JUBCOR 2024

CONFERENCE & EXHIBITION

INNOVATIVE SOLUTIONS FOR CORROSION CHALLENGES

Jubcor Presentation

CARBAMATE CORROSION OF STAINLESS-STEEL UREA GRADE WELDS DUR TO IMPROPER WELDING

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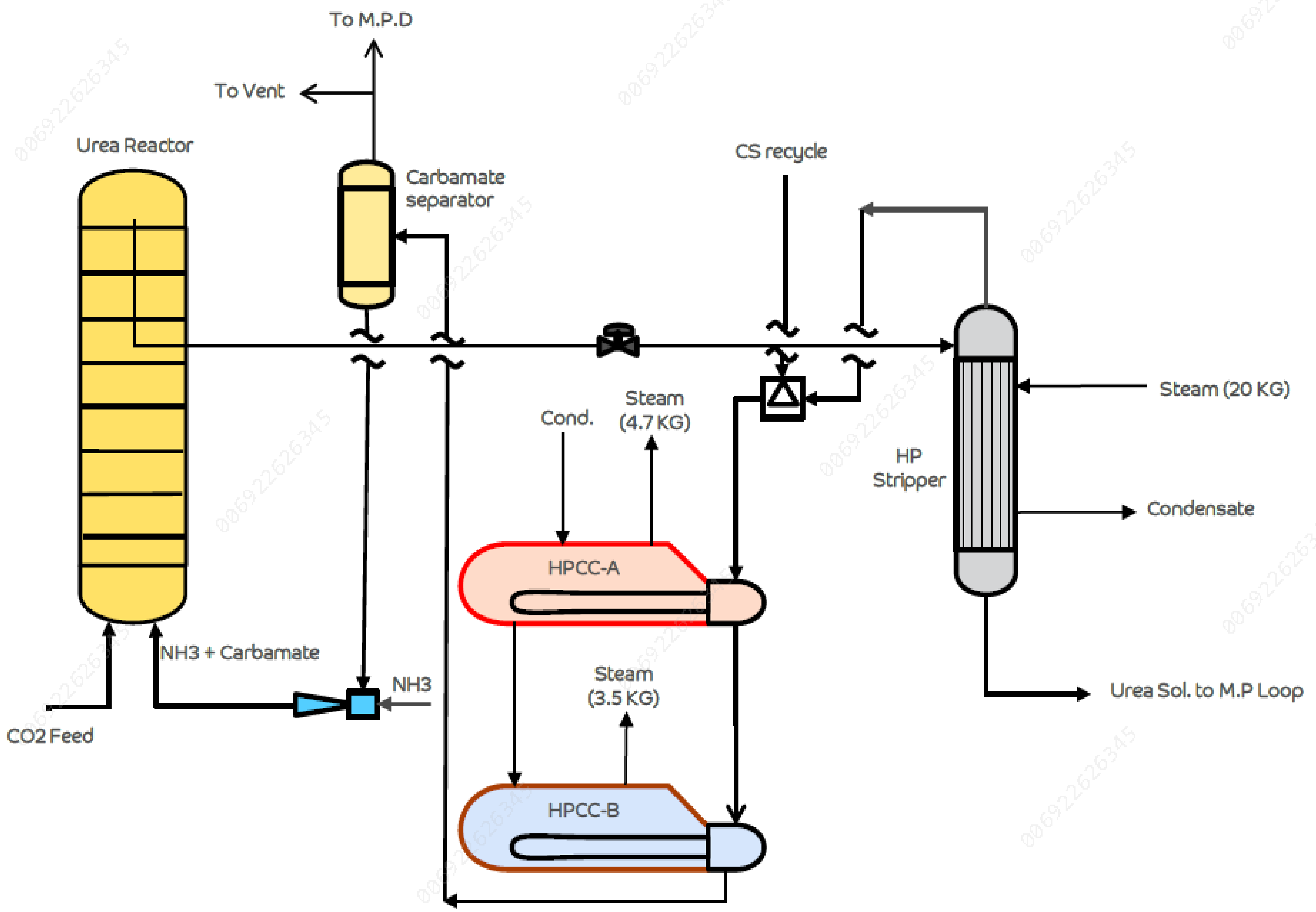
ABSTRACT

Urea carbamate is very corrosive. Hence, the tubes HP equipment are constructed from special stainless steel grades welded to a carbon steel tubes with weld overlay of the same stainless steel grade similar to the tubes. Chemical composition, ferrite number are critical factor that can affect the corrosion resistance of the stainless steel weld in carbamate solution. Under the High Temperature High Pressure deep-etching reaction environment, there is the probability of leakage all the time in urea synthesis equipment, in case stainless steel lining leaks, the High Temperature High Pressure medium can produce heavy corrosion and stress corrosion cracking to carbon steel shell (500mm/year), finally leads to serious accident.

This paper describes the reason behind weld failure and methodologies adopted to assess the condition of the urea grade stainless steel welds to ensure safe continued operation and prevent process safety consequences of the High Pressure Carbamate Condenser (HPCC). The study concluded that deviation from the developed WPS can affect the corrosion resistance of the weld resulting in a leak that can damage tube sheet behind the weld overlay. The paper also discusses the mandatory requirements to ensure that the welds have an acceptable corrosion resistance to the carbamate solution.

Process Description

The high pressure carbamate condensers generate low pressure steam by condensing ammonia and CO2 into ammonium carbamate solution.
The waste heat is utilized to generate steam at two stages,
In HPCC A, 6 kg/cm2 steam generated which supplies steam to MPD A, LPD, and distillation column, and at the second stage,
Steam at 4 kg/cm2 is generated form HPCC B which is used to heat vacuum concentrator, granulation air heaters and used as re-injection steam in CO2 compressor turbine. The blowdown from HPCC B is then sent to condensate accumulator.



Corrosion in Urea High pressure Synthesis

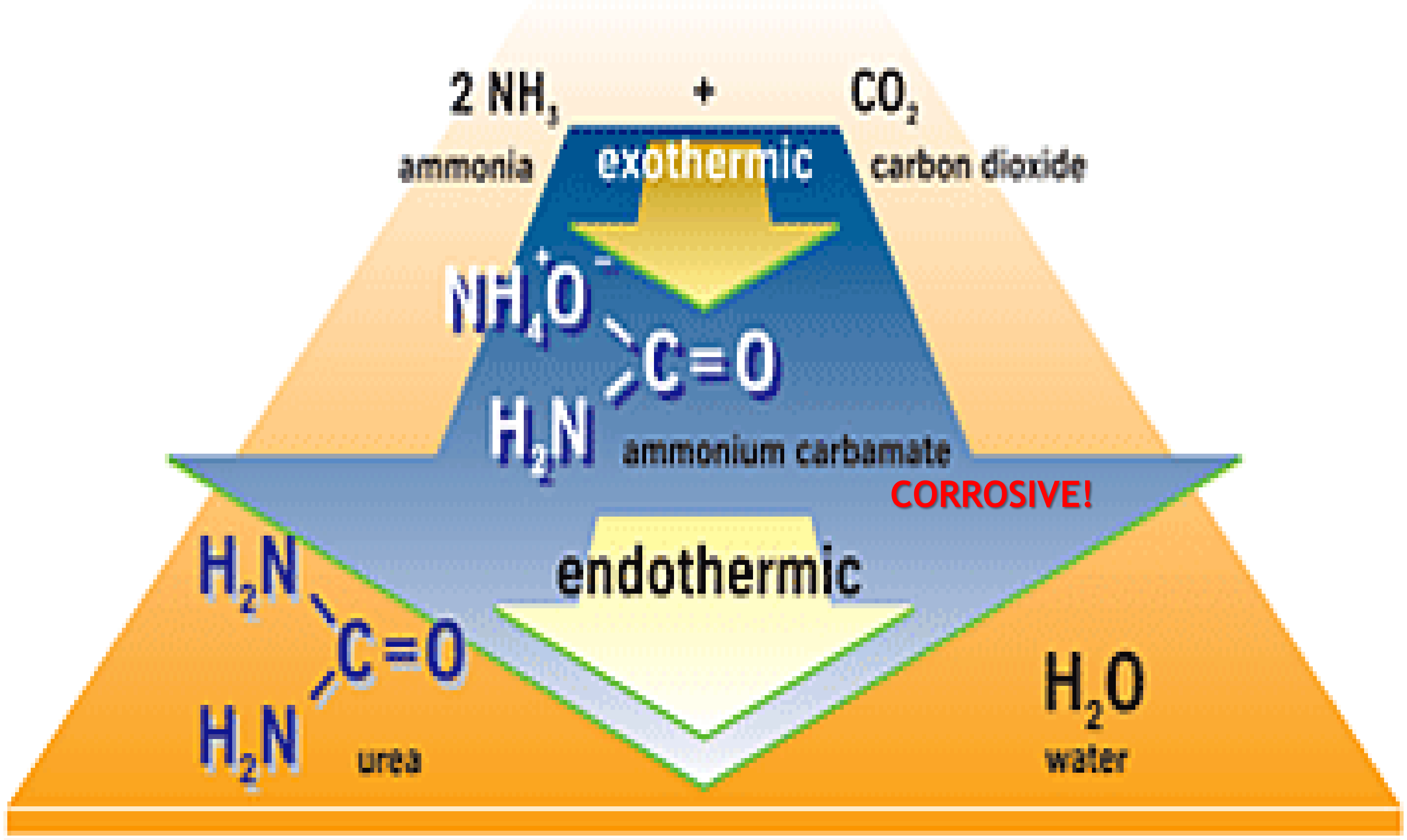
- Urea is produced by 2-step reaction between ammonia and carbon dioxide at 188-190°C and 150 kg/cm²:

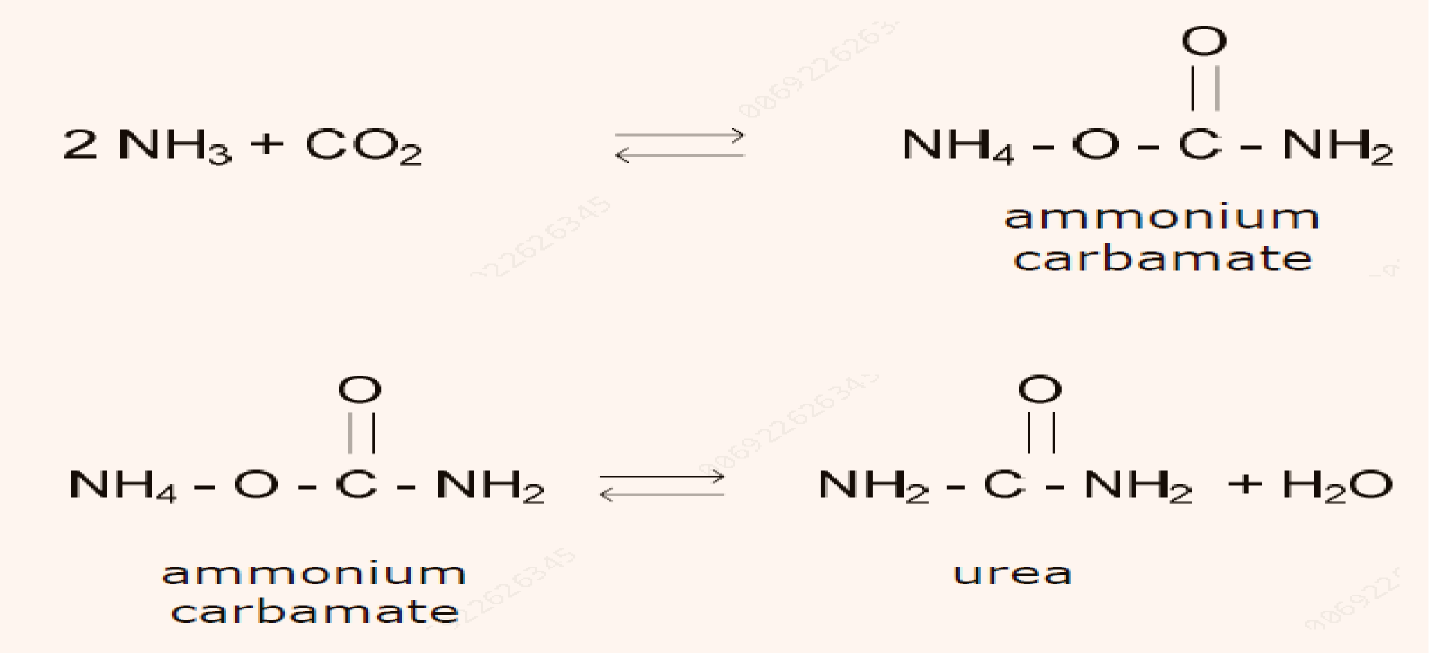
$$2NH_2NH_3 + CO_2 \longleftrightarrow H_2NCOONH_4 \longleftrightarrow H_2NCOONH_2 + H_20$$

- The reaction intermediate is ammonium carbamate which is also the main corrosive species. Process fluids contain also ammonia, urea, water and carbon dioxide, all corrosive for carbon steel.

- Corrosion by ammonium carbamate is considered general and may reach high rates if the material is not passivated.

- AISI 316L UG type stainless steel, highly alloyed SS as 25Cr-22Ni-2Mo, super Duplex stainless steel, Titanium and Zirconium are commonly used as corrosion resistant materials in urea synthesis environments. The corrosion prevention methods have been established mainly through experiences in commercial plants. Corrosion is prevented by injecting air into the process fluid to induce passivation of stainless steels. Too low an oxygen concentration results in activation and high corrosion rates of these stainless steels.





Overview of Materials of Construction in Urea Synthesis Section

01

Lead (lined reactor)

This material was used in the first generation of urea plants for reactor lining

02

Austenitic Stainless steel

Ordinary SS 316L was used first. In early 1960's SS 316 UG was used In late 1960's and early 1970's 310 UG was used after introducing the stripper in Urea plants.

03

Super duplex stainless steel

Special grades of super duplex are used by different licensors

04

Titanium

Used as reactor liner, and for the strpper tubes

05

Zirconium

Tubes, and Bi metallic tubes in urea stripper

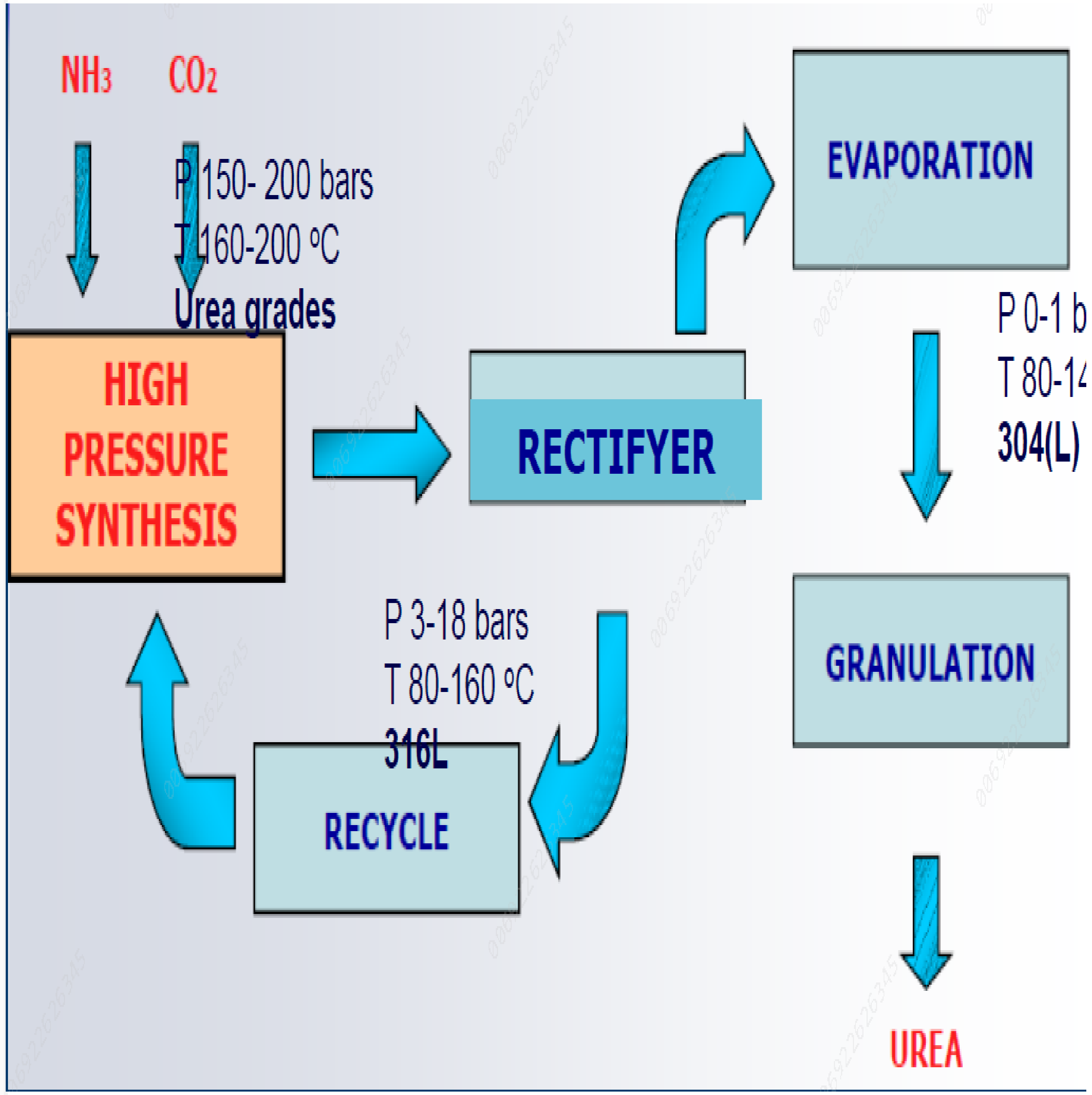
Note: the use of Nickel alloy is prohibited in Urea synthesis section

Materials of Construction in Urea Plants

Over the past two decades, the urea industry have witnessed spectacular metallurgical developments for process equipment.

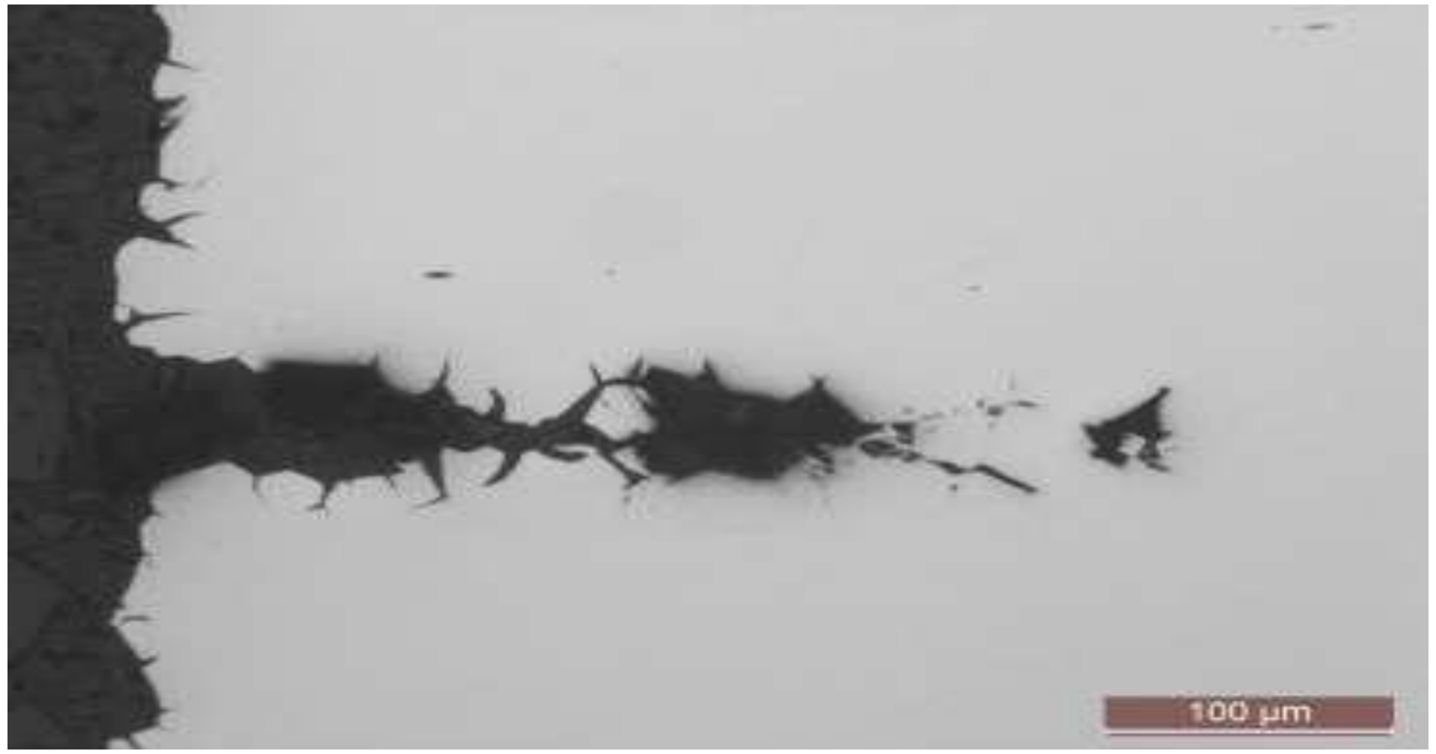
Ordinary 316L alloy was the initial choice but it was soon found to be inadequate in this service due to the preferential attack of the ferrite and sigma present in small amounts. This led to the development of urea grade 316L UG with a low ferrite content attained by balance composition and maintaining a high level of purity. For many years, use of 316L UG along with injection of air remained the standard material for critical parts like reactor lining, carbamate condenser, and HP decomposer as no other better austenitic stainless steels were available. Under passive conditions corrosion rate of carbamate varies between 0.01 and 0.1 mm/year but under condensing condition (from NH_3–CO_2–H_2O vapour) the rate increases to 0.2 mm/year as in freshly formed condensate availability of oxygen is low. In practical situation this phenomenon causes accelerated corrosion in cold spots, especially in 316L UG steel. SS 316 Land SS 316 L (urea grade) have significant difference. American Society for Testing and Materials (ASTM) allows a large tolerance range for composition of 316 L. For example, 316 L urea grade-is produced to a well-defined composition, which enables maximum corrosion resistance.

Subsequent research carried out with the participation of the process licensers and alloy manufacturers led to the development of a new grade of alloy 310 MoLN. by Sandvik having a balanced composition of Cr, Ni and Mo (25Cr–22Ni–2Mo). The main objective was to increase the passivation characteristic and stability of protective film by increasing the chromium content from 18 to 25%.



HP Section (Synthesis): Intergranular Corrosion Mechanism

- Intergranular attack is highly localized corrosion at and adjacent to the grain boundaries in a metal's structure while the grains remain relatively free from attack.
- Since little corrosion takes in place on the grains, the alloys disintegrates by grain separation. The grain fall out.
- Intergranular attack is caused by the corrosive action of a specific chemical environment on the metal grain boundaries that are susceptible to attack from impurities. The enrichment or depletion of one of the alloying elements at grain boundaries may also cause attack.
- Many alloys are susceptible to intergranular corrosion in specific environments. However, intergranular attack is caused by depletion of chromium resulting from sensitization.
- When a SS has a carbon content above 0.03% and the alloys is held in or cooled slowly through the temperature range (371°C to 816°C), chromium and carbon are removed from solid solution and form chromium-carbides along grain boundaries. The chromium-depleted zone near the grain boundary is corroded because it does not contain sufficient chromium to resist attack in corrosive environments.
- Sensitization can happen during welding or while equipment is at elevated temperatures.



Intergranular Corrosion Testing: An Overview of ASTM A262

Corrosion by ammonium carbamate is considered general and may reach high rates if the material is not passivated.

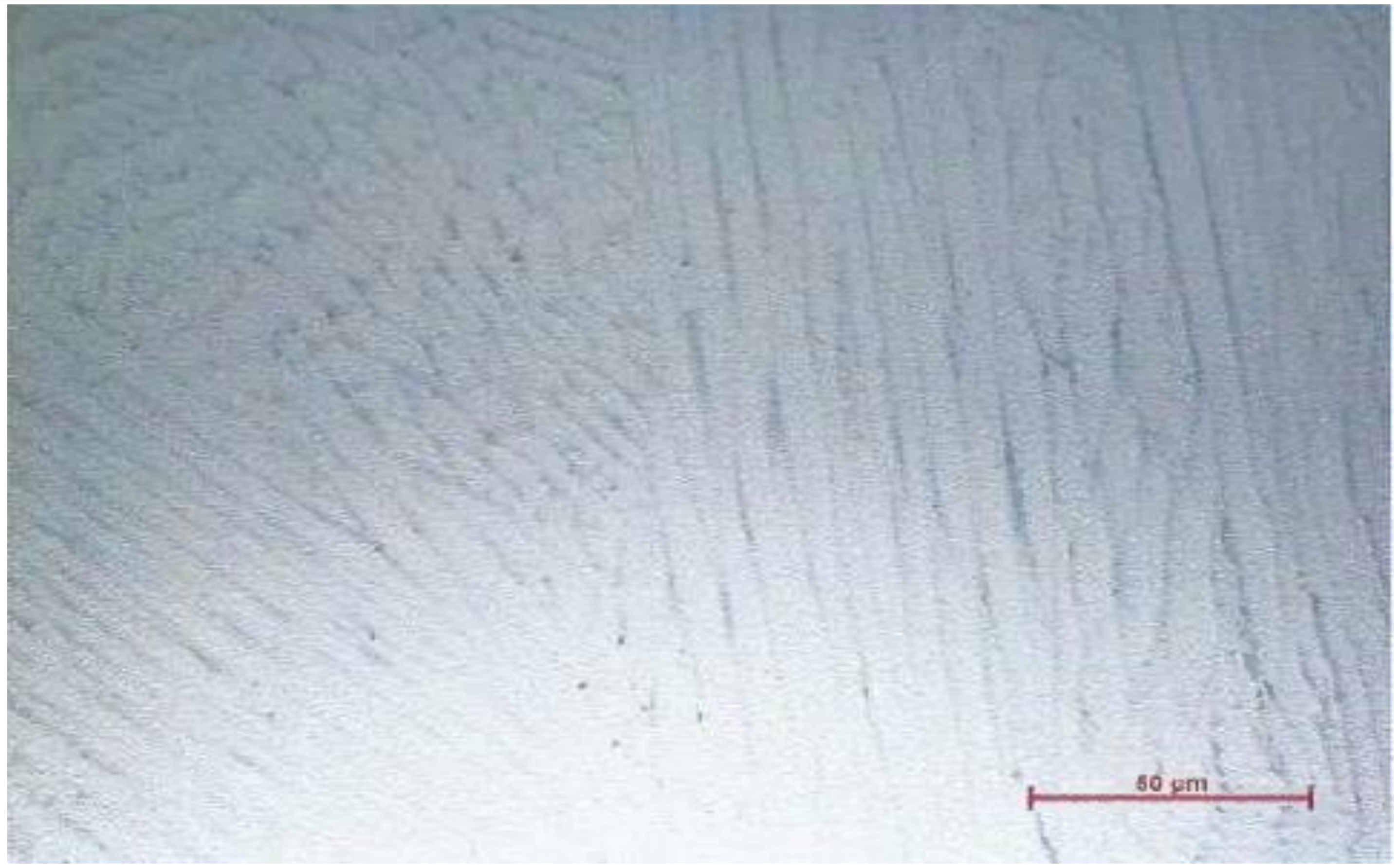
However as secondary phases are preferentially attacked by ammonium carbamate, stainless alloys must have an homogeneous structure free from ferrite, sigma phase and other undesired precipitates.

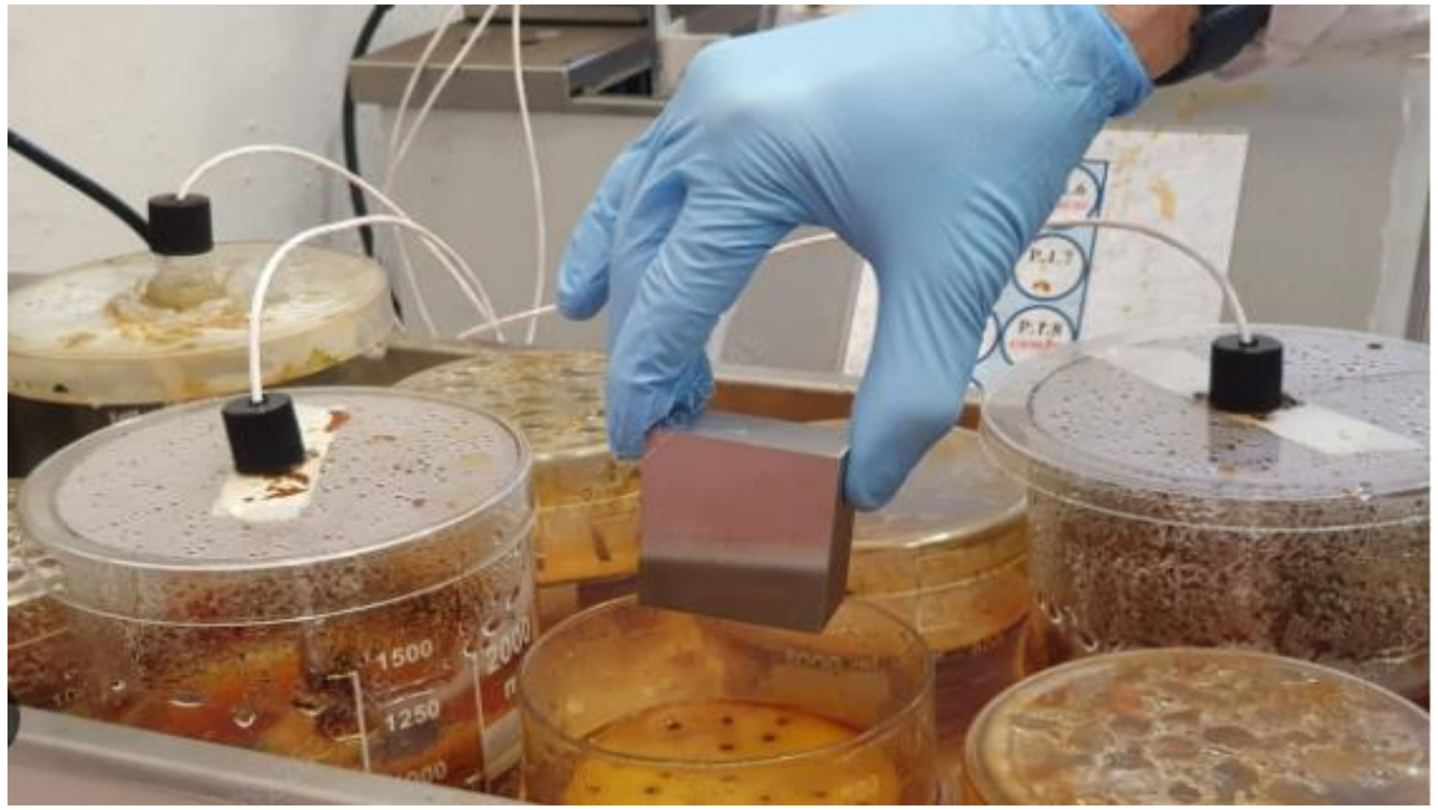
The so-called Huey test (ASTM A262 Practice C) is extensively used as a quality check for stainless steels as it is very sensitive to the presence of intergranular precipitates which are preferentially attacked in urea and ammonium carbamate.

ASTM A262 testing is a popular method of choice due to the variety of practices available and the relatively short turnaround for results. All five methods within this specification involve exposing specimens to a chemical mixture designed to encourage corrosive behavior. At the conclusion off the test, specimens are either visually examined or measured for weight loss and compared to an established corrosion rate for that specific material type.

Huey Test (ASTM A262 Practice C)
The Huey test method uses a nitric acid solution and subjects the specimen to five 48-hour boiling intervals. The samples are weighed at each interval to determine mass loss and degree of susceptibility to intergranular attack. This method is preferable for chromium depletions and corrosion in intermetallic phases. The penetration of selective attack is determined by microscopic examination after the Huey test.

Note: All deposited weld metal shall after final heat treatment, if any, have a fully austenitic structure (max. ferrite content 0.6 %)

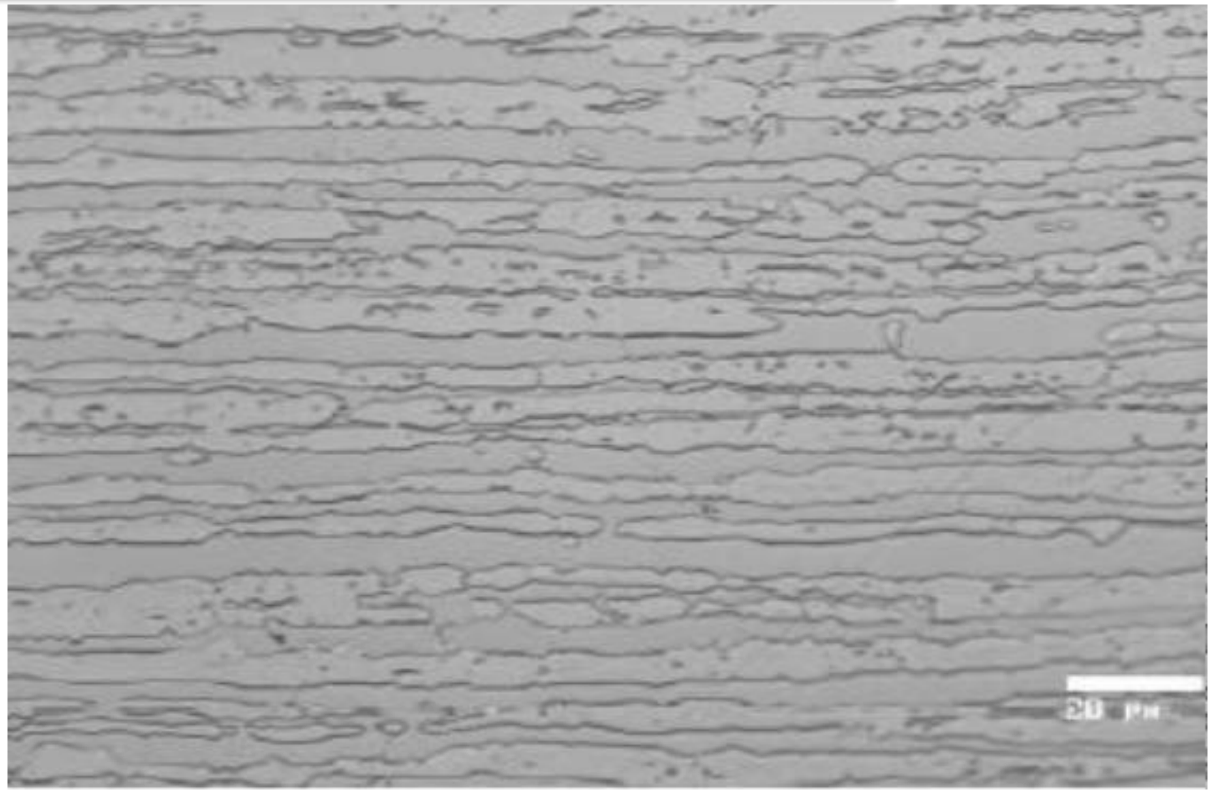


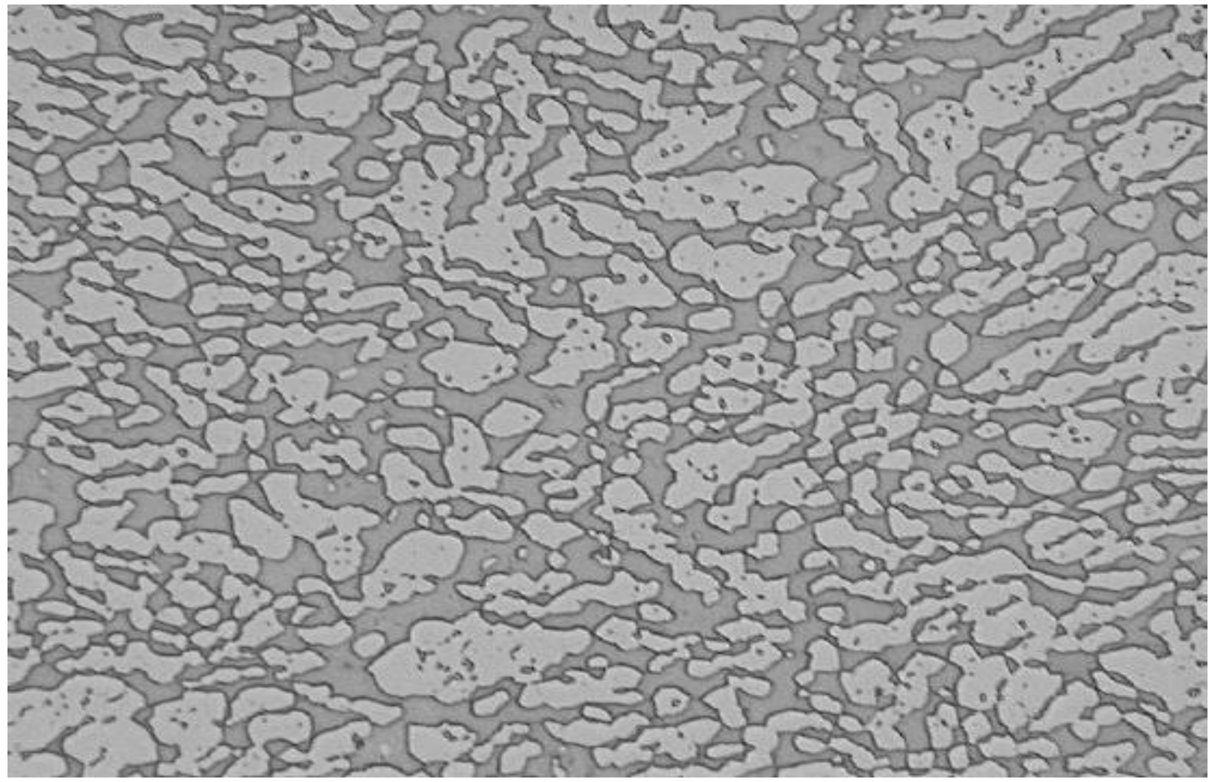


Super Duplex Stainless Steel In Urea Plants

Advantage of Super Duplex stainless steel above Austenitic Stainless steel in Urea Plant

- Lower risk of crevice corrosion and stress corrosion cracking with higher mechanical properties.
- Lower risk for active corrosion in case of flooding in a Stripper
- Less weight (-16%) for HP equipment
- Lower investments costs
- Lower oxygen content is more tolerable.





Super Duplex Stainless Steel In Urea Plants

Mechanical / physical properties of super duplex stainless steel (minimum values)

Material	Yield Strength Rp 0.2 (Mpa) 20°C/225°C	Tensile Strength Rm (Mpa) 20°C/225°C	Elongation A5 (%)	Thermal Expansion 10^{-6}/°C	Module of Elastisity N/mm² at 225°C
Super Duplex Stainless Steel	650/465	800/717	> 25	11.5	184
SS 316 UG	190/135	490/412	> 40	16.5	184
SS 310 UG	270/195	580/495	> 30	16.5	184

Outer Diameter	Temperature	Material		
		SS 316 UG	SS 310 UG	Super Duplex Stainless Steel
25mm	187°C	1.5	1.00	0.50

Minimum tube wall thickness in relation to materials and tube dimensions under operating conditions

LEAK OF UREA HPCC-A

HPCC A in one urea plant was replaced in 2020 during TA. In September 2022 leak was confirmed as the steam conductivity in the shell side increased. Plant kept running after conducting RA along with given guidelines from Process Licensor by keeping steam conductivity analysis under close monitoring and giving the maximum limit 100 μS/cm as maximum limit.

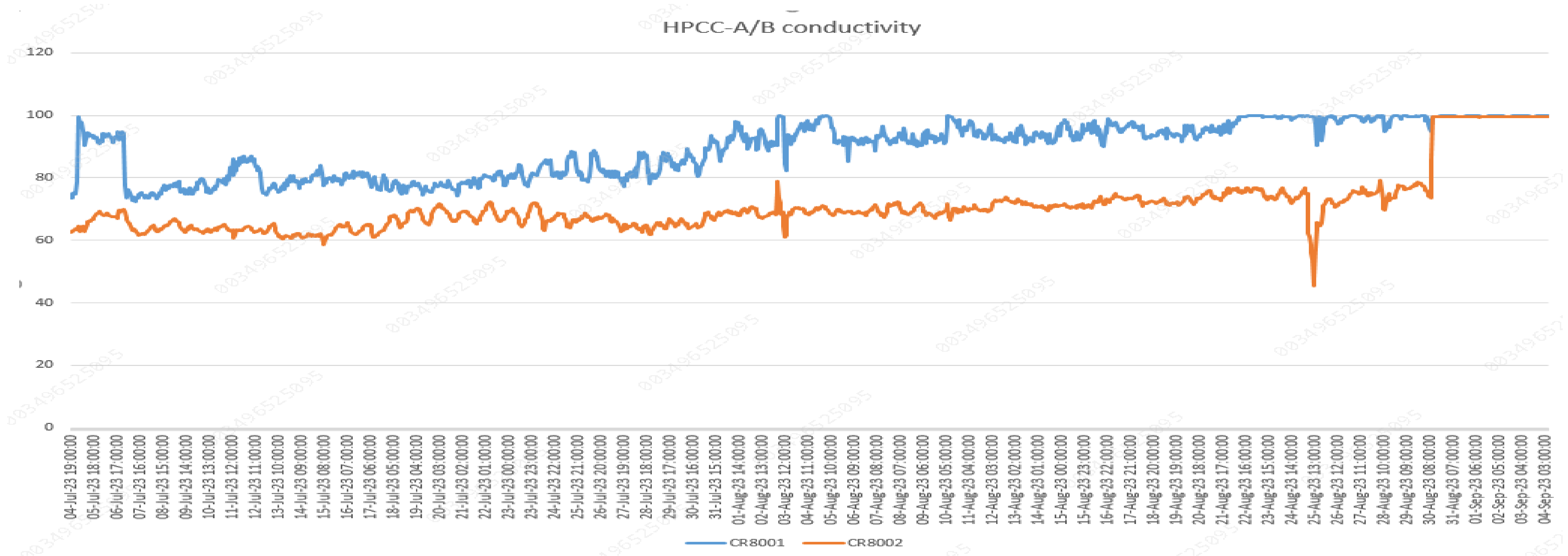
Urea Plant underwent safe SD as the conductivity of the steam sharply increased to 120 μS/cm in HPCC A.
The equipment was manufactured in 2020 according to the following codes

- ASME Sec. VIII Div.1 for shell side U-stamp
- ASME Sec. VIII Div.2 Cl.2 for tube side U2-stamp
- TEMA 9th edition.
- Licensor specification and Standards.

Tubes: 877 U-tubes 25/22/2; Tube size: 19.05 x 2.11 mm.
Tube sheet C.S+ weld overlay 10 mm (SS 310 UG)

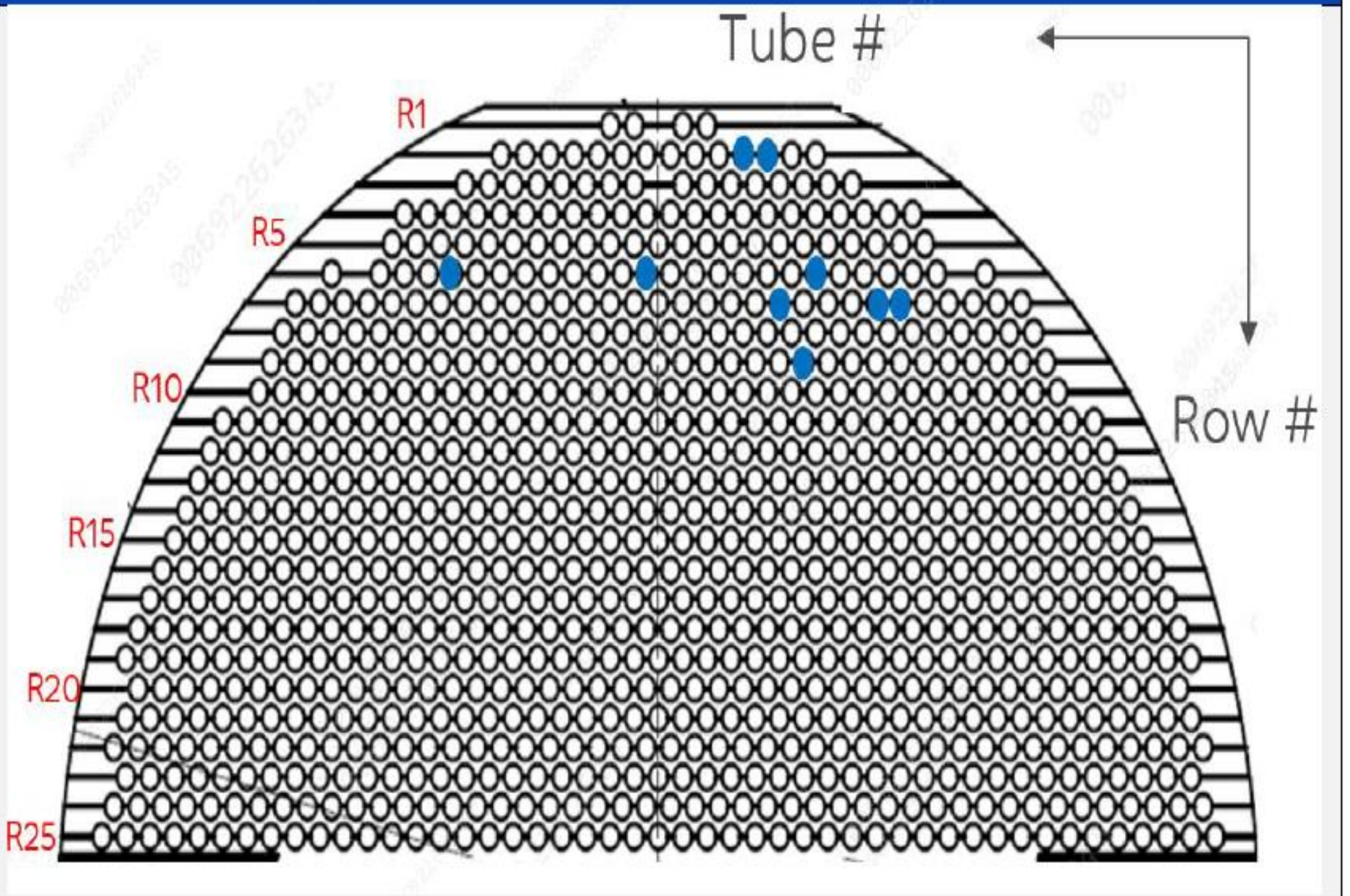
Leak Identification And Monitoring

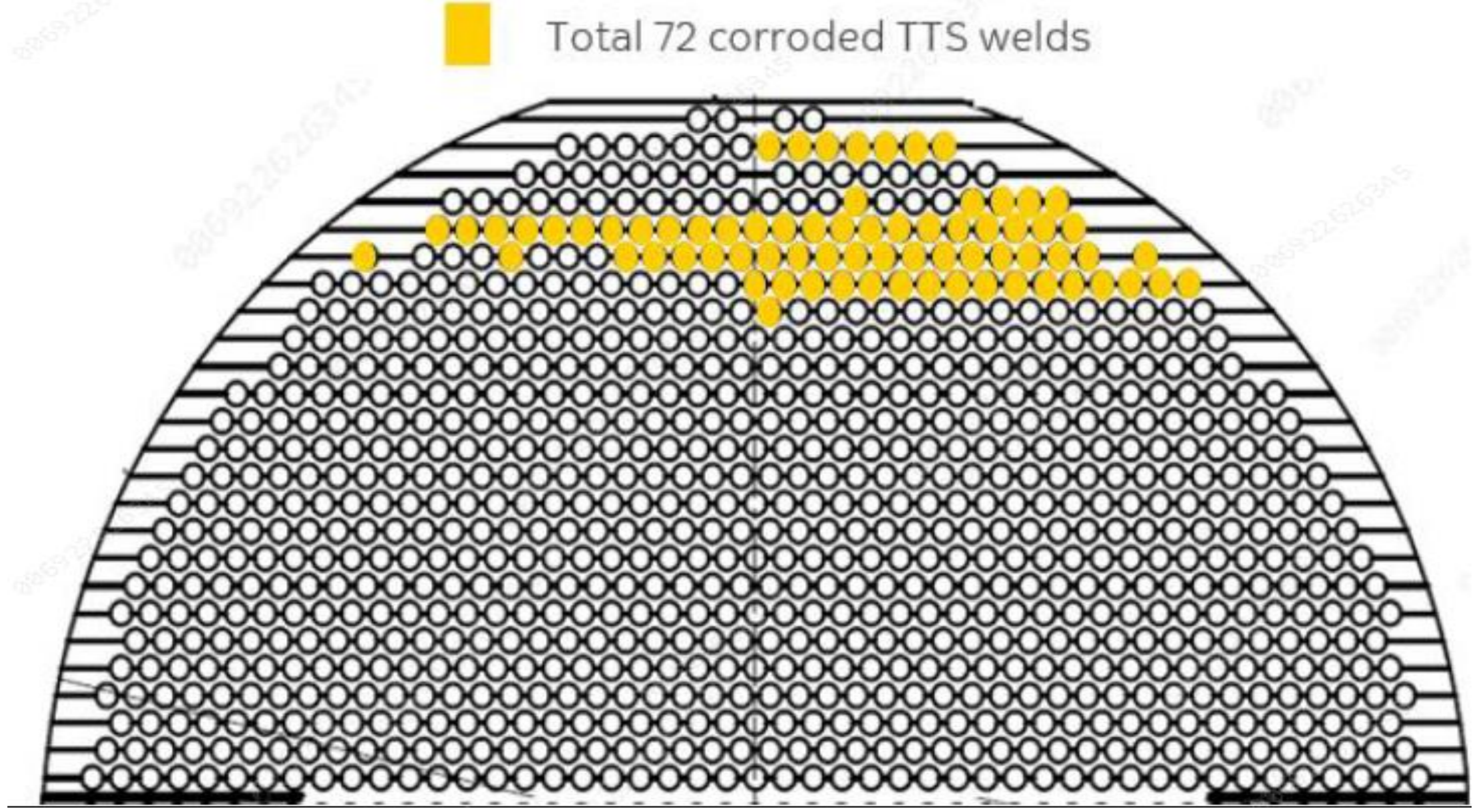
RIP 2020	SEP-2022	SEP-2022	Feb-2023	AUG-2023
HPCCA/B Were replaced	Conductivity started to increase from 7 to 24 us/cm. As per process & Process licensor evaluation, HPCC-A found leaking.	Risk assessment was conducted and risk found minor. Based on OEM guideline, max limit of conductivity was set (100 us/cm).	Conductivity increased from 24 to 70 us/cm	• Conductivity reached to 100 us/cm. (max recommended value by licensor)



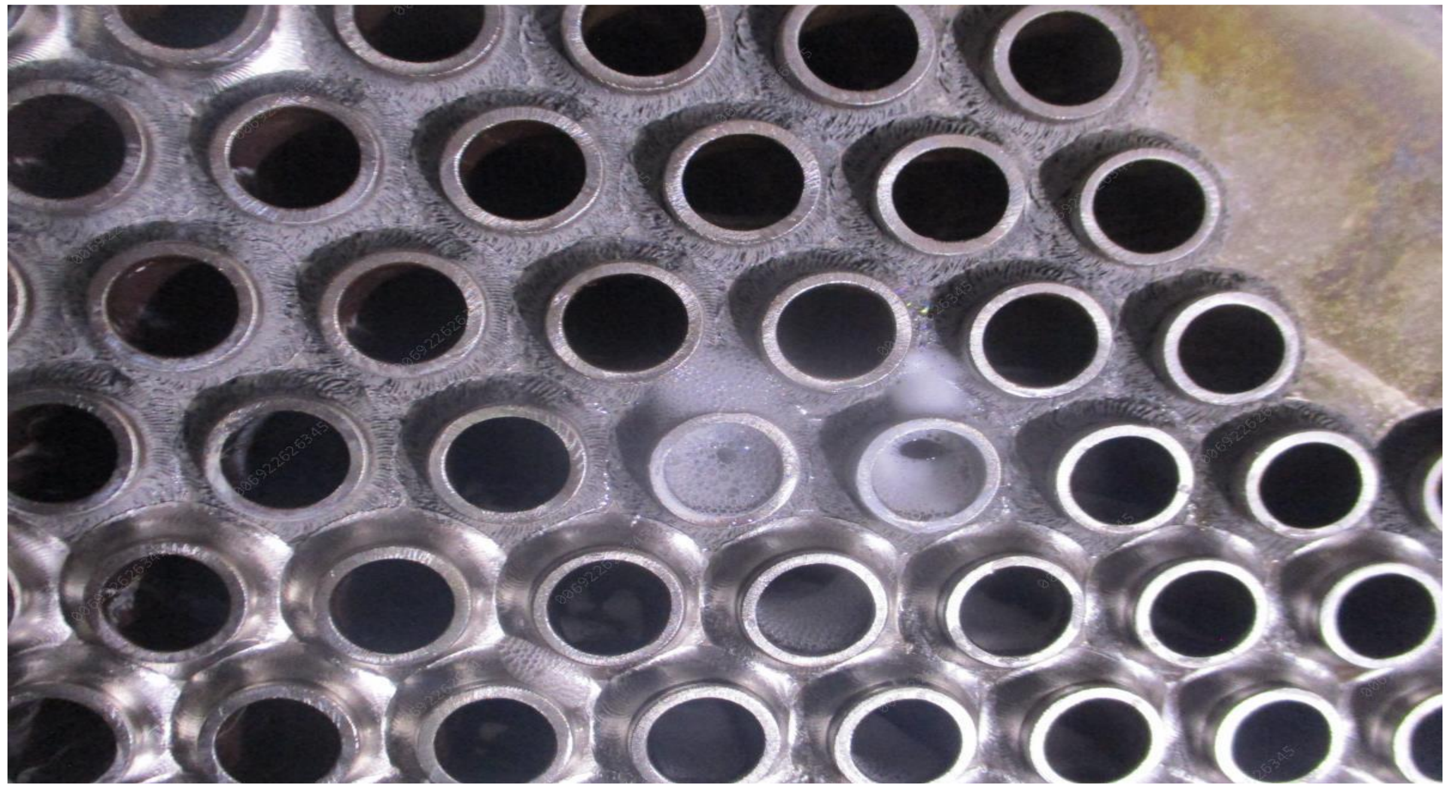
Inspection Findings

During initial inspection, the exchanger was tested by pneumatic test at 4.9kg/cm² to identify the leak locations. Nine tubes were found leaking from TTS weld. Row number and tube number of each tube found leaking during the test is shown in Table.1. The condition of the TTS weld of the leaking tubes showed signs of corrosion as shown in the photos below Fig. 1 and 2.
72 TTS welds found corroded in upper part of the tube sheet. The location of the corroded TTS is shown in marked tube sheet layout.

Row number	Tube number	Pneumatic test pressure	Photo
R2	T3, and T4	2kg/cm²	
R6	T7, T14	4kg/cm²	
	T22	4.9kg/cm²	
R7	T6, T7	2kg/cm²	
	T11	4kg/cm²	
R9	T11	4kg/cm²	

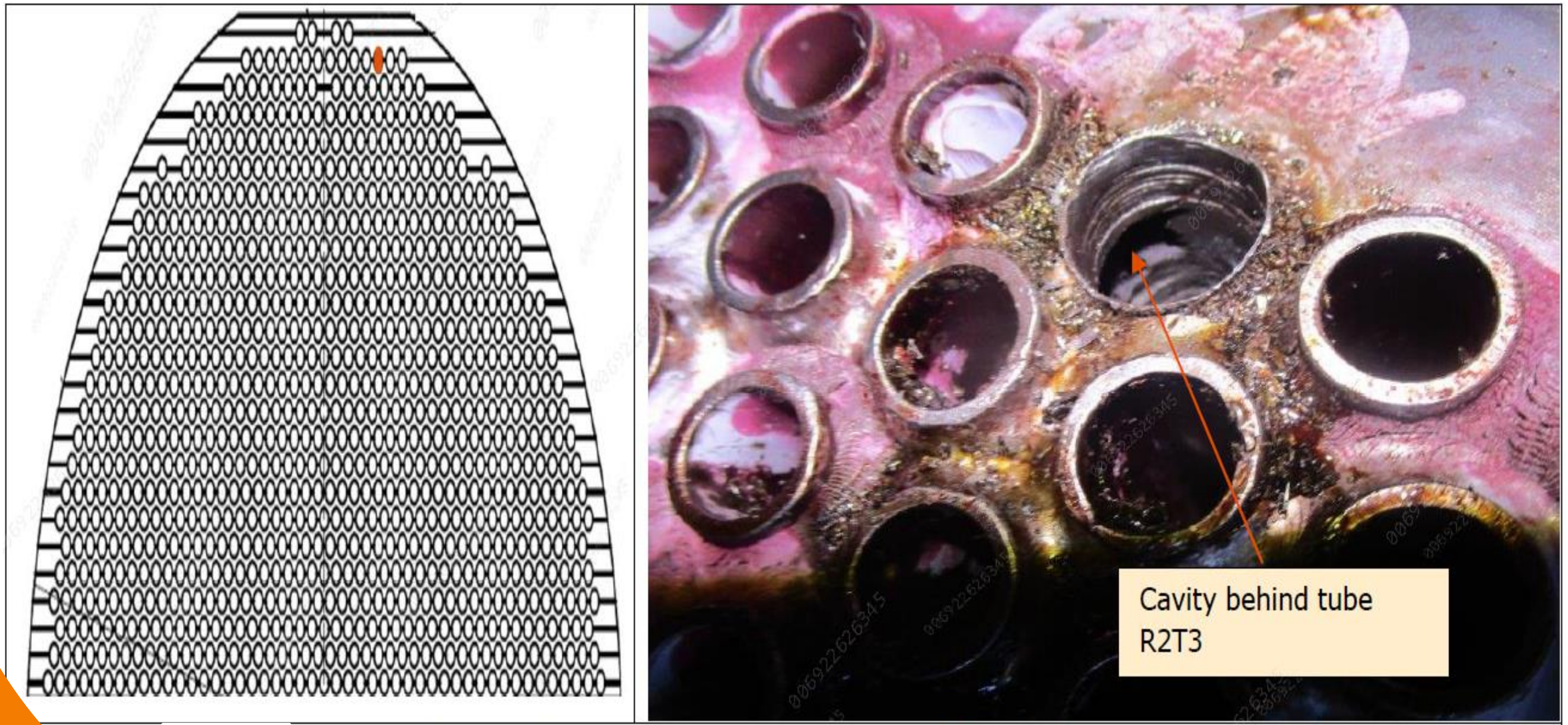


corroded TTS in the upper part of inlet tube sheet



Inspection Findings

Drilling was done for tubes found leaking. No corrosion in the CS tube sheet observed behind the liner. Full removal of the tube up to 40mm from the tube sheet was measured by inserting a plug of 19.08 OD and 40mm length. Corrosion in the CS portion was observed behind Tube T3 in Row 2 after removing the tube from within the tube sheet, therefore the surrounded tubes were also drilled and the liner removed to check the extent of corrosion behind the liner.



corrosion observed in CS portion behind Tube T3 in Row 2 after removing the tube

corrosion cavity

Finite Element Analysis (FEA)

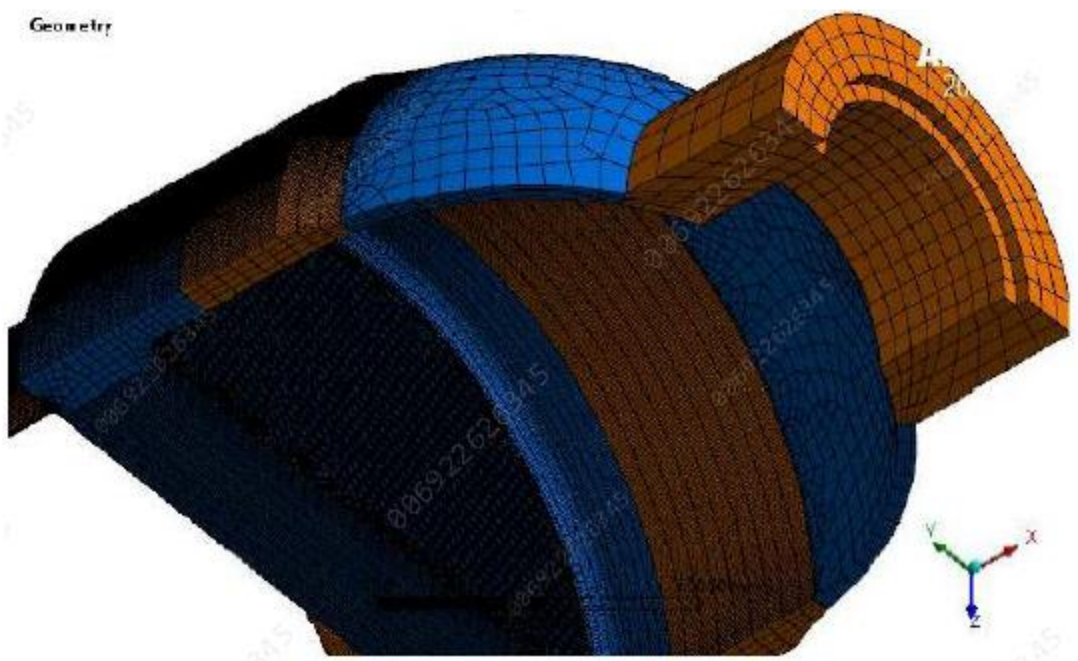
FE Analysis was conducted to check the compliance of the tube sheet with the existing cavity and the pass partition box with the code prescribed stress limits.

Design methods of ASME sec. VIII Div.2
The analysis was carried out adopting the finite element program ANSYS. Inc. product 2020,R2

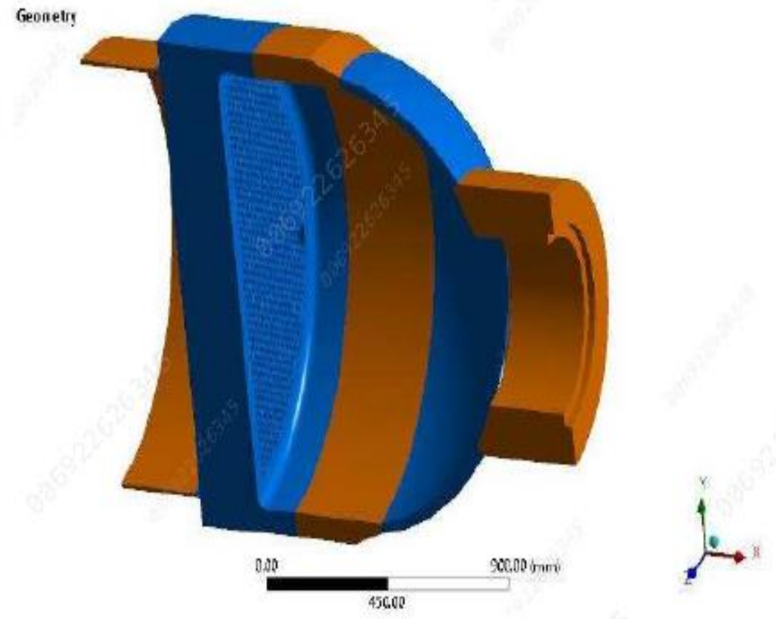
FEA proved that the components are in compliance with the criteria according to ASME sec. VIII Div.2.

FEA was carried out to check for:

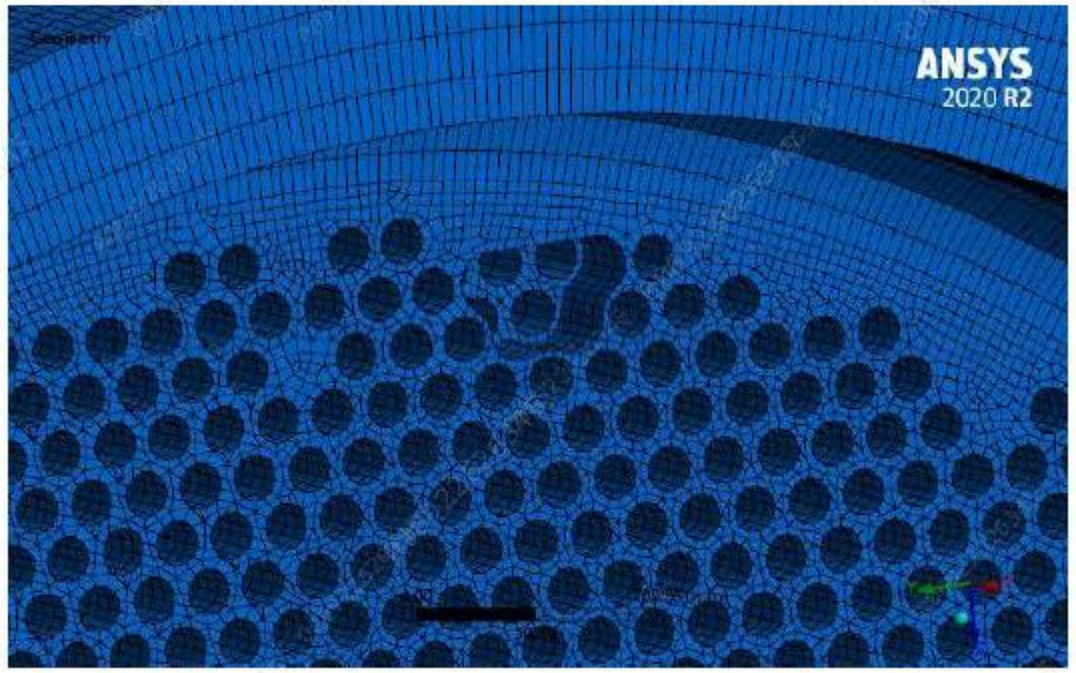
1. Protection against plastic collapse
2. Protection against local failure



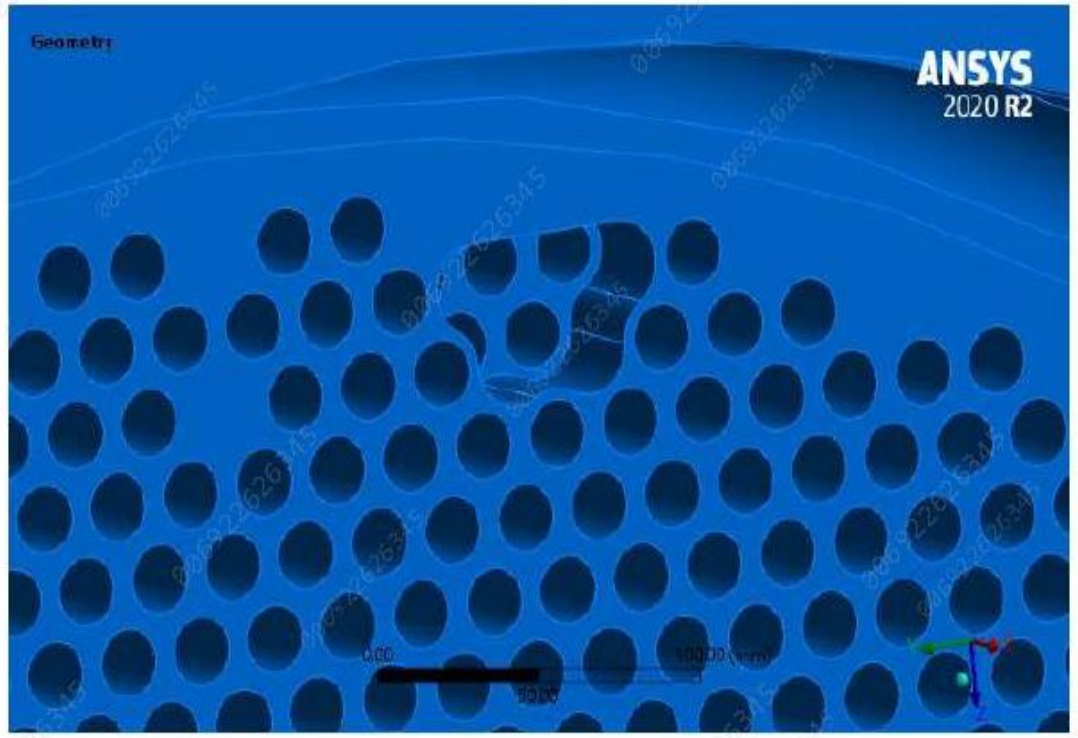
Detail of finite element model.



Geometrical Model



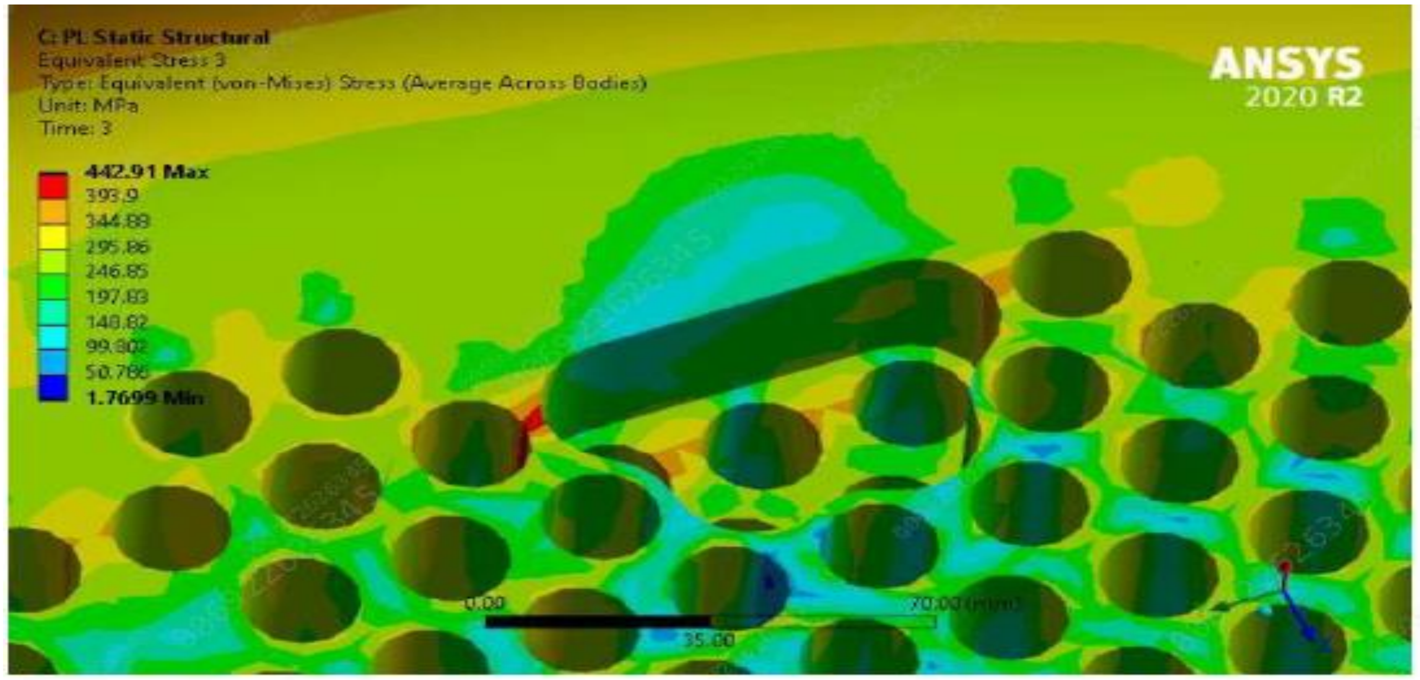
Detail of finite element model.



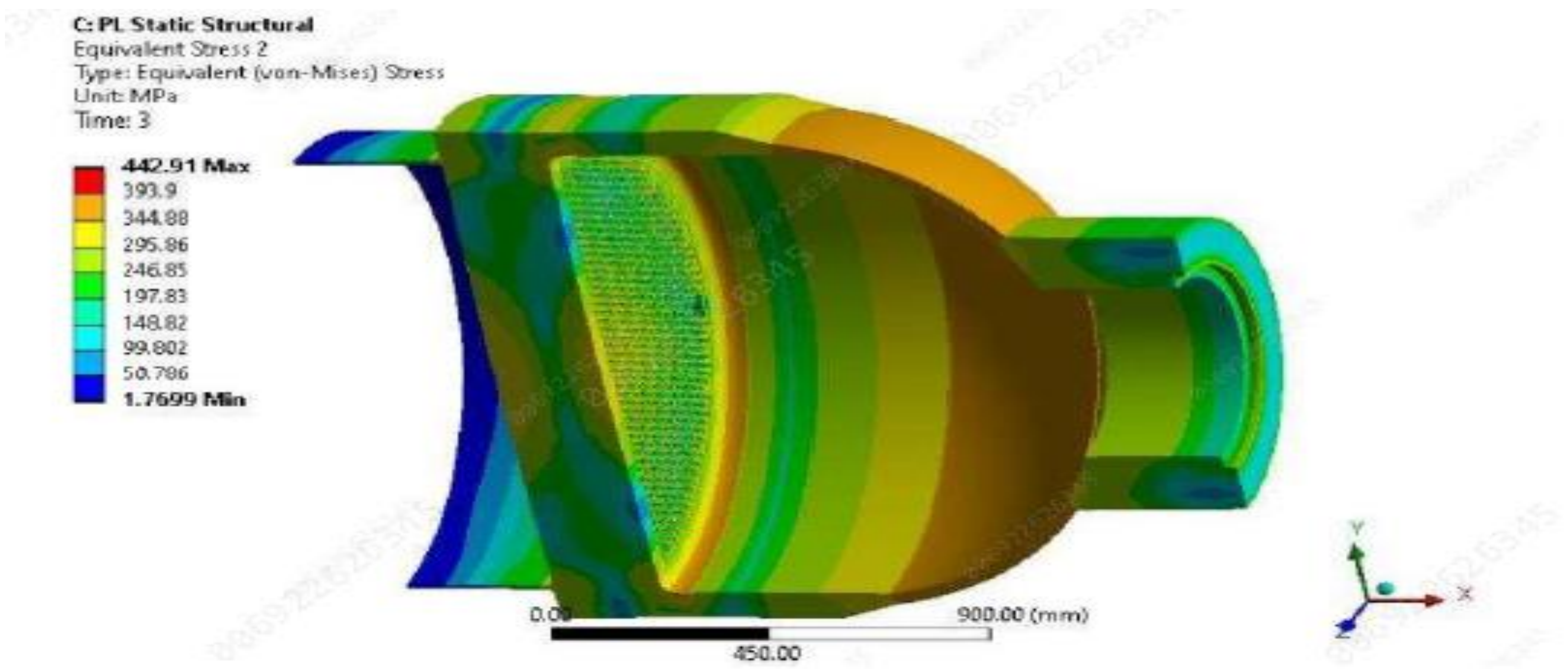
Detail of Geometrical Model.

Protection against plastic collapse

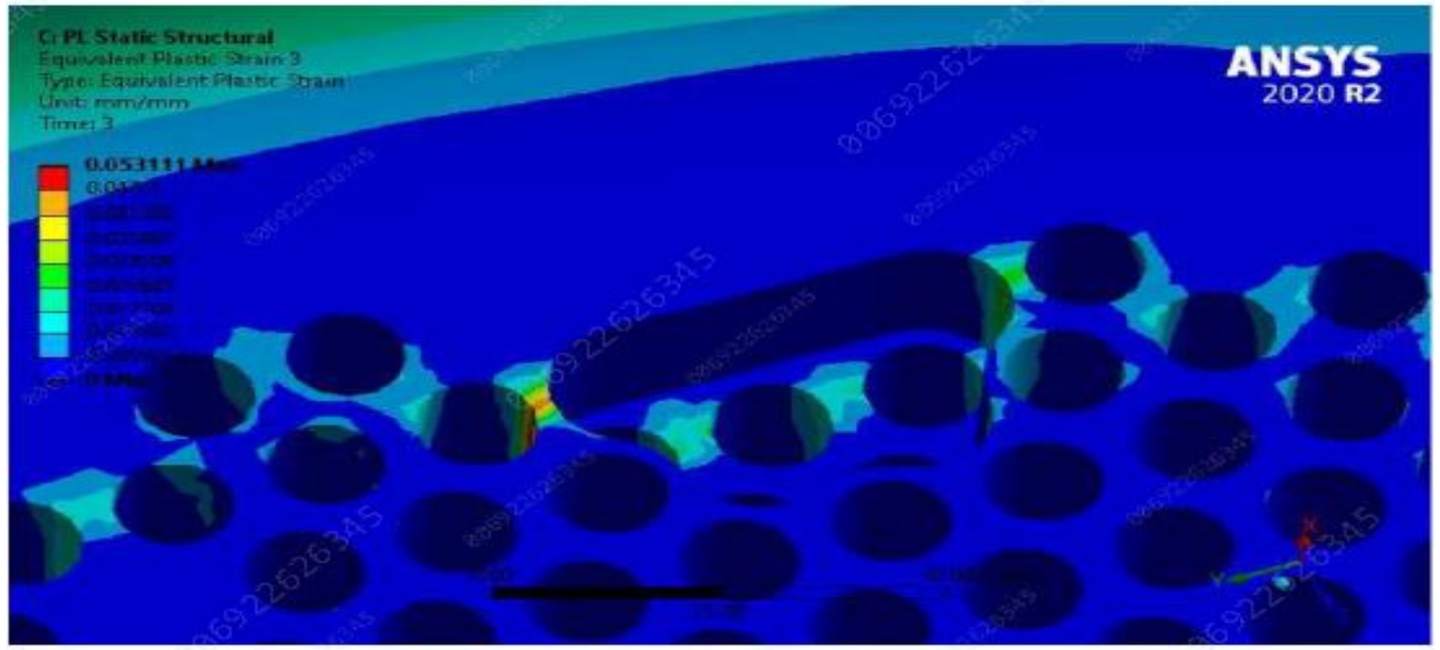
Finite Element Analysis (FEA)



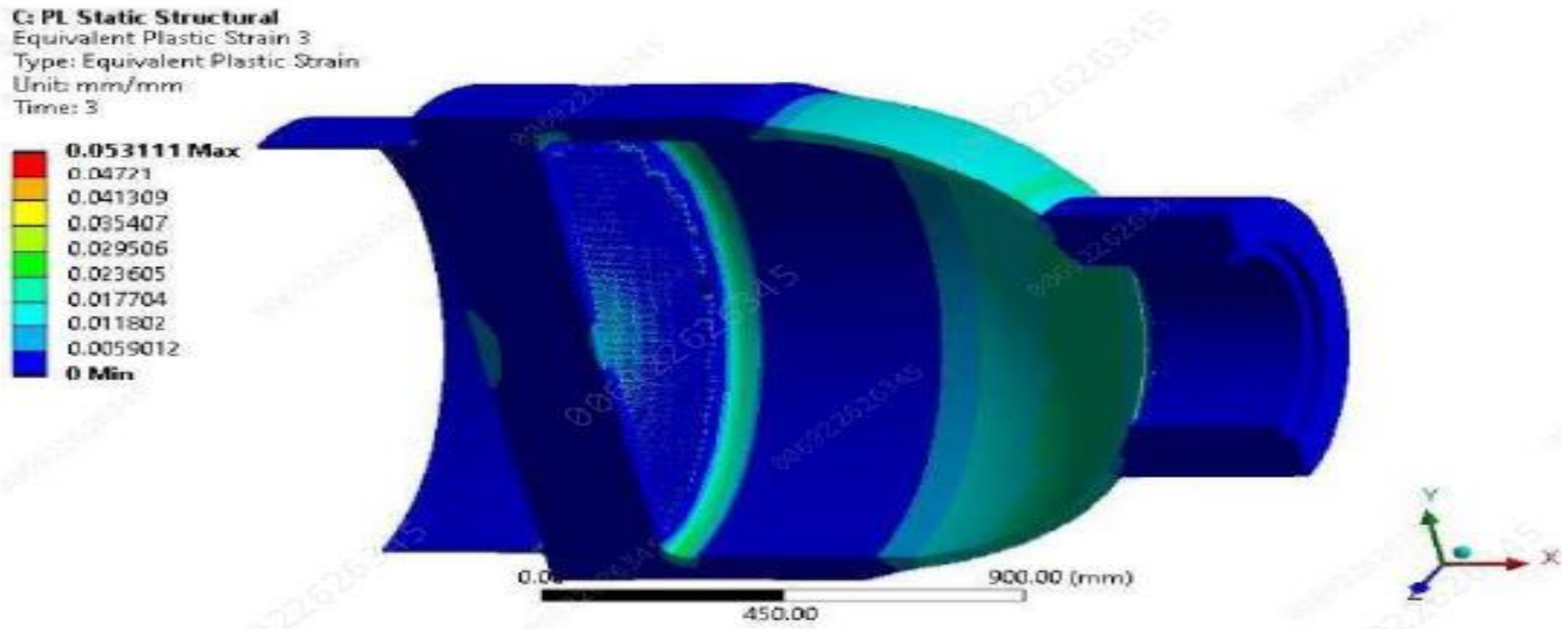
LC1-Von Mises Equivalent stress contours [MPa]



LC1-Von Mises Equivalent stress contours [MPa]



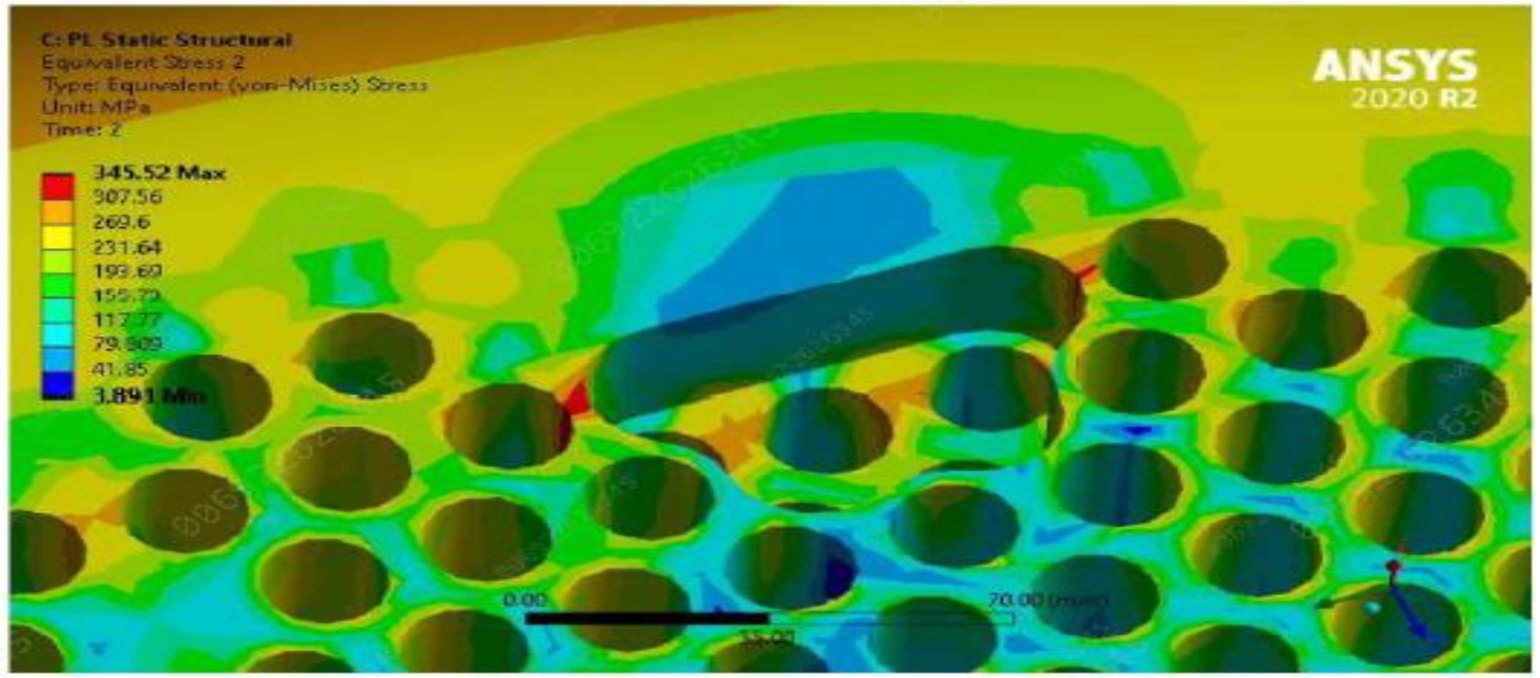
LC1- Equivalent plastic strain contours [mm/mm]



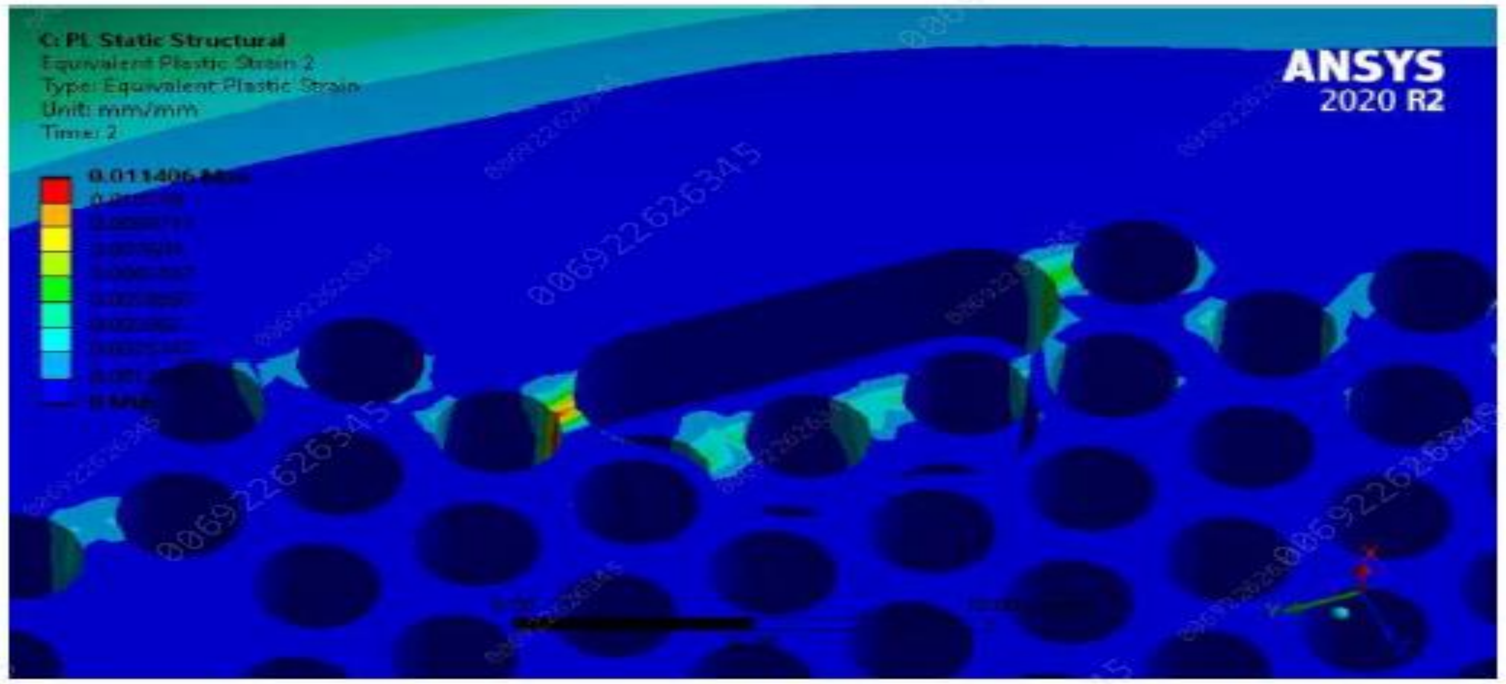
LC1- Equivalent plastic strain contours [mm/mm]

Protection against plastic collapse

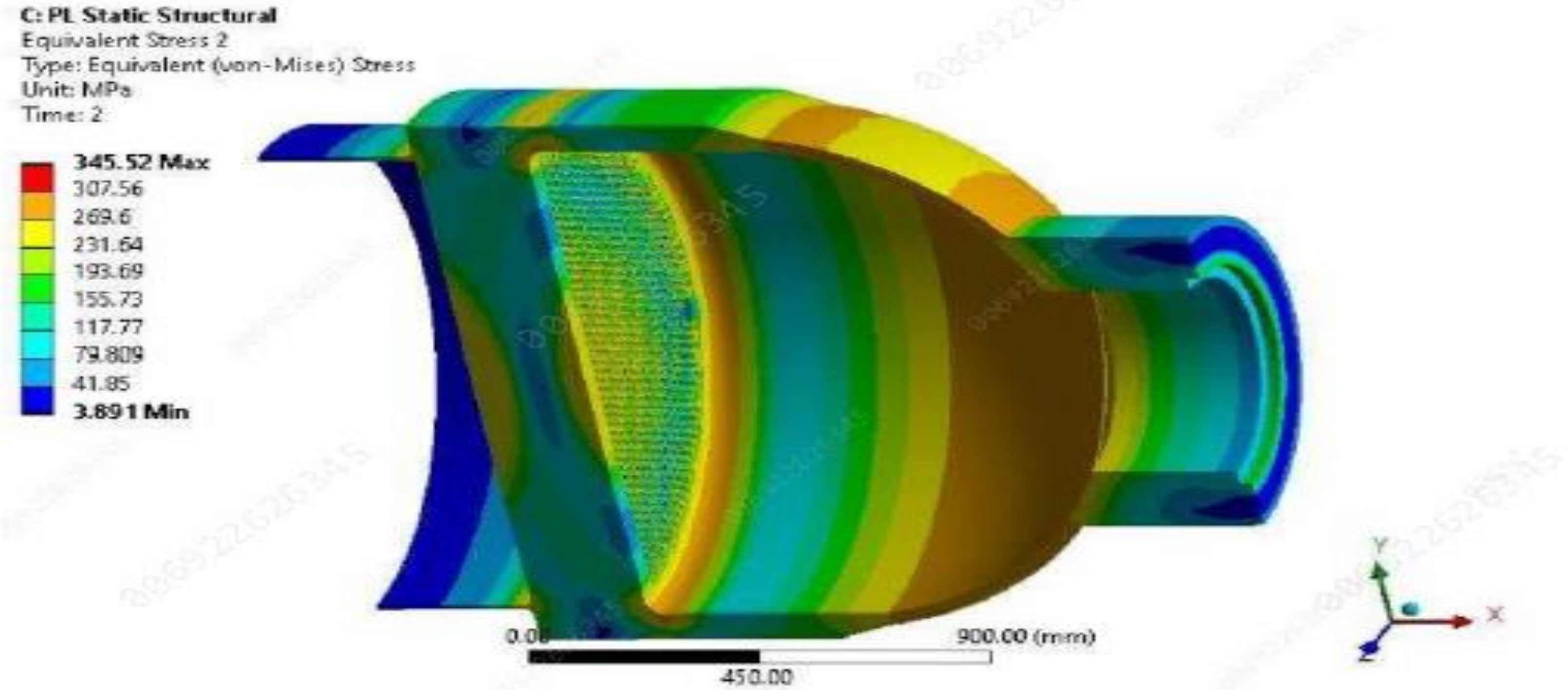
Finite Element Analysis (FEA)



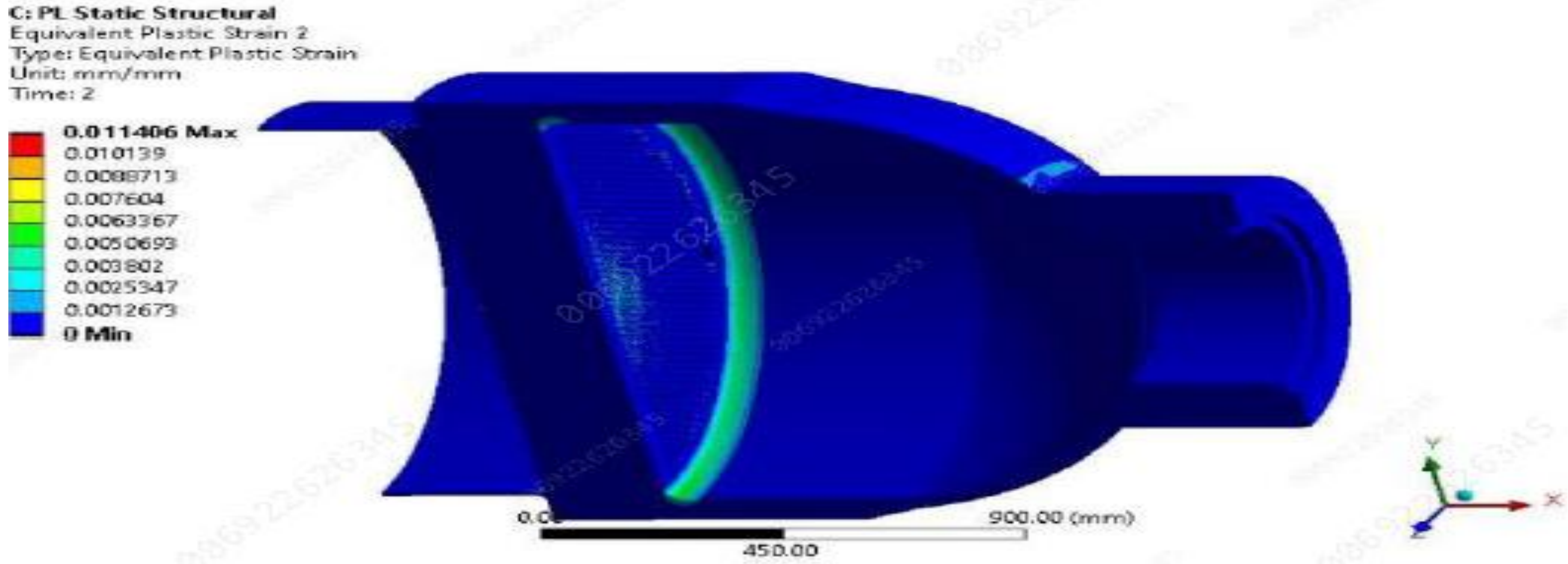
LC2-Von Mises Equivalent stress contours [MPa]



LC2- Equivalent plastic strain contours [mm/mm]



LC2-Von Mises Equivalent stress contours [MPa]



LC2- Equivalent plastic strain contours [mm/mm]

Protection against local failure

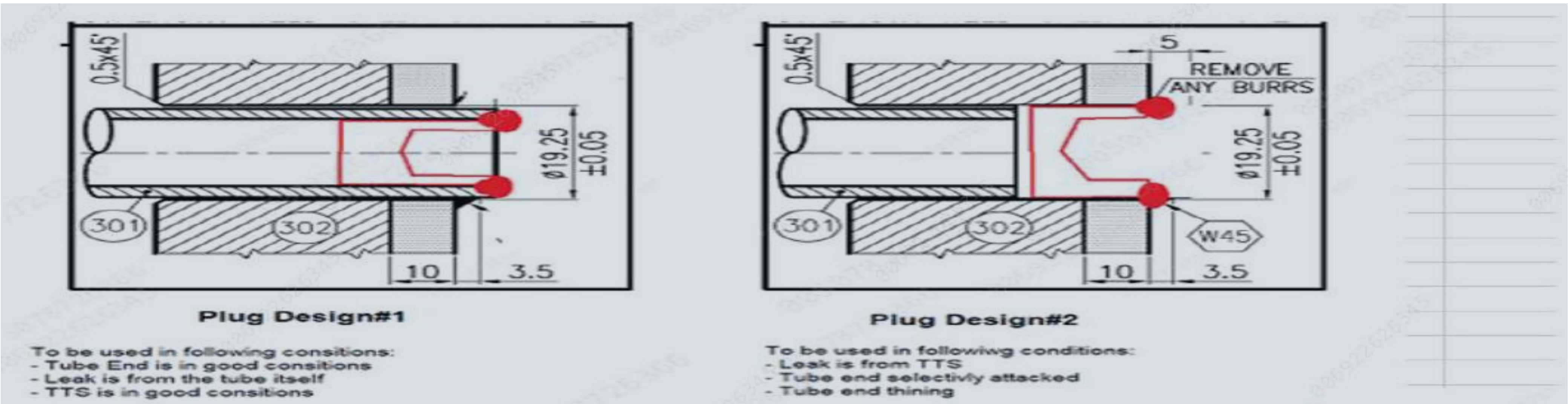
Repair Methodology

The repair procedure was developed based on the findings and the size of corrosion cavity. After taking the measurement of the cavity, five solid bars of 22mm diameter and 3mm length was installed inside the cavity. Tow plates above Row#2 were placed to fill the gap. material of the plug, and plates is 25.22.2 as confirmed by PMI. The edges of the tube sheet overlay were smoothened and bevel prepared in order to be welded with a plate of 25.22.2 material that was placed on top of the cavity. the weld was tested by DPT and found accepted. Ferrite was also measured and found to be less than 0.3. PMI of the was done on the final weld pass and the plate. Material was matching to 25.22.2.

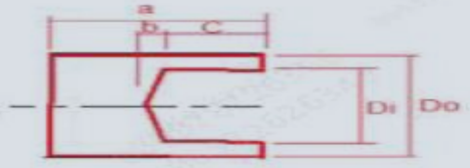
Other tubes found leaking during initial inspection were plugged using a hollow plug inserted inside the tube sheet groove after removing the 40mm of the tube within the tube sheet by drilling. Plug material was verified by PMI and found to be matching with 25.22.2 material. The plug design is #2. Plug weld repair was tested by DPT and found accepted. Ferrite was measured and found to be less than 0.3.

Corroded TTS welds were repaired by fusing the existing weld without filler wire and apply two weld passes on the existing weld and ensuring the interpass temperature does not exceed 100°C and using 1.6mm filler wire diameter. Welding was done using 25.22.2 filler wire of 1.6mm diameter. Filler wire material was verified by PMI prior to welding. The weld repair was tested by DPT and found accepted. Ferrite was measured and found to be less than 0.3.

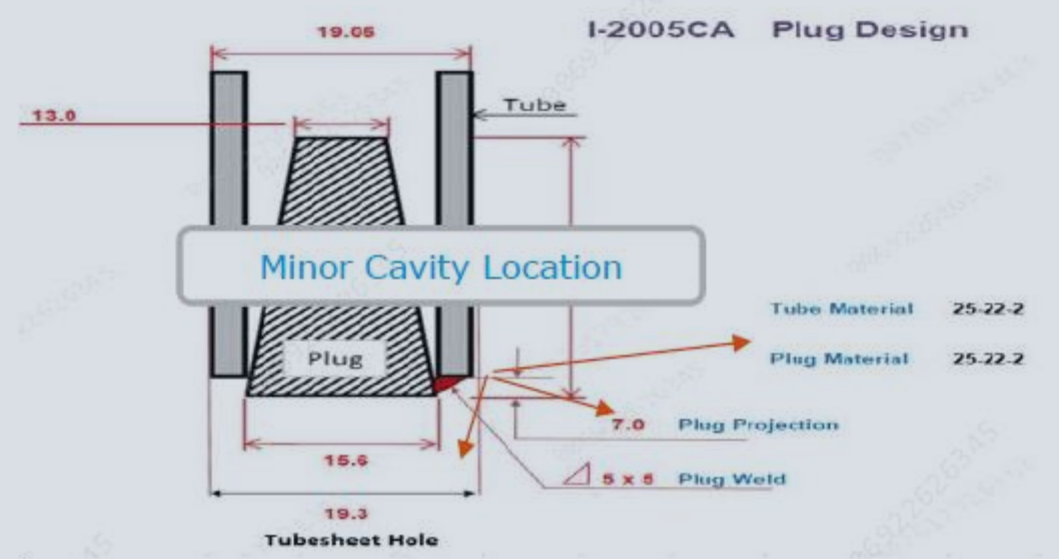
Repair Methodology



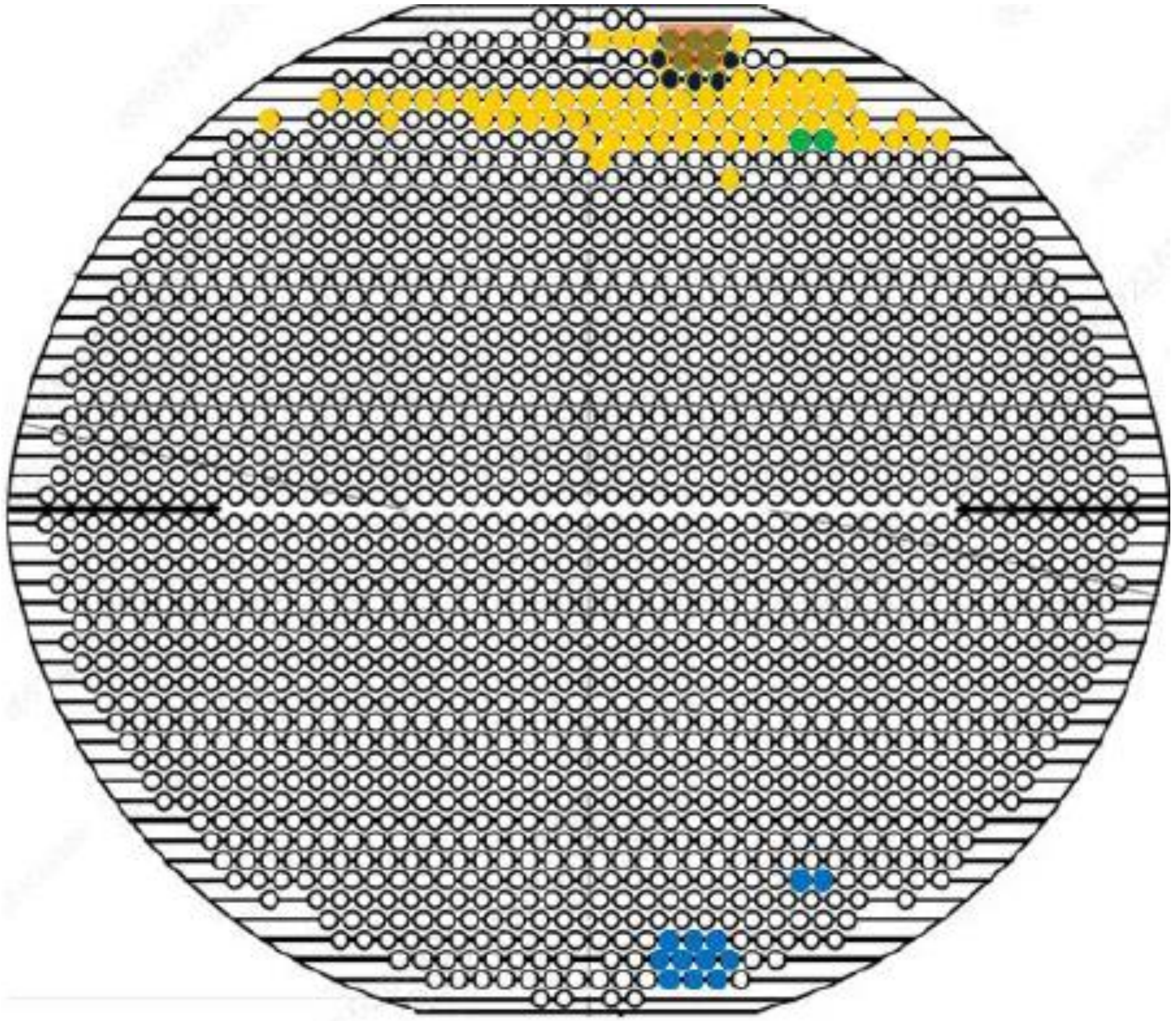
	a	b	c	Di	Do
Plug Design#1	40	3	10	7	14.7
Plug Design#2	40	3	10	11	19.05



Plug design#1 was used for all tubes in the bottom part of the tube sheet. Plugs were extended 5mm from tube end.
Plug design#2 was used for two tubes in Row #7 (T6, and T7), Plugs were extended 5mm beyond the tube sheet



This plug design was used for tubes around the corrosion cavity

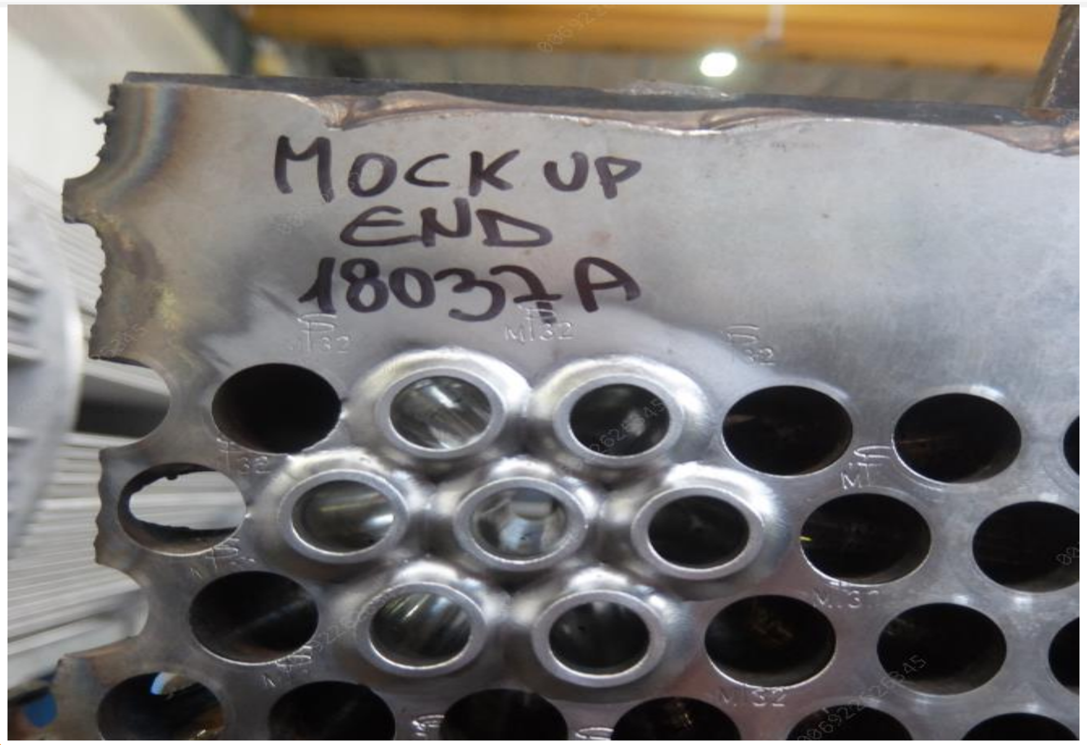


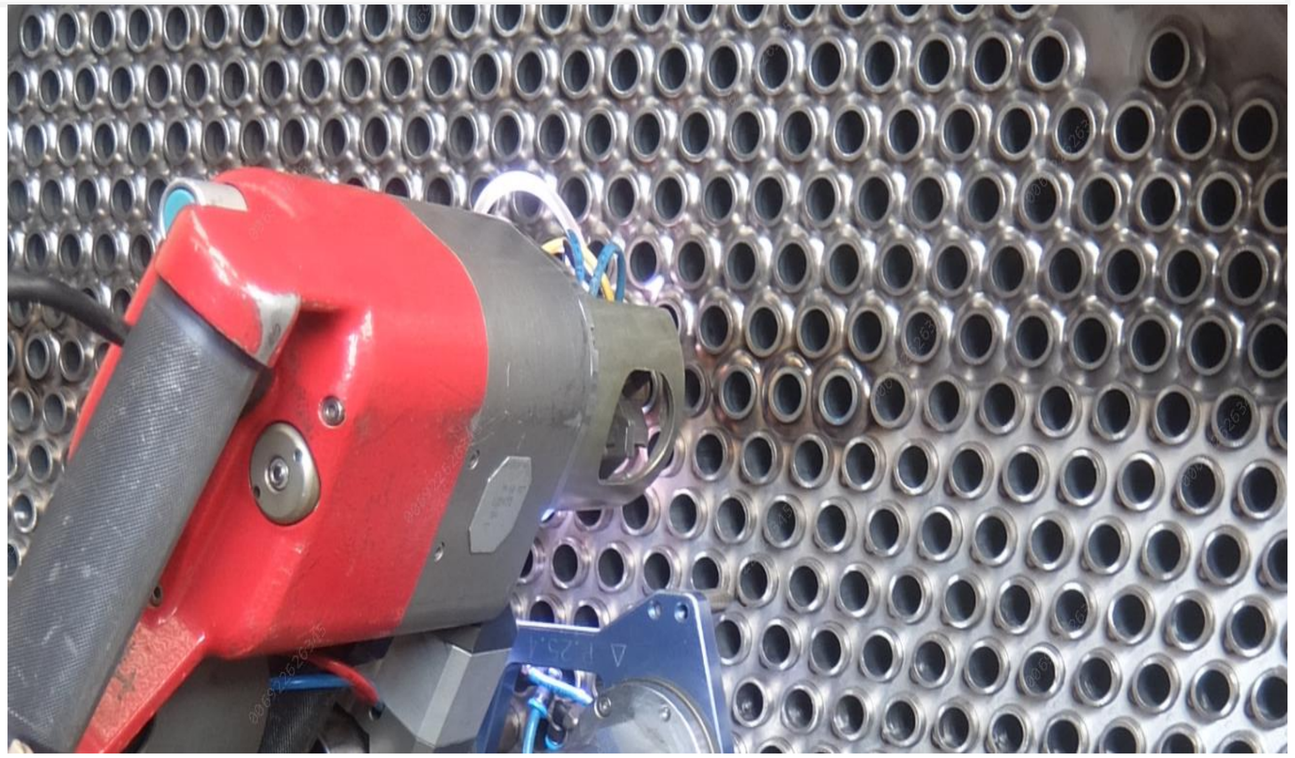
- Tubes plugged by drill plug, design#2
- TTS weld repaired by welding
- TTS weld repaired by welding and tube plugged by tapered plug
- Tubes plugged by Hollow plug, design#1
- Corrosion cavity

Corrosion Assessment

Welding records during fabrication and mock up were reviewed. Findings are summarized as follows:

- OEM confirming the wavy surface due to pulsed current were used while WPS 8037A-45Showing No pulsed current, and beads is string not weave.
- The auto welding is an approved welding technique but there no recorded pictures nor witnessed party to check the welding steps.
- Mock up was not witnessed.
- The wavy surface is a result from uncontrolled pulsed current which was done to lower the heat input and not to burn through the tubes but it should have being set to the minimum to have a smooth surface. It is very important to have as smooth as possible surface (excellent surface roughness) for stainless steel material to have a very good corrosion resistant.





ELECTRICAL CHARACTERISTICS (QW-409)				
Process:	GTAW			
Current Type:	DC			
Pulsing Current:	No			
Polarity:	EN			
Tung. El. Type:	EWTh-2			
Tung. El. Ø:	2.4			
Transfer Mode:	N.A.			
Other:	QW-409.1 QW-409.4 QW-409.8 not used			

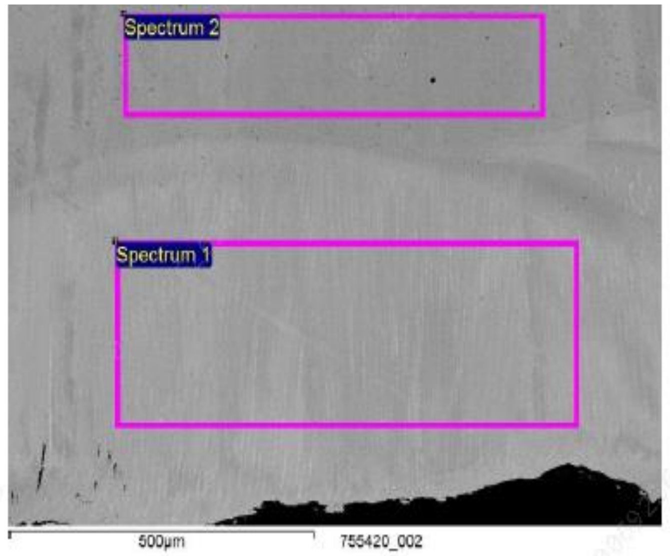
TECHNIQUE (QW-410)	
String/Weave beads:	String
Orifice/Cup size (mm):	11
Initial Cleaning:	Machining
Interpass Cleaning:	/
Method of Back Gouge:	/
Oscillation:	N.A.
Single/Multi pass/side:	Multi pass
Single/Multi Electrode:	Single
Electrode Spacing (mm):	N.A.
Electrode Stick out (mm):	N.A.
Closed/Out of Chamber:	N.A.
Manual or Automatic:	Machine
Supplemental Device/s:	N.A.
Peening:	NO
Other:	QW-410.11 QW-410.15 QW-410.64 n.u.

Corrosion Assessment

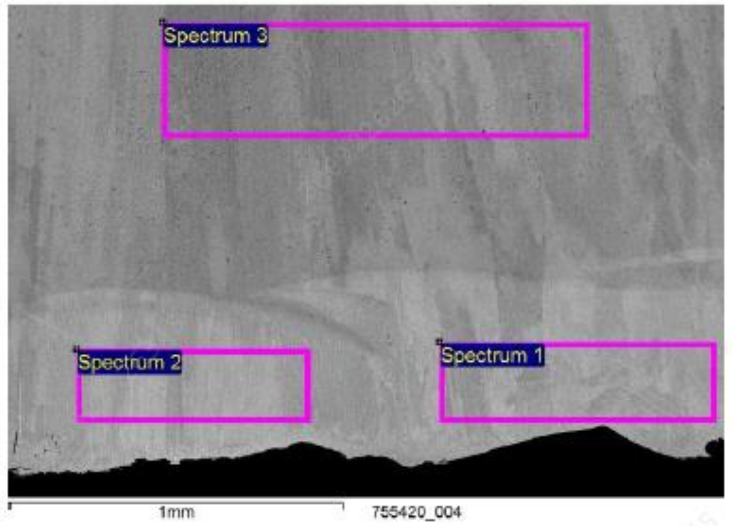
A Sample was taken from the TTS during the repair. The Sample was sent to CoE lab for Analysis. Result is as follows:

- The chemical composition result of the TTS weld material does not match the specification of the design filler wire material ASTM A312 grade S31050.
- Signs of corrosion were observed on a selected area which is at the top of the inlet urea process side suggesting that there was a mixing of filler wires used during the fabrication.
- The analysis of the weld at the front side of the tube sheet showed high nickel, moly, and less other elements.
- the result of the weld at the tube sheet is different from the subsequence welds.
- **<u>Based on the above analysis, it was concluded that the root cause was due to using improper filler wire during fabrication</u>**

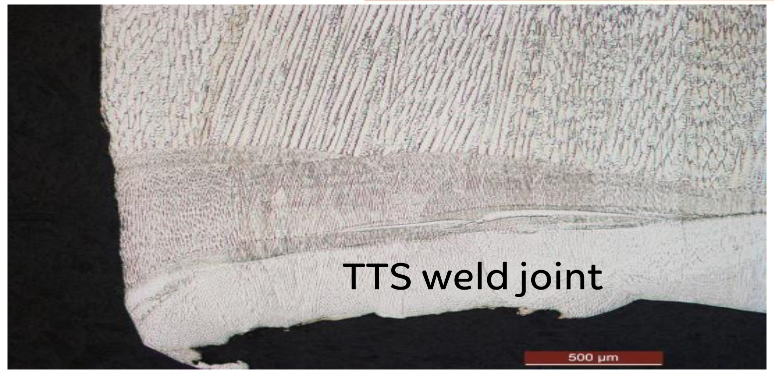
Top Sample		Bottom Sample (TTS weld joint)		ASTM312 S31050
Elements	Conc.%	Elements	Conc.%	Conc.%
Fe	Bal.	Ni	37.89	20.5-23.5
Cr	22.47	Fe	Bal.	Bal.
Ni	19.51	Cr	24.14	24.0-26.0
Mn	2.98	Mo	4.284	1.6-2.6
Mo	1.982	Mn	2	2.0
Si	0.484	Nb	1.14	---
Al	0.18	Al	0.29	---
Cu	0.145	Si	0.21	0.4
V	0.047	Cu	0.118	---
C	0.0351	Ti	0.061	---
S	0.01	V	0.059	---
		C	0.0306	0.025
		S	0.007	0.015
		P	0.003	0.02



Spectrum	C	Si	Cr	Mn	Fe	Ni	Mo
Spectrum 1	8.26	0.30	22.65	1.28	17.53	44.71	5.27
Spectrum 2	7.68	0.62	23.73	3.34	42.34	20.21	2.08
Mean	7.97	0.46	23.19	2.31	29.94	32.46	3.67



Spectrum	C	Si	Cr	Mn	Fe	Ni	Nb	Mo
Spectrum 1	8.23	0.23	22.50	1.22	19.10	41.36	1.78	5.58
Spectrum 2	7.44	0.23	22.25	1.30	17.63	43.24	2.10	5.80
Spectrum 3	7.26	0.52	23.79	3.52	42.21	20.34		2.37



Conclusion and Recommendations

- The use Nickel alloys in Urea HP synthesis is not allowed as it can get attacked by the corrosive carbamate solution.
- Reputable Manufacturers with sufficient experience shall be approved for HP equipment.
- Mock up shall always be a hold point and witnessed by inspection prior to manufacturing the equipment.
- OEM of Urea HP equipment shall have stringent quality plan. The quality plan shall ensure that Urea grade filler wires are not mixed with other alloys' filler wires. It shall also ensure that Nickel Alloy filler wires are kept away from the HP equipment being fabricated in the workshop.
- PMI of each TTS weld using spectrometer equipped with micro tip shall be used to enable the verification of the chemical composition of TTS welds. This shall be considered as hold point.
- The same welders or welding machines/operators for automatic welding shall be welding the tube to tube sheet weld joint.
- All welding parameters followed during mock up shall be strictly followed during welding the tube to tube sheet welds.
- MTC of the filler materials which to be used for fabrication shall be reviewed and approved prior to welding.

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