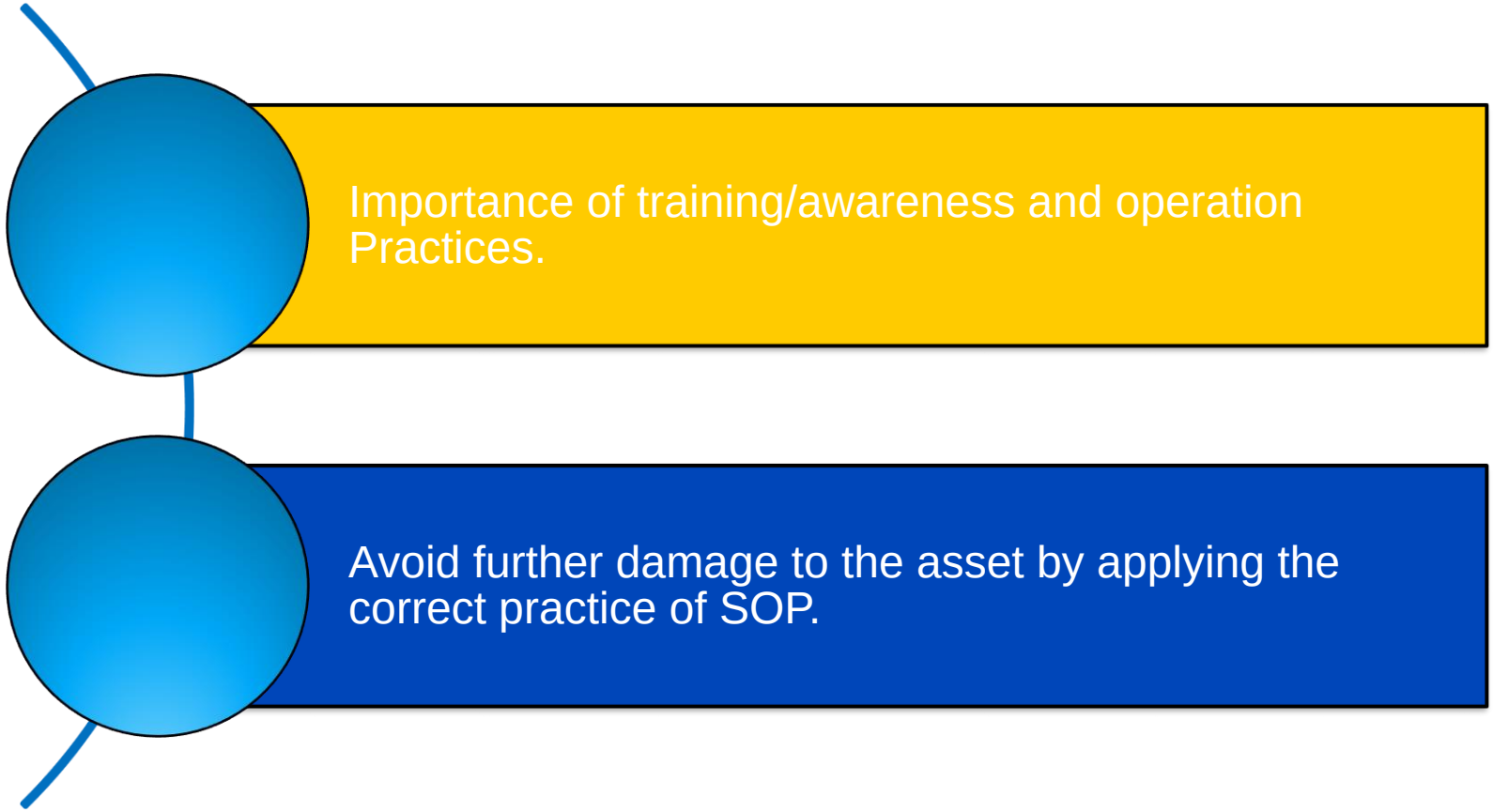


Not able to control the pH

RECOMMENDATIONS

- Controlling of chlorides of the feed which are from up stream.
- Controlling PH effectively.
- Selecting a suitable material of construction for Condenser.
- Importance of training/awareness and operation Practices.
- Avoid further damage to the asset by applying the correct practice of standard operating procedure.

KEY LEARNINGS

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