

# REFORMER AND SHIFT CATALYST EXPERIENCE



# COMPANY PROFILE

**Incorporated in 1969 at Tuticorin, Tamil Nadu**  
**Commercial Production from 1975**  
**Installed Urea Production Capacity – 512000 MTPA**



# COMPANY PROFILE

**Revamps and Capacity Augmentation in 50 Years**  
**Present Urea Production Capacity – 759200 MTPA**



# AMMONIA PLANT

**Installed Capacity in 1975**

**Capacity Augmentation in 1996 to 1998**

**Gas Conversion Revamp in 2021**

**- 1100 MTPD (Nap + Steam) / ICI Process**

**- 1260 MTPD (Nap + Steam) / Casale Converter**

**- 1320 MTPD (NG + Steam) / KBR**



# Catalyst Upset – Case Study

1. **Primary Reformer Catalyst**
  2. **High Temperature Shift Catalyst**
-

# Catalyst Upset – Case Study

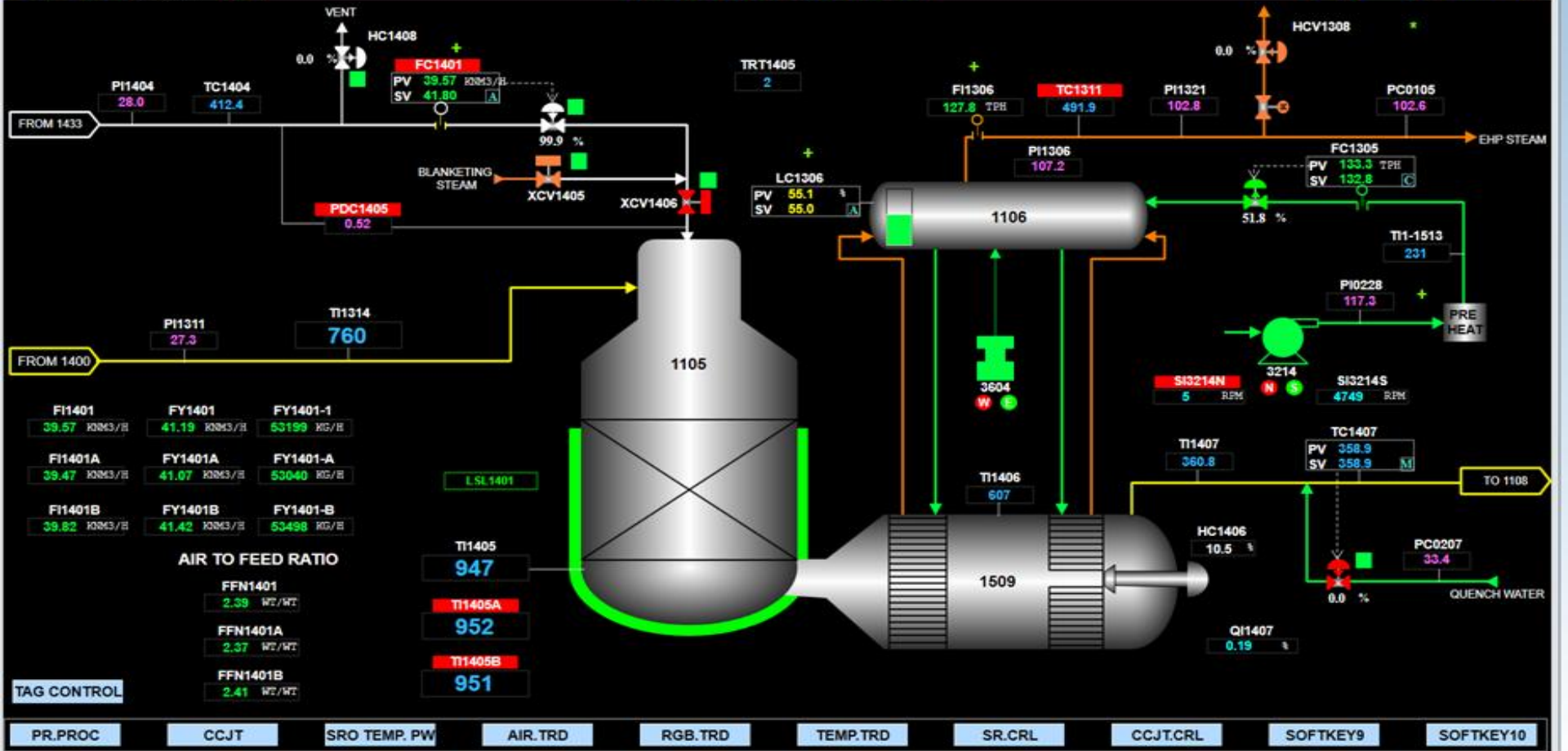
1. Primary Reformer Catalyst
  2. High Temperature Shift Catalyst
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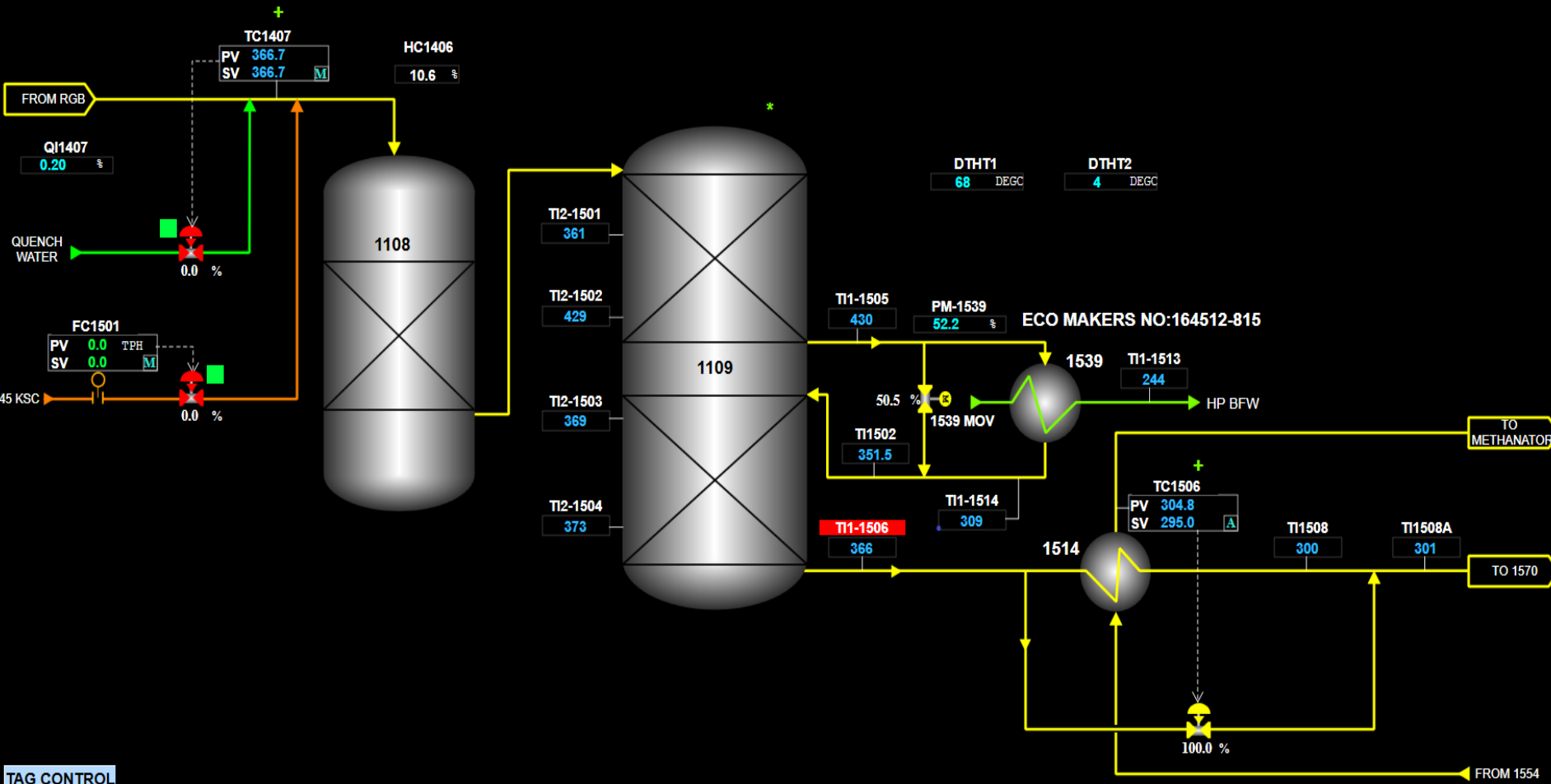
# REFORMER – Configuration

1. **Top Fired with 90 Guns (10 Rows X 9 Guns)**
2. **264 Catalyst Tubes (8 Rows x 33 Tubes) of 4 inches diameter and 13 Mts length**
3. **Balanced Draft Furnace with design Heat Flux of 75 KW/M<sup>2</sup>**
4. **Furnace operating under – 2 mm WC Pressure**
5. **Convection Module with Heat Recovery System for Process Steam, Combustion Air and Super Heated Steam**









TAG CONTROL

# REFORMER – CASE STUDY

Catalyst Vessel	Supplier	Quantity (m3)	Charged On	Replaced on	Life (Months)
Primary reformer	A	17.88	Apr-04	Apr-07	36
		11.88			
	B	17.80	Oct-10	Mar-17	78
		11.60			

# REFORMER – CASE STUDY

12

1. After serving for above 6 years, pressure drop of Catalyst in Primary reformer was on increasing trend during end of 2016 and hence it was planned to go for catalyst replacement
2. Availability of NG was foreseen in the next few years, but only 60% of the total quantity was allocated
3. Operation with Mixed Feed of Naphtha + NG was foreseen
4. Supplier – X recommended **3 layer Catalyst** for Mixed Feed

# REFORMER – 3 Layer Catalyst

1. **Top Layer** - 23% Ni, 7% K<sub>2</sub>O - 40% Volume
2. **Middle Layer** - 18% Ni, 1.8% K<sub>2</sub>O - 20% Volume
3. **Bottom Layer** - x % Ni, 0 % K<sub>2</sub>O - 40% Volume

The above combination of triple decker catalysts has been considered as the plant is expected to operate on natural gas after 3-4 years. This proposed combination of catalyst will allow SPIC to operate the reformer to operate on 100% naphtha, any combination of naphtha and natural gas and 100% natural gas.

## **Case 1 – 100% naphtha**

Parameters	Unit	S/C@3.6	
		SOR	EOR
Exit pressure	kg/cm <sup>2</sup> g	30.9	30.1
Pressure drop <sup>^</sup>	kg/cm <sup>2</sup>	2.4	3.2
Peak heat flux	kW/m <sup>2</sup>	120.6	117.6

# REFORMER – CASE STUDY

1. Pre dispatch inspection was found normal with respect to Quality
  2. Loading done through **UNIDENSE** mechanism
  3. Effective loading was carried out and pressure drop variation was +/- 3%
  4. Commissioned on 13<sup>th</sup> March 2017
-

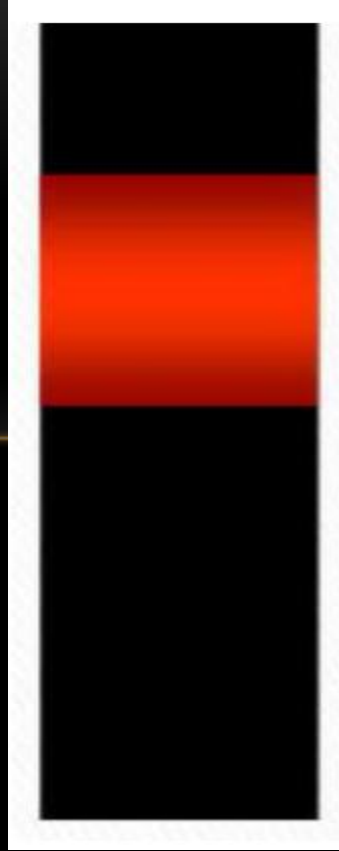
# REFORMER – Naphtha Feed

NAPHTHA QUALITY REPORT		
Density @ 15oC	GM/CC	0.685
IBP	DEG C	43.5
10 % v/v		52
50 % v/v		70
90 % v/v		105
FBP		130
Total Sulphur	PPM	143
Olefins	%	0.35
Aromatics	%	6.4
Reid Vapour Pressure (RVP) @ 37.8 Deg. C	Kg/cm2	0.7
Residue on evaporation	mg/100 ml	1.1
Lead	ppb	3
Chloride (In-Organic) ASTM D 4929	ppm	0.3
C/H ratio	-	5.36
Gross Calorific value (IS 1448 Calculation)	Kcals/KG	11414

# REFORMER – Hot Band / Hot Patches

16

**Hot  
Band**



**Hot  
Patches**

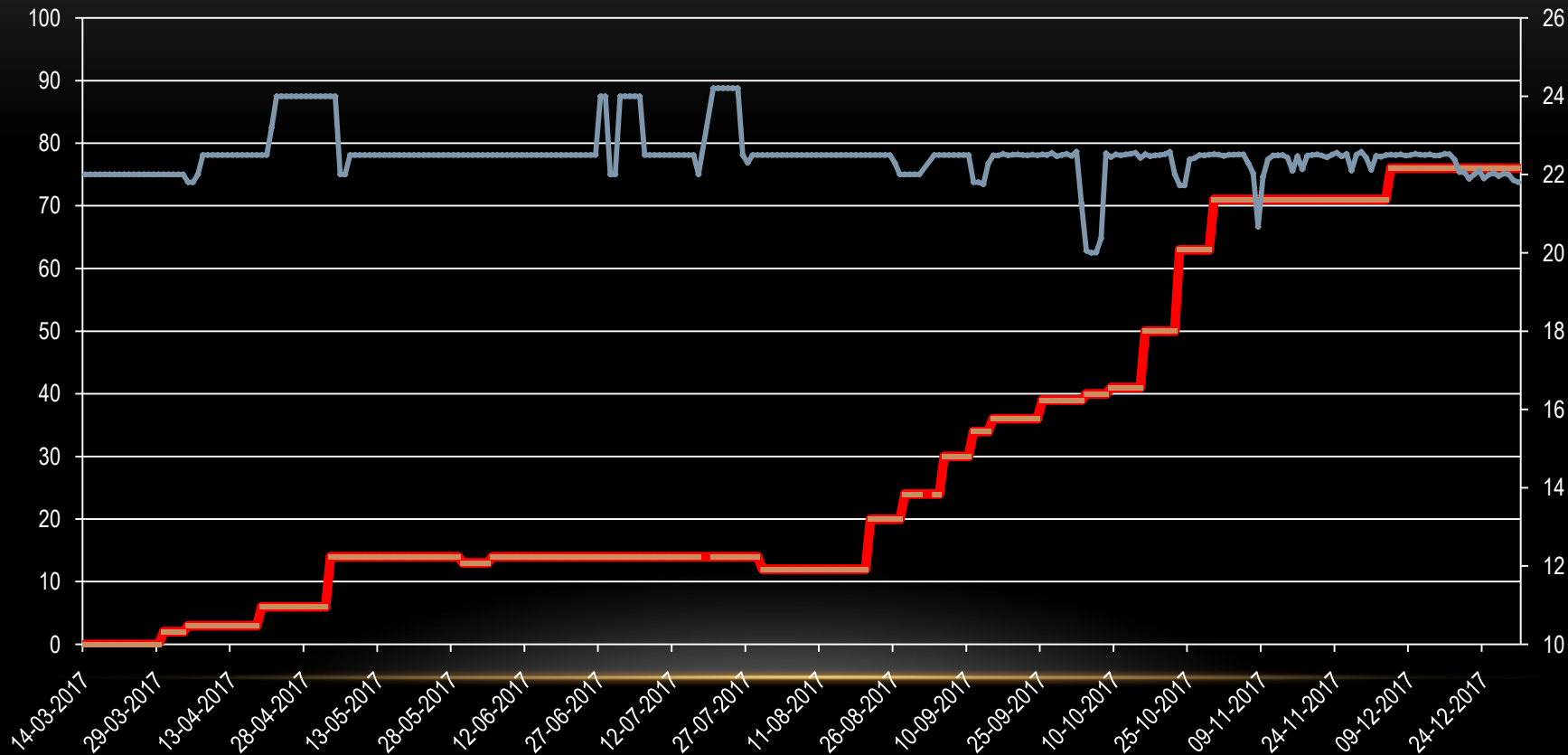




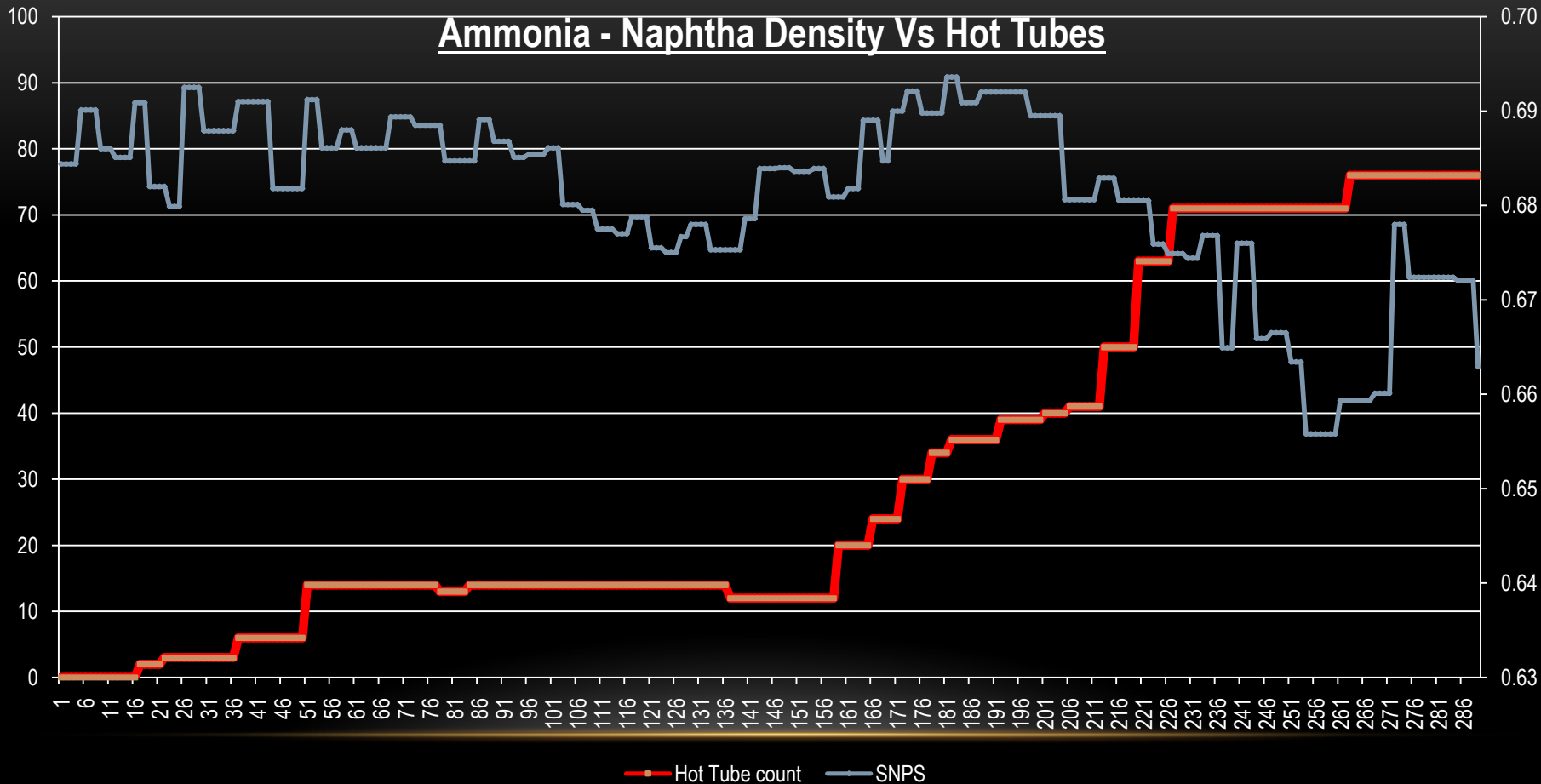
# Ammonia - Sweet Naphtha Flow Vs Hot Tubes

Hot Tube count

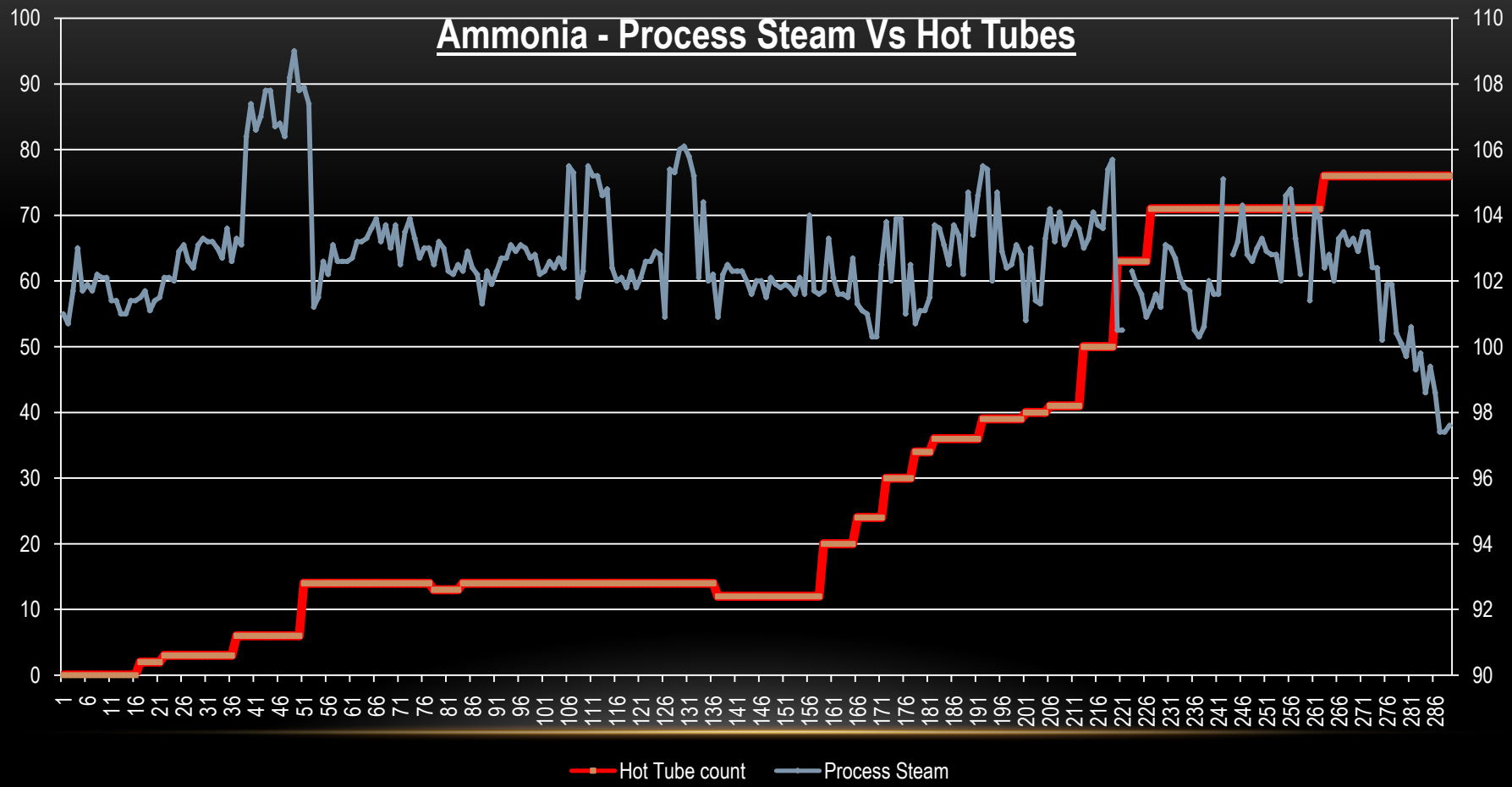
Plant Load



# Ammonia - Naphtha Density Vs Hot Tubes



# Ammonia - Process Steam Vs Hot Tubes



**AMMONIA PLANT - REFORMER - BURNER CONDITION on 01st Jan 2018**

From North

Br.	A	Br.	B	Br.	C	Br.	D	Br.	E	Br.	F	Br.	G	Br.	H	Br.
	TUBE		TUBE		TUBE		TUBE		TUBE		TUBE		TUBE		TUBE	
1	1	11	1	21	1	31	1	41	1	51	1	61	1	71	1	81
	2		2		2		2		2		2		2			
	3		3		3		3		3		3		3			
2	4	12	4	22	4	32	4	42	4	52	4	62	4	72	4	82
	5		5		5		5		5		5		5			
	6		6		6		6		6		6		6		6	
	7		7		7		7		7		7		7		7	
3	8	13	8	23	8	33	8	43	8	53	8	63	8	73	8	83
	9		9		9		9		9		9		9			
	10		10		10		10		10		10		10		10	
	11		11		11		11		11		11		11		11	
	12		12		12		12		12		12		12		12	
4	13	14	13	24	13	34	13	44	13	54	13	64	13	74	13	84
	14		14		14		14		14		14		14			
	15		15		15		15		15		15		15		15	
	16		16		16		16		16		16		16		16	
5	17	15	17	25	17	35	17	45	17	55	17	65	17	75	17	85
	18		18		18		18		18		18		18			
	19		19		19		19		19		19		19		19	
6	20	16	20	26	20	36	20	46	20	56	20	66	20	76	20	86
	21		21		21		21		21		21		21			
	22		22		22		22		22		22		22		22	
	23		23		23		23		23		23		23		23	
7	24	17	24	27	24	37	24	47	24	57	24	67	24	77	24	87
	25		25		25		25		25		25		25			
	26		26		26		26		26		26		26		26	
8	27	18	27	28	27	38	27	48	27	58	27	68	27	78	27	88
	28		28		28		28		28		28		28			
	29		29		29		29		29		29		29		29	
	30		30		30		30		30		30		30		30	
9	31	19	31	29	31	39	31	49	31	59	31	69	31	79	31	89
	32		32		32		32		32		32		32			
	33		33		33		33		33		33		33		33	
10	32	20	32	30	32	40	32	50	32	60	32	70	32	80	32	90
	33		33		33		33		33		33		33			

**Hot tubes**

**1**

**3**

**11**

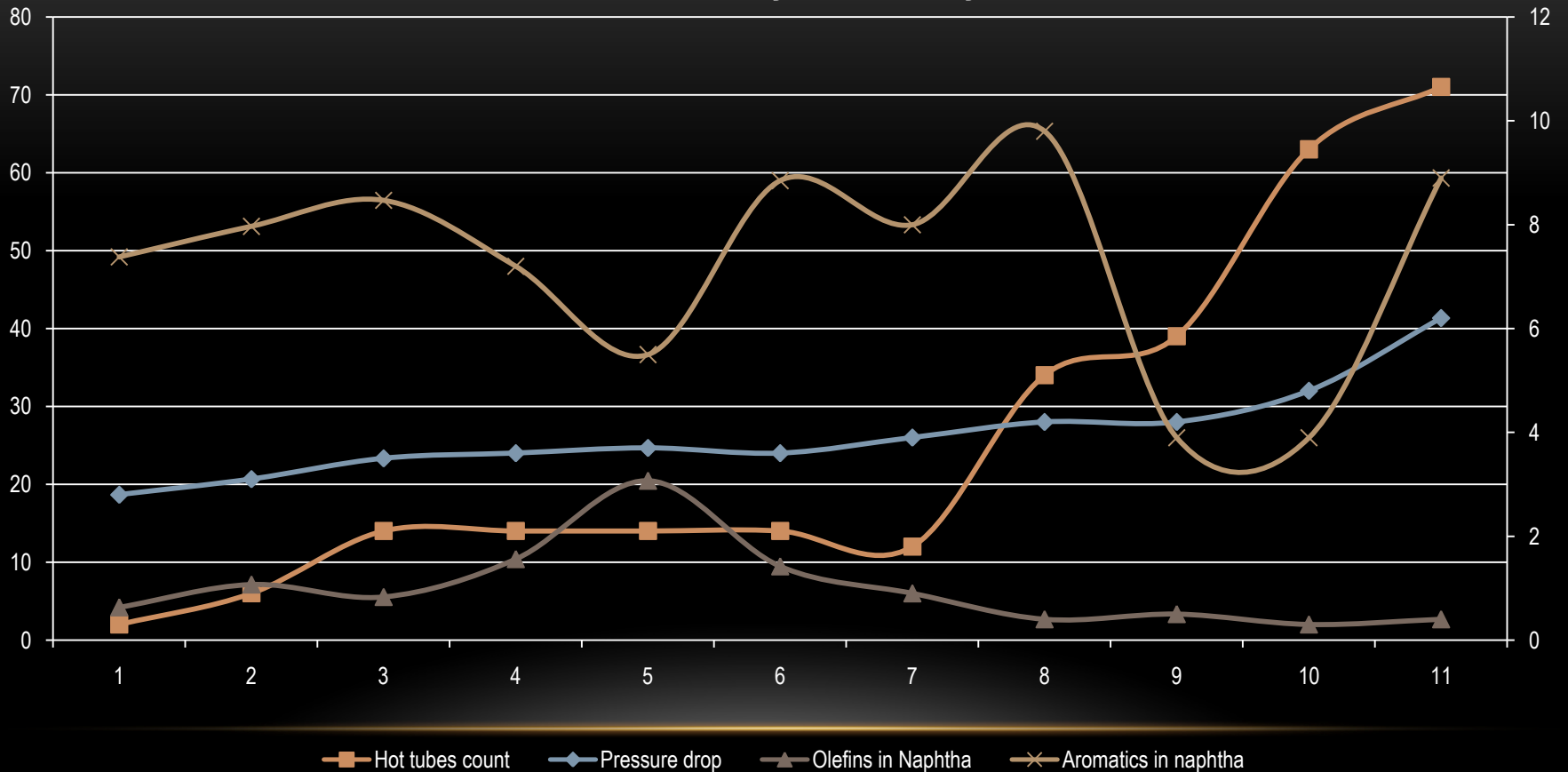
**14**

**25**

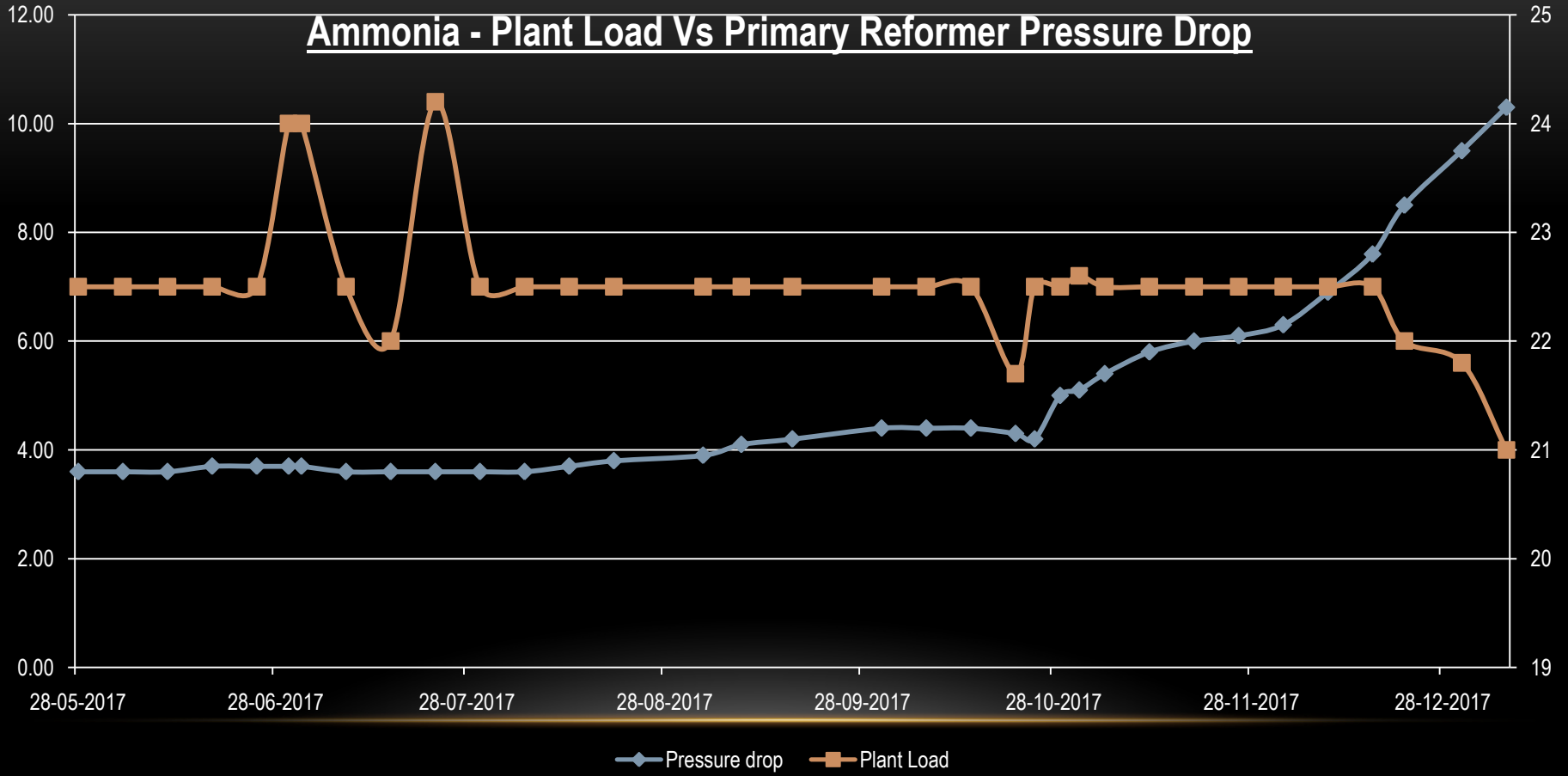
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**5**

# Ammonia - Naphtha Quality Vs Primary Reformer



# Ammonia - Plant Load Vs Primary Reformer Pressure Drop



# SUMMARY OF OBSERVATIONS

1. Hot tubes started to appear from March 2017 end and it went up to 76 numbers out of 264 in 10 months
2. Pressure drop started at 3.5 Ksc and reached up to 10.5 Ksc. Increase of 7 ksc in 10 months
3. Plant load was 22.5 TPH Naphtha, predominantly
4. Increased inlet pressure due to abnormal pressure drop resulted in limiting the plant load
5. Increased steam consumption to manage the situation resulting in higher energy consumption
6. Hot bands were prevailing in the bottom half where less or non-potash catalyst is present

# Action Plan

- 1. Stopping the plant in January 2018**
- 2. Replacement of catalyst through catalyst loading mechanism**
- 3. Tubes internal & external cleaning**
- 4. Tubes inspection**
- 5. Catalyst inspection and analysis**
- 6. Total duration of 12 days**



# OBSERVATIONS after Stoppage

- Average pressure drop in each tube before commissioning was 0.936 Ksc and after processing 10 months during removal it was 1.107 Ksc. An increase of 0.1827 Ksc which is about 18%.
- Black colouration over the catalyst layer was noticed in the top layer catalyst up to 2 meters.
- Out of 264 tubes, DP could not be checked in 4 tubes (G33, H31, H32 & H33) as air was backing up.
- Catalyst removal was not easy in many tubes between 3 to 5 meters.

# Catalyst Samples

Table 1: List of samples collected

## Reformer spent catalyst Sample details - SPIC

S No	Tube #	Elevation	Category
1	B2	Top	Cold
2	B2	1	Cold
3	B2	2	Cold
4	B2	3	Cold
5	B2	4	Cold
6	B2	5	Cold
7	B2	6	Cold
8	B2	7	Cold
9	B2	8	Cold
10	B2	9	Cold
11	B2	10	Cold
12	B2	11	Cold
13	B2	12	Cold
14	B2	13	Cold

S No	Tube #	Elevation	Category
15	H29	Top	High DIP
16	H29	1	High DIP
17	H29	2	High DIP
18	H29	3	High DIP
19	H29	4	High DIP
20	H29	5	High DIP
21	H29	6	High DIP
22	H29	7	High DIP
23	H29	8	High DIP
24	H29	9	High DIP
25	H29	10	High DIP
26	H29	11	High DIP
27	H29	12	High DIP

S No	Tube #	Elevation	Category
28	F22	Top	Hot
29	F22	1	Hot
30	F22	2	Hot
31	F22	3	Hot
32	F22	4	Hot
33	F22	5	Hot
34	F22	6	Hot
35	F22	7	Hot
36	F22	8	Hot
37	F22	9	Hot
38	F22	10	Hot
39	F22	11	Hot
40	F22	12	Hot
41	F22	Bottom	Hot

S No	Tube #	Elevation	Category
42	H33	Top	High DP
43	H33	1	High DP
44	H33	2	High DP
45	H33	3	High DP
46	H33	4	High DP
47	H33	5	High DP
48	H33	6	High DP
49	H33	7	High DP
50	H33	8	High DP
51	H33	9	High DP
52	H33	10	High DP
53	H33	11	High DP
54	H33	12	High DP
55	H33	Bottom	High DP

S No	Tube #	Elevation	Category
56	G33	Top	Cold
57	G33	2	Cold
58	G33	4	Cold
59	G33	6	Cold
60	G33	8	Cold
61	G33	10	Cold
62	G33	12	Cold
63	G33	Bottom	Cold

S No	Tube #	Elevation	Category
64	D15	Top	Hot
65	D15	2	Hot
66	D15	4	Hot
67	D15	6	Hot
68	D15	8	Hot
69	D15	10	Hot
70	D15	12	Hot
71	D15	Bottom	Hot

S No	Tube #	Elevation	Category
72	Catalyst dust collected during unloading		



# Spent Catalyst Analysis Report

*Based on the analysis observations, the most likely sequence of events is that, during certain periods, insufficient naphtha conversion has been achieved in the upper 60% of the reformer tube compared with the previous double decker loading. This is likely due to the use of low potash catalyst in the mid-section and further worsened by some slight deviations in naphtha composition and some poisoning of the catalyst at the inlet. The unconverted higher hydrocarbons slipping into the hotter part of the tube (lower 40%) appear to have cracked across the catalyst in the lower part of the tube, forming whisker carbon. This appears to have lifted nickel off the surface of the catalyst, causing deactivation and hot banding on the tubes. It has also likely created the rough service texture left behind, causing some weakening of the pellets and the build of some dust and, consequently, increasing pressure drop.*

# REFORMER – 2 Layer Catalyst

1. **Top Layer** - 23% Ni, 7% K<sub>2</sub>O - 60% Volume
2. **Bottom Layer** - 16% Ni, 0 % K<sub>2</sub>O - 40% Volume

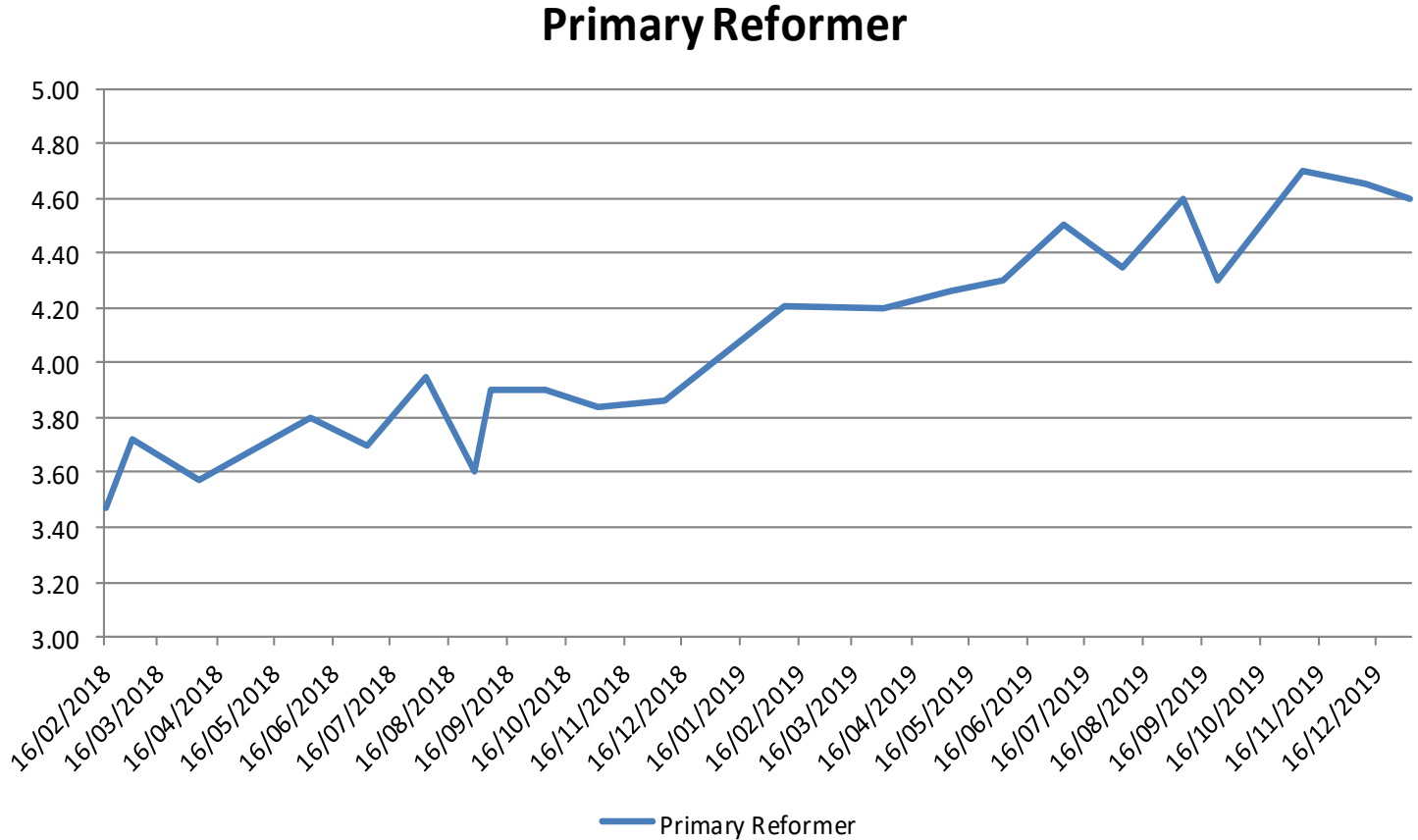
We have considered the following cases to simulate the performance of primary reformer catalysts:

- Case 1 – Plant operates on 100% naphtha from SOR to EOR (5 years)
- Case 2 – Plant operates on naphtha + natural gas. For this case, out of total feedstock flow of 9156 Nm<sup>3</sup>/hr, we have considered 20% of NG flow (1831 Nm<sup>3</sup>/hr) + 80% of naphtha (7325 Nm<sup>3</sup>/hr). The maximum allowable natural gas is 20% of the total feed stock on molar basis i.e., % {natural gas/(natural gas + naphtha)}

For case 2 (naphtha + NG) the inlet, steam to carbon and exit conditions were considered same as case 1.

# REFORMER – CASE STUDY

Date	Primary Reformer
16/02/2018	3.47
02/03/2018	3.72
06/04/2018	3.57
04/06/2018	3.80
04/07/2018	3.70
03/08/2018	3.95
29/08/2018	3.60
07/09/2018	3.90
05/10/2018	3.90
02/11/2018	3.84
07/12/2018	3.86
08/02/2019	4.21
01/04/2019	4.20
06/05/2019	4.26
03/06/2019	4.30
05/07/2019	4.50
05/08/2019	4.35
05/09/2019	4.60
24/09/2019	4.30
07/11/2019	4.70
10/12/2019	4.65
03/01/2020	4.60



# REFORMER – CASE STUDY

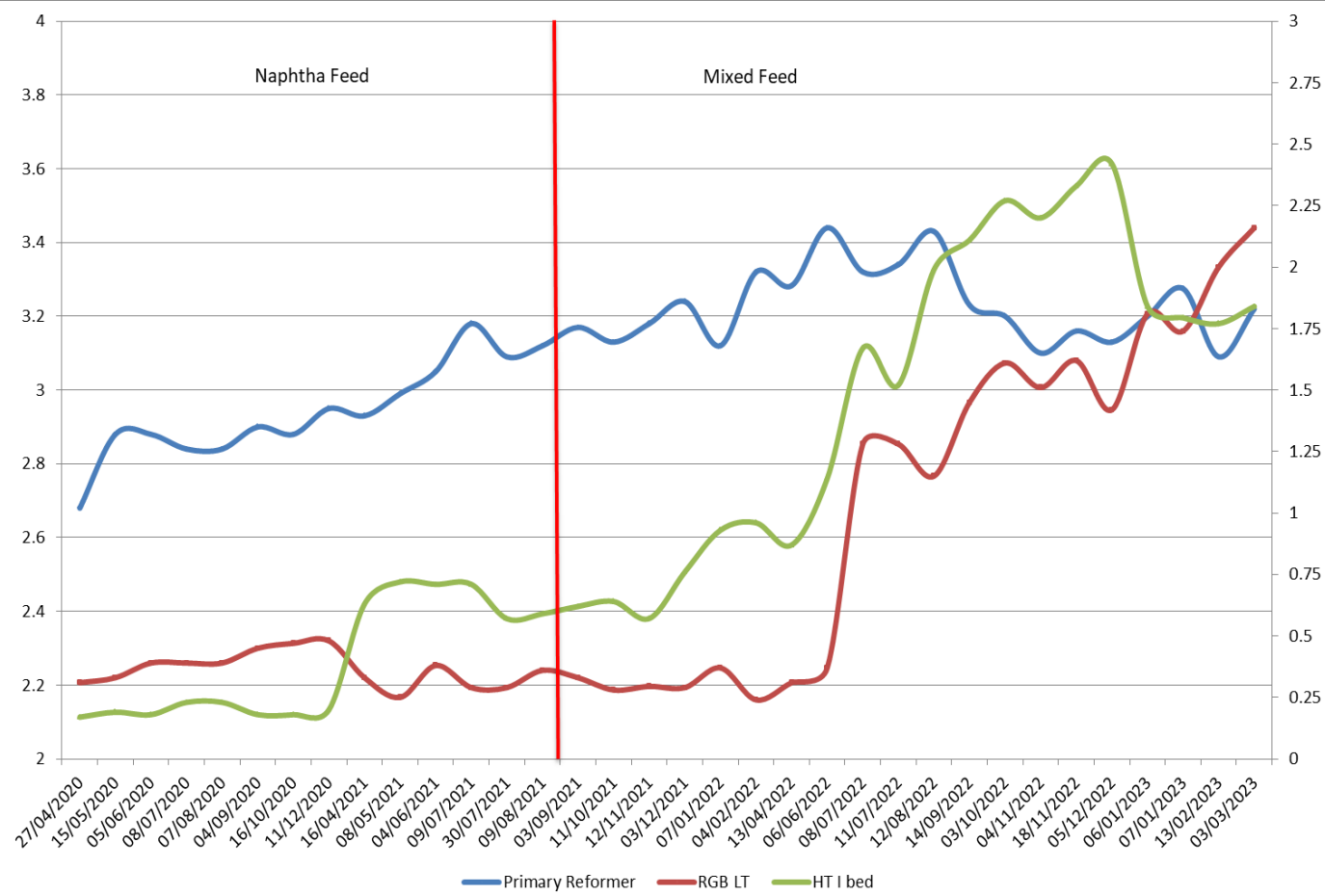
Catalyst Vessel	Supplier	Quantity (m3)	Charged On	Replaced on	Life (Months)
Primary reformer	A	17.88	Apr-04	Apr-07	36
		11.88			
	B	17.80	Oct-10	Mar-17	78
		11.60			
	X	11.20	Mar-17	Jan-18	10
		5.60			
		11.20			
	X	16.80	Jan-18	Apr-20	27
		11.20			

# REFORMER – CASE STUDY

1. Catalyst received from Supplier – x was in service from 2018 to 2020
2. As bulk of outlet pigtail replacement was planned in 2020, catalyst replacement was needed
3. As the possibility of Mixed Feed operation was still there and considering various other factors Catalyst Procurement was done from Supplier – B instead of Supplier – X
4. Plant started to process NG as feed from end of August 2021
5. Since then till today Plant is being operated with **MIXED FEED**

# REFORMER – CASE STUDY

Pressure Drop Data (Kg/cm2)				
Date	Primary Reformer	RGB LT	HT I bed	
27/04/2020	2.68	0.31	0.17	
15/05/2020	2.88	0.33	0.19	
05/06/2020	2.88	0.39	0.18	
08/07/2020	2.84	0.39	0.23	
07/08/2020	2.84	0.39	0.23	
04/09/2020	2.90	0.45	0.18	
16/10/2020	2.88	0.47	0.18	
11/12/2020	2.95	0.48	0.20	
16/04/2021	2.93	0.33	0.63	
08/05/2021	2.99	0.25	0.72	
04/06/2021	3.05	0.38	0.71	
09/07/2021	3.18	0.29	0.71	
30/07/2021	3.09	0.29	0.57	
09/08/2021	3.12	0.36	0.59	
03/09/2021	3.17	0.33	0.62	
11/10/2021	3.13	0.28	0.64	
12/11/2021	3.18	0.29	0.57	
03/12/2021	3.24	0.29	0.76	
07/01/2022	3.12	0.37	0.93	
04/02/2022	3.32	0.24	0.96	
13/04/2022	3.28	0.31	0.87	
06/06/2022	3.44	0.37	1.14	
08/07/2022	3.32	1.28	1.67	
11/07/2022	3.34	1.28	1.52	
12/08/2022	3.43	1.15	1.99	
14/09/2022	3.23	1.45	2.11	
03/10/2022	3.20	1.61	2.27	
04/11/2022	3.10	1.51	2.20	
18/11/2022	3.16	1.62	2.33	
05/12/2022	3.13	1.42	2.42	
06/01/2023	3.20	1.81	1.84	
07/01/2023	3.28	1.74	1.79	
13/02/2023	3.09	2.00	1.77	
03/03/2023	3.22	2.16	1.84	

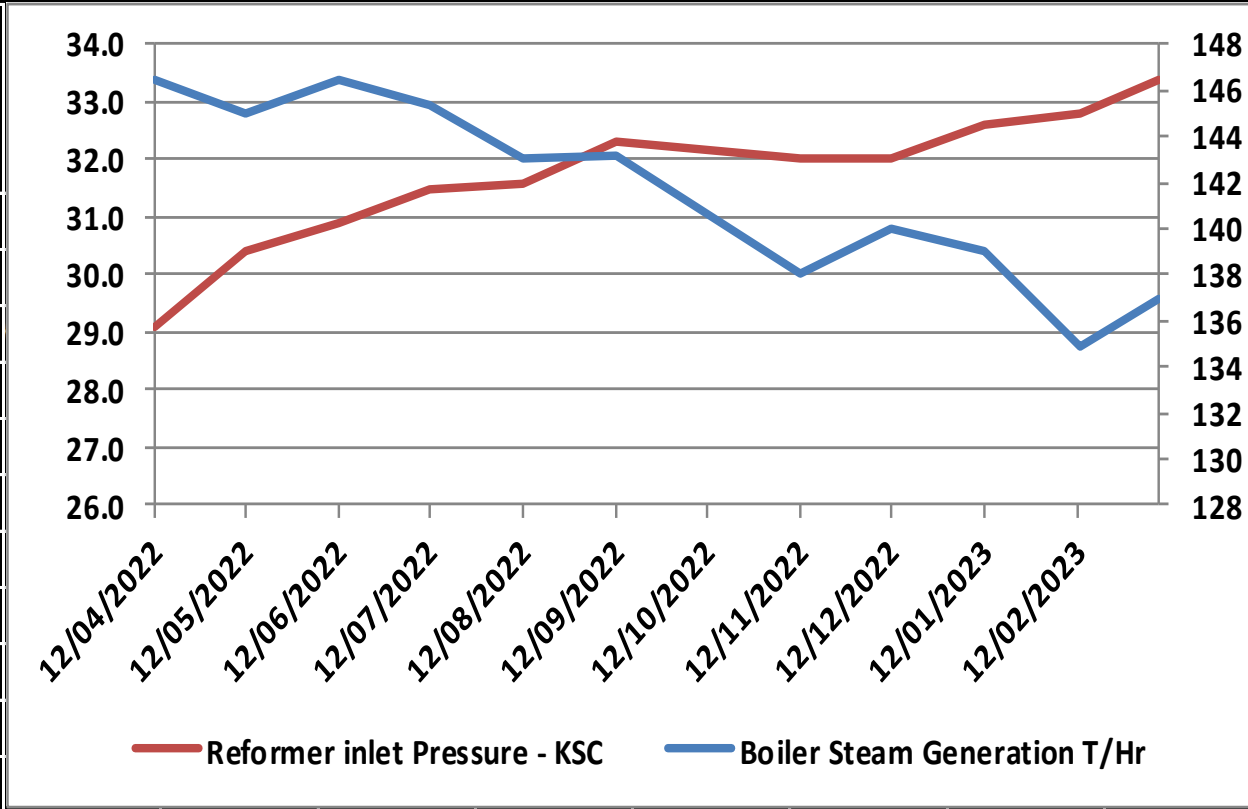




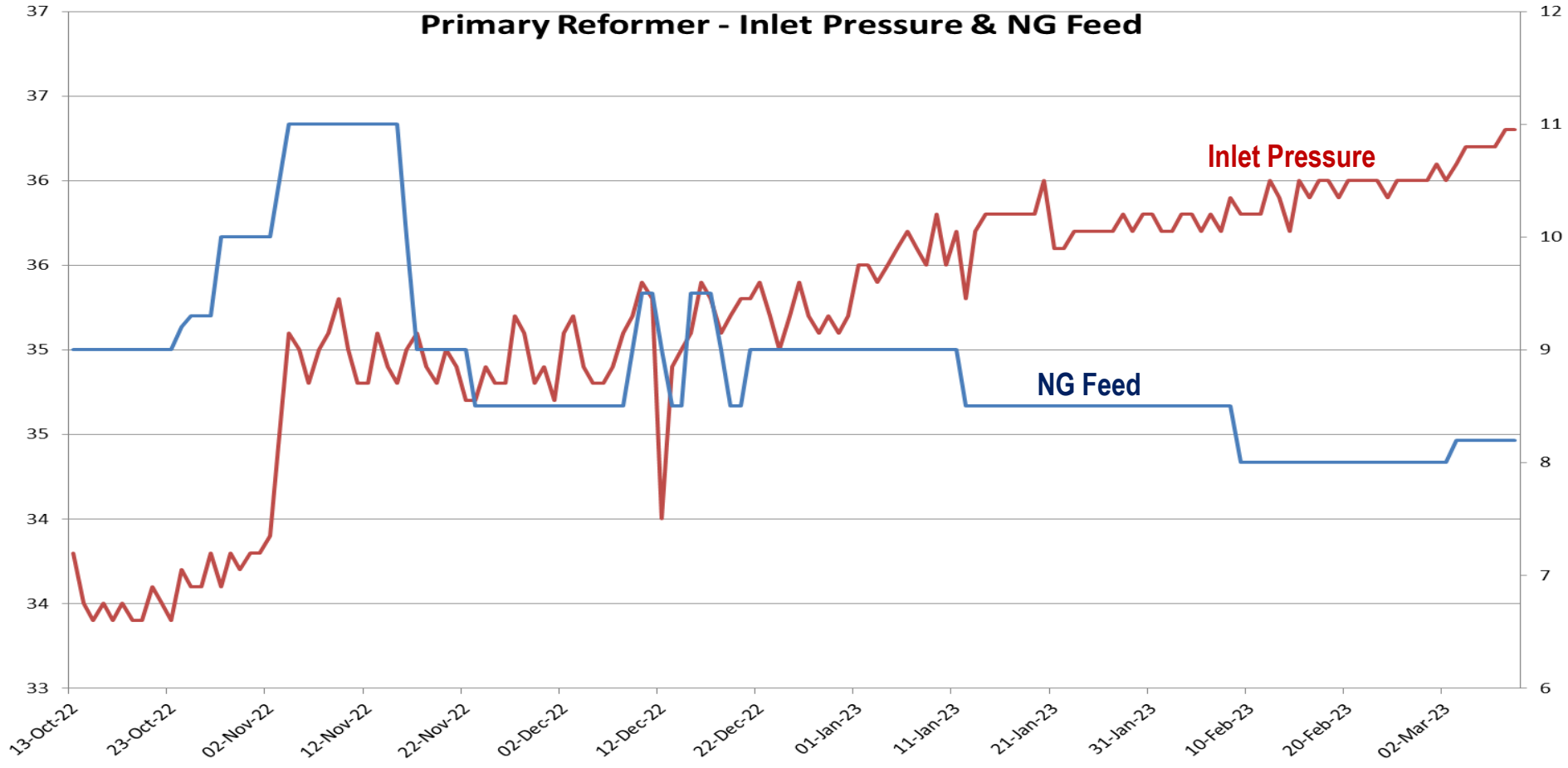
# REFORMER – CASE STUDY

## Effect of Fouling in RGB and high Pressure Drop in Boiler & HT shift

Date	Boiler Steam Generation T/Hr	Reformer inlet Pressure - KSC
12/04/2022	147	29.1
12/05/2022	145	30.4
12/06/2022	147	30.9
12/07/2022	145	31.5
12/08/2022	143	31.6
12/09/2022	143	32.3
12/11/2022	138	32.0
12/12/2022	140	32.0
12/01/2023	139	32.6
12/02/2023	135	32.8
10/03/2023	137	33.4



# REFORMER – CASE STUDY



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	X	11.20	Mar-17	Jan-18	10
		5.60			
		11.20			
	X	16.80	Jan-18	Apr-20	27
		11.20			
	B	16.80	Apr-20	Mar-23	35
		11.20			

# SUMMARY OF FAILURE ANALYSIS

- 1. 60% of the High Potash and 40% of Non – Potash Catalyst is the ideal combination for processing Naphtha.**
- 2. 2 Layer Catalyst Combination to process Naphtha can handle up to a maximum of 40% NG, however a low potash Catalyst can not handle Naphtha even for a short period of time**
- 3. Potash leaching is suspected and getting deposited in RGB and HT Shift**

# ACTION PLAN

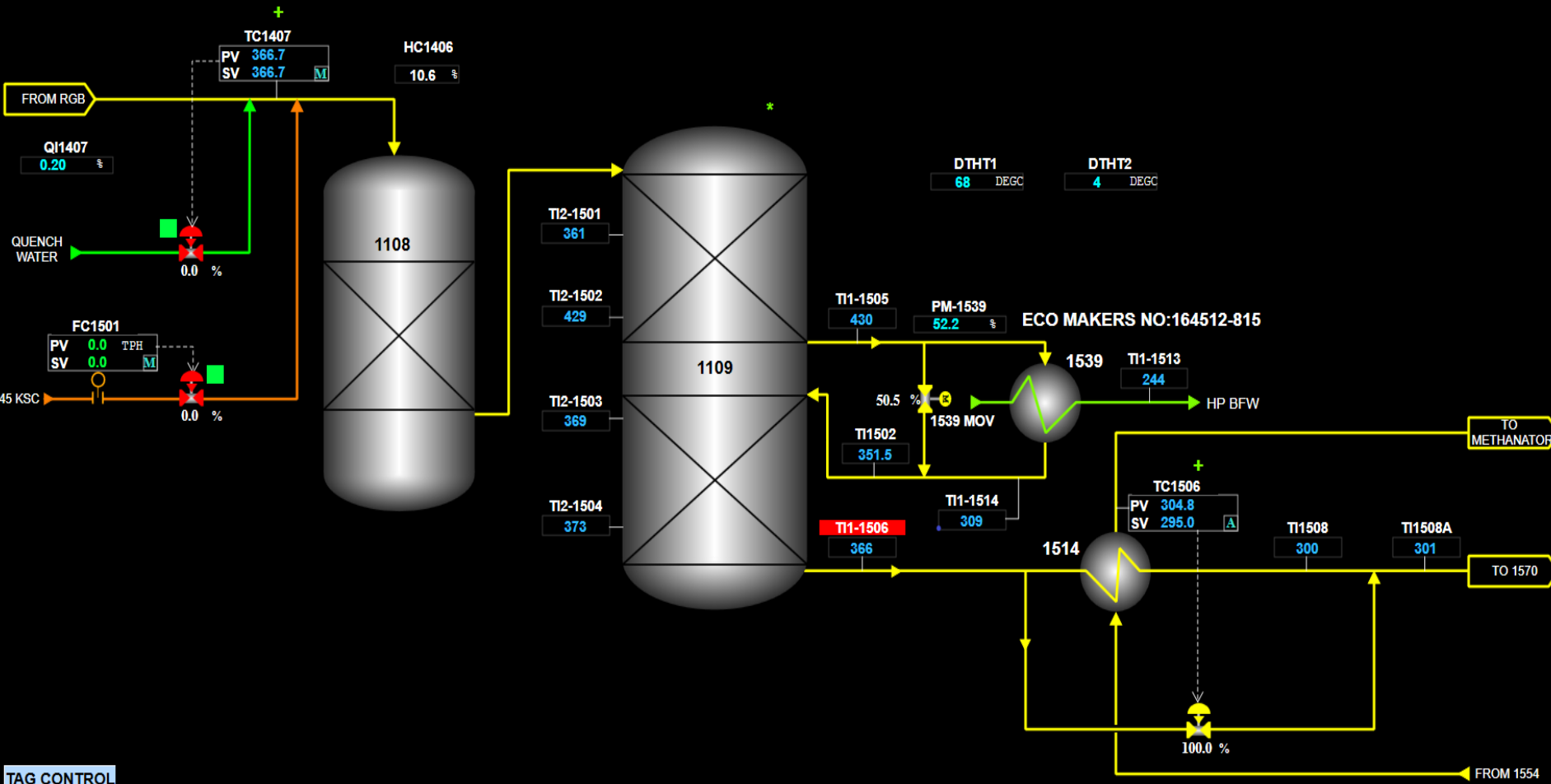
- 1. Cleaning of tubes to be done for Low Temperature compartment of Reformed Gas Boiler.**
- 2. Catalyst Skimming has to be done in HT – Shift Catalyst in the First Bed**

## Request to Catalyst Vendors

**SPIC is still open to have discussions with Catalyst Vendors who can provide the right combination of Primary Reformer Catalyst than can handle both Naphtha and NG at any proportion without affecting its performance and the downstream sections.**

# Catalyst Upset – Case Study

1. **Primary Reformer Catalyst**
  2. **High Temperature Shift Catalyst**
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TAG CONTROL

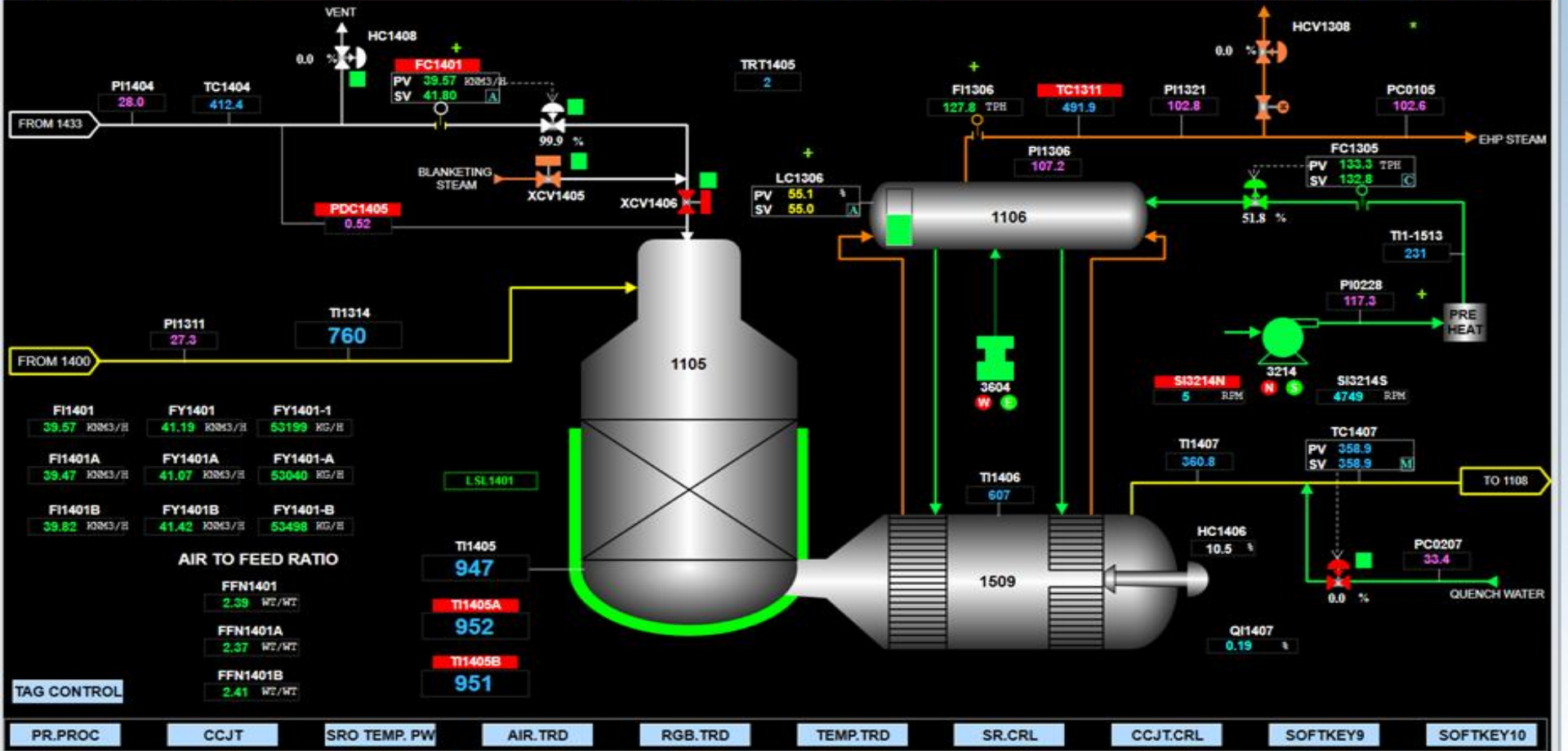


# HT Shift Catalyst

- 1. Chromic Oxide - 8.0%**
- 2. Copper Oxide - 1.8%**
- 3. Ferric Oxide - Balance**
- 4. Shape - Tablet**
- 5. Volume - 36 Kilo Liters**

# Case Study - Sequence of Events

- 1. Plant had to be stopped on Emergency due to vibration in Synthesis Gas Compressor on 15<sup>th</sup> March 2019**
- 2. Reformer Loop purging was completed with Steaming till all the Hydrocarbon and gases are removed**
- 3. Next step was to carryout cooling down operation with Nitrogen Circulation**
- 4. Nitrogen Compressor was lined up and Steam was isolated**
- 5. It is a conventional procedure to keep the Process Air Compressor running for Instrument Air Service and it is charged up to inlet of Process Air Heater.**



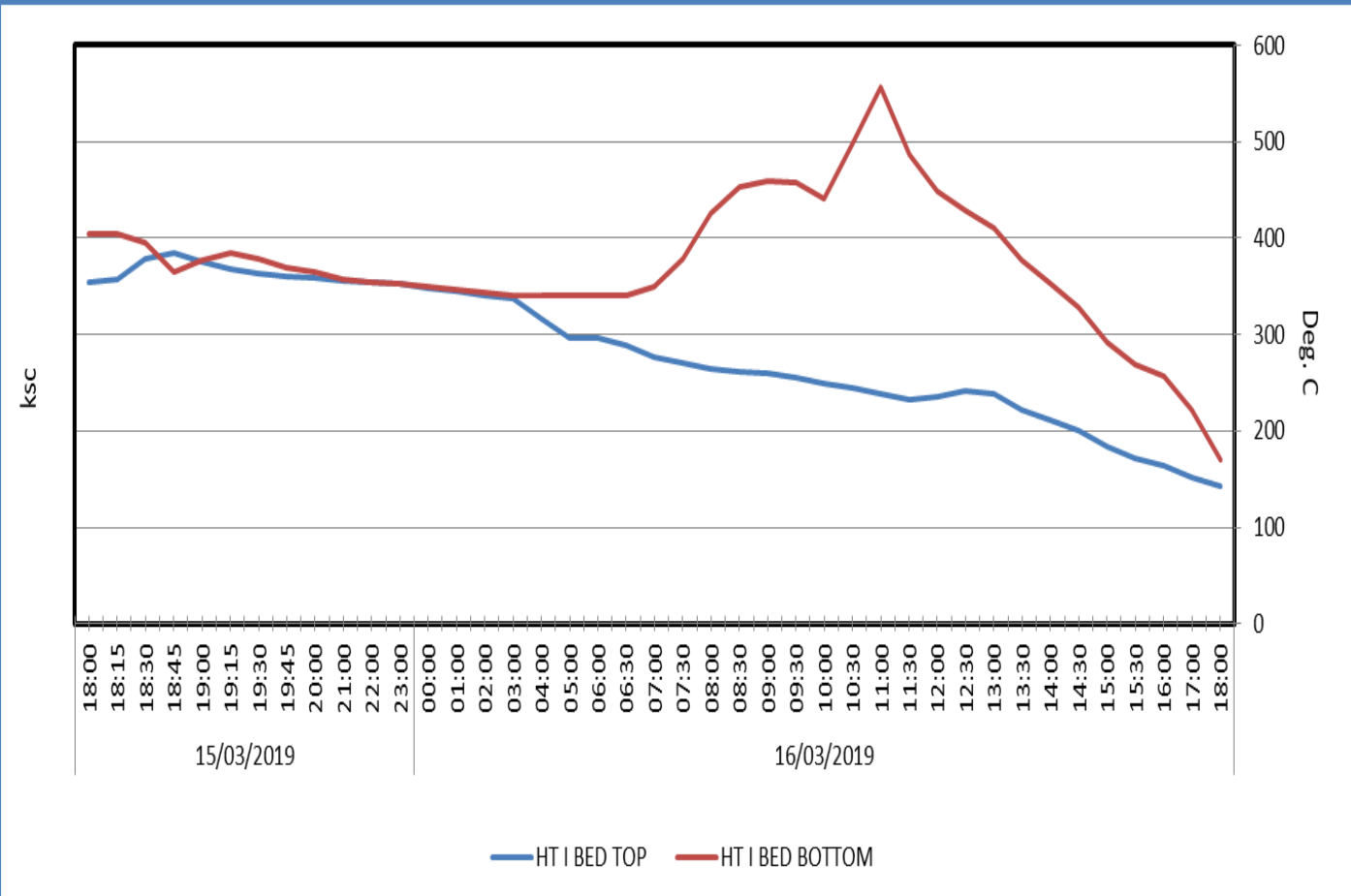
FI1401	FY1401	FY1401-1
39.57 K0M3/B	41.19 K0M3/B	53199 KG/B
FI1401A	FY1401A	FY1401-A
39.47 K0M3/B	41.07 K0M3/B	53040 KG/B
FI1401B	FY1401B	FY1401-B
39.82 K0M3/B	41.42 K0M3/B	53498 KG/B

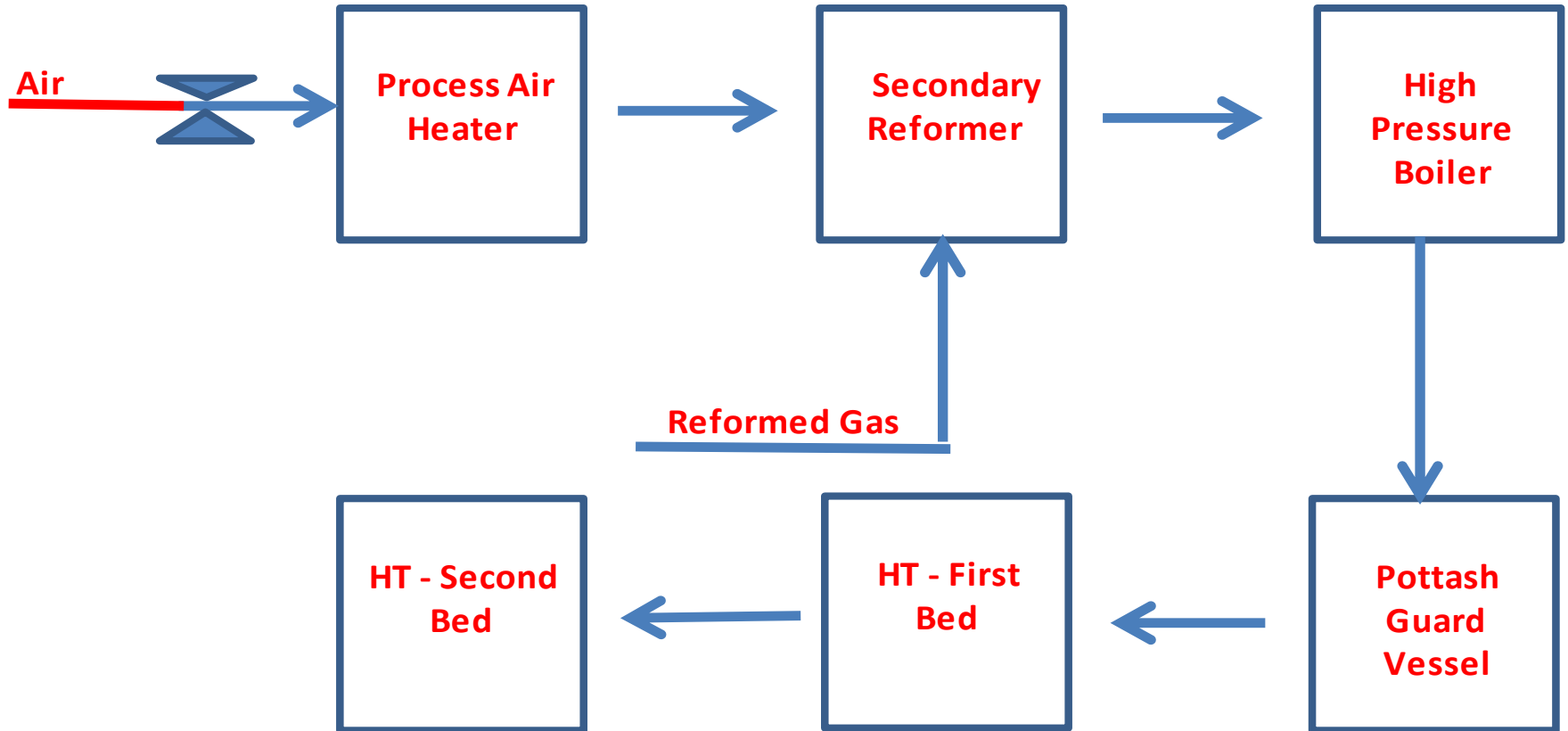
AIR TO FEED RATIO	
FFN1401	2.39 WZ/WZ
FFN1401A	2.37 WZ/WZ
FFN1401B	2.41 WZ/WZ

# Run Away Reaction

TIME	HT-I-TOP	HT-I-BOT
00:00	348	349
01:00	345	346
02:00	341	343
03:00	338	340
04:00	316	340
05:00	297	340
06:00	297	340
06:30	289	341
07:00	277	349
07:30	270	378
08:00	265	426
08:30	262	453
09:00	260	459
09:30	255	457
10:00	249	441
10:30	244	499
11:00	239	556
11:30	233	487
12:00	236	448
12:30	241	428
13:00	238	410
13:30	221	377
14:00	211	352
14:30	200	329
15:00	183	292



# RCA



## Consequence of Upset

- 1. Catalyst activity had reduced by rapid oxidation**
- 2. Inlet Temperature had to be maintained above 375 deg C to sustain the reaction**
- 3. Loading had shifted from First Bed to Second Bed.**
- 4. However the pressure drop was normal**
- 5. Plant had to be operated at optimum load till the next catalyst charge was made ready by Oct 2019**
- 6. Lost the Catalyst life of about 5 years**

# Consequence of Upset

## HISTORICAL HTS CATALYST PERFORMANCE -SPIC

Date	7/5/12	04/03/15	12/10/16	05/06/17	03/02/18	02/07/18	18/02/19	01/04/19	05/07/19
MOS	1	31	74	82	1	6	13	15	18
REPORTED									
Production Rate	1125	1127	1150	1008	1035	1035	1035	1039	1044
HTS Inlet Temp	360	361	364	370	340	342	345	376	376
HTS Outlet Temp	426	420	424	429	406	405	406	436	436
DT Measured, Deg C	66	59	60	59	66	63	61	60	60
DT Calculated, Deg C	65.3	61	53.8	86.9	69.5	66	60.9	61.2	59.2
HTS CO Slip	2.82	3.90	3.83	4.14	2.4	2.62	3.72	3.88	4.13
Delta P HTS	0.54	0.88	0.77	0.72	0.19	0.14	0.67	0.32	0.5
ATE, Deg C	21	65.2	76.9	(-) 0.9	16.3	30.5	79.7	51.0	60.6

## Catalyst Replacement History

HT SHIFT CONVERSION					
Catalyst Vessel	Supplier	Quantity (m3)	Charged On	Replaced on	Life (Months)
HT 1ST bed	B	42.23	Apr-01	Apr-07	72
	B	36.4	Apr-07	Feb-18	89
	B	36	Feb-18	Oct-19	20
	B	36	Oct-19	Mar-23	41



## Learning & Outcome

- 1. Minor Mistakes during a shutdown and startup of an Ammonia Plant can become very costly**
- 2. SOP was modified in such a way that similar mistake do not happen again**
- 3. The Case Study was communicated to the Operation and Maintenance Team for awareness**

## Catalyst Replacement History

Catalytic Vessel	Volume - KL	From	To	Service - Months
Secondary Reformer	26.2	Apr-96	Mar-23	283
Methanator	36.5	Aug-90	Mar-23	351
Converter	54.81	Apr-96	Mar-22	270

## Conclusion

*Life of the Catalyst depends on maintaining better operating conditions and exposure to less process upsets with respect to its parameters outside the limits and eliminating poisonous substance*

THANKS