CHAMBAL FERTILISERS AND CHEMICALS LIMITED

Operating Experience of Shift & Synthesis Convertors Catalysts in Ammonia Plant

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CHAMBAL FERTILISERS AND CHEMICALS LIMITED

Agenda

- About Chambal Fertilisers and Chemical Limited (CFCL)
- Plants overview at CFCL
- Brief narrative of Ammonia Plant
- Brief narrative of Shift Convertors Catalysts with case study
- Brief narrative of Synthesis Convertor Catalyst with case study

About CFCL

- Flagship company of K.K. Birla group.
- Located at Gadepan 35 km from Kota on NH-76
- Total land acquired about 400 Hectares out of which 34.75% is covered with green belt.
- Three Nitrogenous Fertilizer Manufacturing Units at Gadepan, Kota (Rajasthan)
- Largest private sector fertilizer complex in India with capability of 3.4 MMTY Urea.
- The Company has a vast marketing network comprising 15 regional offices, 2,200 dealers and 22,000 village level outlets.

CFCL Plants Overview

	Ammonia plant	Urea plant
CFCL – I Jan 1994	Haldor Topsoe, Denmark Reassess :1520 MTPD Revamp : 1767 MTPD	Snamprogetti, Italy Reassess :2620 MTPD Revamp : 3100 MTPD
CFCL – II Oct 1999	KBR, USA Reassess :1520 MTPD Revamp : 1710 MTPD	Toyo, Japan Reassess :2620 MTPD Revamp : 3000 MTPD
CFCL – III Jan 2019	KBR, USA Design : 2200 MTPD	TOYO, Japan Design :4000 MTPD

Brief narrative of Ammonia Plants

A. Desulfurization of the NG feed: Sulfur removal from NG gas feed by using de-sulfurizer.

B. Synthesis Gas Production:

1. Primary and Secondary Reforming- Steam Reforming
2. CO Conversion to CO2 – **Water Gas Shift Reaction**

C. Synthesis Gas Purification

1. Carbon Dioxide Removal
2. Carbon Oxide Conversion to Methane – Methanation

D. Ammonia Synthesis and Refrigeration

1. Syngas Compression
2. Conversion of Synthesis Gas to Ammonia
3. Refrigeration and Product Separation

Water Gas Shift Reaction

WGSR is the reaction of an equimolar mixture of Steam and Carbon Monoxide and the process is moderately exothermic.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \; ; \quad \Delta H^\circ = -41 \text{ kJ/mol}$$

Equimolar Exothermic

It is an important step in the overall process as it provides a source of hydrogen at the expense of carbon monoxide, which is important for use in ammonia synthesis.

High Temp. and Low Temp. Shift Reactor

- WGSR is an exothermic equilibrium reaction.
- The equilibrium conversion decreases with increasing temperature. However, the kinetic rate of reaction is favored by high temperature.
- Shift conversion, i.e. conversion of CO to CO2, is done in two steps using a high temperature reaction catalyst which is operated in the kinetic regime and a low temperature reaction catalyst which is operated in the equilibrium regime.

Shift Reaction Catalysts

HTS Reactor

- Cu-promoted Fe-Cr based
- Reaction temperature range: 350-430°C
- Rugged up to temperature ~500°C

LTS Reactor

- Cu-ZnO based as traditional Fe-Cr has low volumetric activity for WGS at low temperatures
- Reaction temperature range: 200-220°C
- Sensitive to temperatures over 230°C

HTS Catalysts at CFCL

Description	CFCL-1	CFCL-2	CFCL-3
Name of catalyst* (Present)	ShiftMax 120	C-12-4	ShiftMax 120
Last recharge	APR-2022	MAY’2013	AUG’2018
Previous recharge	APR’2010	MAY-1999	NA
Volume (M3)	74	70	74

Note: Name of Catalyst mentioned above table is trade name of Catalyst supplier.

HTS Catalyst Poison

- Residual Sulphur: Potent poison for downstream LTS catalyst
- Levels of Chromium (VI) salts: Weakens the catalyst pellet and is also carcinogenic.
- Chlorine content carried over with steam.
- Over-reduction from Fe_3O_4 (active phase) to FeO and Fe at low S/G ratio.
- Fouling due to catalyst dust from upstream secondary reformer.

LTS Catalysts at CFCL

Description	CFCL-1	CFCL-2 (LTG/LTS)	CFCL-3
Name of catalyst* (Present)	LSK-2 +LK-821	LSK-2 +LK-821/ LSK-2 +LK-821	ShiftMax 120
Last recharge	APR-2019	MAY’2021	AUG’2018
Previous recharge	APR’2012	March 2015/ MAY-2013	NA
Volume (M3)	109.8	23/70	117

Note: Name of Catalyst mentioned above table is trade name of Catalyst supplier.

LTS Catalyst Poison

- Sulphur from upstream HTS catalyst.
- Chlorine content carried over with steam.
- Condensation of steam:
  - Significant strength reduction
  - Catalyst deactivation
  - Thermal shock
  - Catalyst breakage blocking active sites and increasing pressure drop.
  - Leaching of other catalyst poisons.

Key Parameters monitored in CFCL

- %CO slip at HTS and LTS outlet.
- Overall Delta T across the reactors
- Temperature Profile across the reactor bed.
- Differential pressure across the reactors.
- Approach to equilibrium (ATE) monitored as per Catalyst evaluation report provided Catalyst suppliers.

WETTING OF LTS CATALYST IN AMMONIA-2 PLANT
A CASE STUDY

Case Study- Wetting of LTS Catalyst

NORMAL OPERATION

- To operate in the equilibrium regime, high temperature shift gas from HTS (424°C) is cooled down in **shift waste heat steam generators** (AEA-302A/B) before entering LTS at an inlet temperature of 200°C.
- Boiler Feed Water, at a pressure of 115 kg/cm2g and temperature of 176°C, enters through the tube side of BFW preheater after absorbing heat from the HTS outlet shift gas and is fed to RGB steam drum at a temperature of 315°C.
- The process gas enters LTS at an inlet temperature of ~200°C and leaves at a temperature of ~217°C with %CO slip at outlet to be 0.12%.

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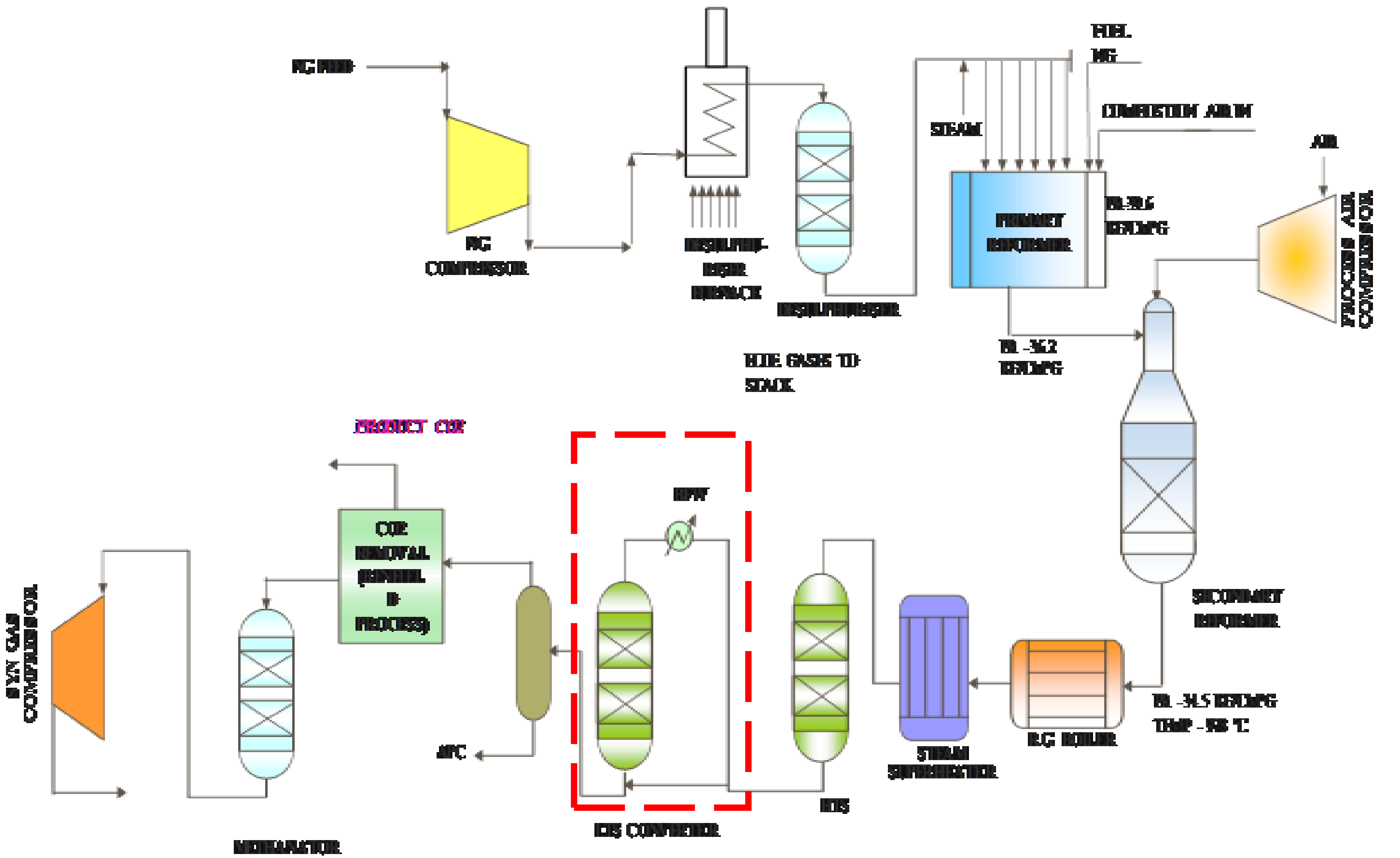
AMMONIA - 2 PROCESS FLOW BLOCK DIAGRAMS (KELLOGG PROCESS)



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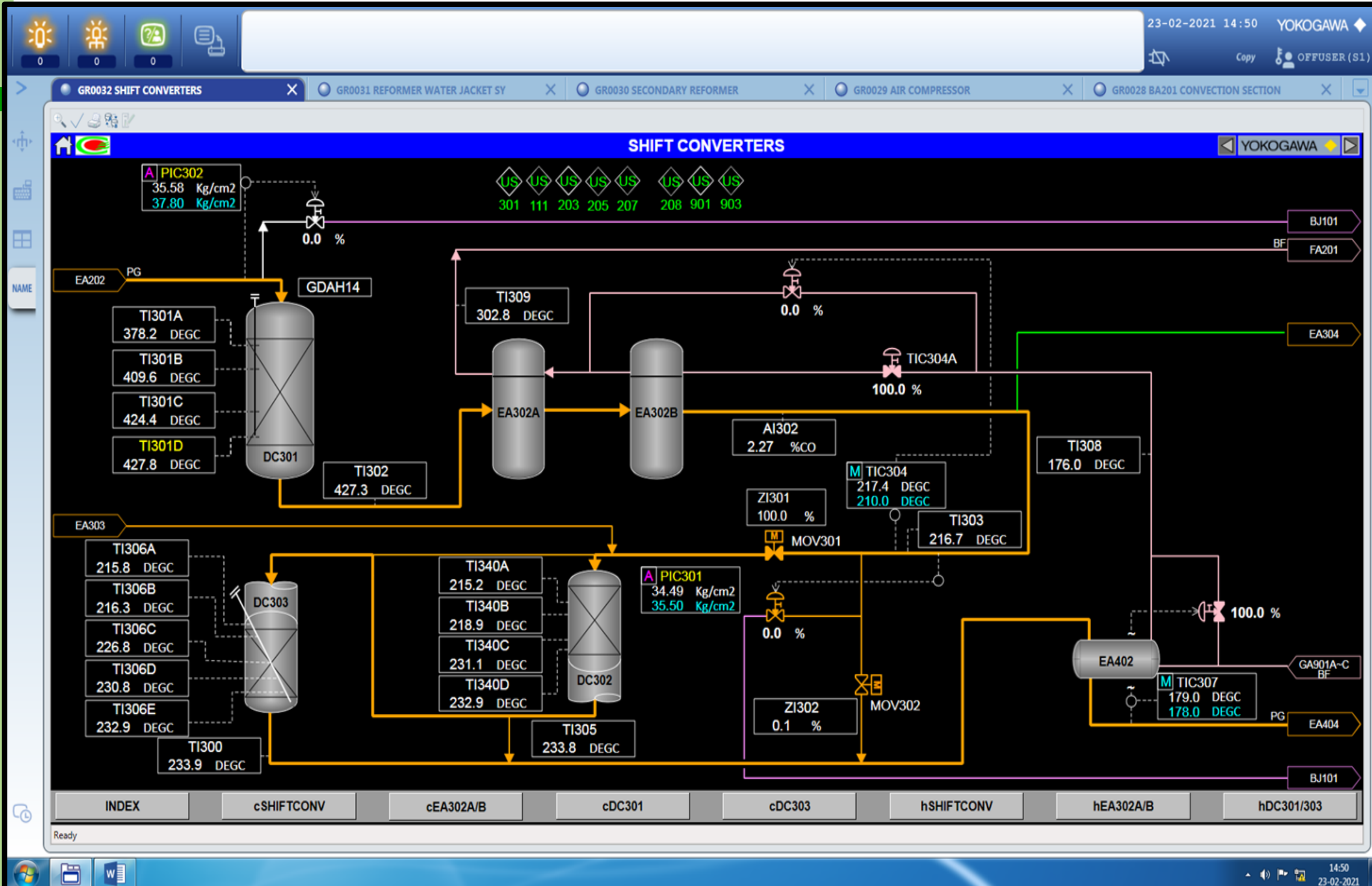

Amm-2 Shift Conversion section schematic

OBSERVATIONS IN 2015

- LTS inlet (outlet of EA302A/B) temperature of the process gas started to decrease gradually.
- Despite of a lower inlet temperature, the CO slip at LTS/LTG slip had dropped down from 0.16% to 0.14%.
- Downstream CO2 Removal unit (Benfield section) seemed to picking up a lot of surplus heat.
- The total Ammonia process condensate flow had increased from 80 m3/hr. to 100 m3/hr.
- All points highlighted that a leakage had occurred in AEA302A/B exchangers causing BFW ingress in process gas.

ACTIONS TAKEN

- AEA302B upstream BFW inlet valve was throttled and its bypass valve TIC 304 was opened.
- Throttling of BFW flow to front end.
- Reduction of protection steam and S/C ratio from 3.46 to 3.35.
- Increase in HTS inlet temperature.
- Increase in BFW temperature at Deaerator outlet.

IMPACT

- LTS inlet temp. was sustained for a short span.
- Reduction of overall heat recovery from EA302A/B
- Increased heat load in CO2 Removal section
- Reduction of overall steam production from RGB

Final Impact

- LTG/LTS temperatures continued to drop over the course of the next two months and eventually the LTG temperature profile started to succumb as well.
- Increase in Process gas dew point (from 178 ^{0}C to 184 ^{0}C) leading to moisture condensation and deactivating the catalyst.
- Higher CO slip at the LTS/LTG outlet.

Description	Tag	21.07.15	21.08.15	07.09.15	06.10.15	15.11.15	24.11.15
RGB STM GEN	FI921	250.4	257	247.7	243.1	229.9	233.6
EA302A BFW O/L TEMP	TI309	308.9	315.5	316.1	308.7	304.1	311.7
EA 402 PG O/L TEMP	TIC307	177.8	176.4	177.6	179.3	179.6	180.8
APC FLOW TO OSBL	FI901	83.8	87.8	77.8	92.8	105.6	93.7
LTS/LTG I/L TEMP.	TI303	199.5	200.3	200.4	198.6	194.6	187.9
LTG O/L TEMP.	TI305	216	215.6	215.3	214.5	215.4	201.7
LTS O/L TEMP.	TI300	216	216.7	216.3	215.6	216	196.9

Final Steps Taken to Sustain Plant Operation

- To prevent further loss of activity and catalyst damage, it was decided to sacrifice the LTG and place it in series combination with LTS (rather than the usual parallel combination).
- Attempt to place them in series did not prove to be successful
- Eventually, the entire exotherm of shift reaction got killed
- CO slip increased rapidly with Methanator on course for the runaway reaction.
- Finally, safe shut down of the plant was taken .

Root Cause Analysis &Troubleshooting

- Debris deposition on tubes (EA-302A/B) was found to be the main cause of tube rupture.
- Moisture due to seepage of BFW over catalyst in LTG/LTS caused temporary oxidation of catalyst rendering it partially inactive.
- Prior to plant startup, to get rid of the temporary oxidation, the catalyst was slow heated and reduced with the help of syngas for moisture recovery from it.
- The leaky tubes in EA302A/B were plugged.
- Post plant start up, the catalyst performance was deemed satisfactory, though the exotherm had shifted downwards on the LTG bed.
- Loading was shifted from 75:25 to nearly 78:22 in LTS/LTG to maintain a satisfactory combined CO slip at the outlet.

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Recurrence of Leakage in Tubes of LTG/LTS in 2021

- Total charge of LTS and LTG catalyst has been replaced in TAR of April 2021.

- After start-up, gradual decrease in LTG/LTS inlet temp. was observed with similar symptoms indicating tube leakage in EA302A/B though the rate did not seem as severe as that in 2015.

- The BFW flow distribution to front-end and back-end was adjusted and it was ensured that LTG/LTS inlet temperature remained above the dew point by 8-10°C.

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Recurrence of Leakage in Tubes of LTG/LTS in 2021 Contd.

- Energy loss of ~ 3 Gcal/hr. was observed due to excessive heat dumping in the Benfield section. However, plant operations were sustained for the entire year and planned shutdown was taken in Feb-2022.
- Prior to plant startup, the catalyst was slow heated and reduced with the help of syngas for moisture recovery from it.
- We were able to restore the entire activity of the catalysts and the performance of the catalyst had been deemed excellent.

Long-Lasting Solution

- It has been planned to replace the tube bundle of EA-302A/B from alloy steel to SS metallurgy in view of resistance to corrosion.

AMMONIA SYNTHESIS CATALYST

Ammonia Synthesis

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4\,kJ/mol$$

- Favoured by high pressure and low temperature.
- However, reaction rate is enhanced at high temperature.
- Pressure range: 140-250 bar; Temperature range: 350-520°C.
- Around ~30% equilibrium conversion obtained in a single pass.
- **Iron catalyst,** along with promoters, is used in industrial processes of ammonia synthesis

Ammonia Catalyst Poisons

- Oxygenated compounds such as water, carbon monoxide and carbon dioxide
- Sulphur, Chlorine, Arsenic and Phosphorous.
- Cracking of Compressor lubrication oil leaking into the process can form carbon which could act as a physical barrier.

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Main Ammonia Synthesis Converter Catalyst in CFCL

Description	CFCL-1	CFCL-2	CFCL-3
Name of catalyst*(Present)	KM1R+KM1 + KM111	KM1R+KM1	AmoMax10R / AmoMax10
Last recharge	OCT-2016	JUN-1999	AUG’2018
Previous recharge	DEC-1993	NA	NA
Volume (M3)	98.2	85.6	114.2

Note: Name of Catalyst mentioned above table is trade name of Catalyst supplier.

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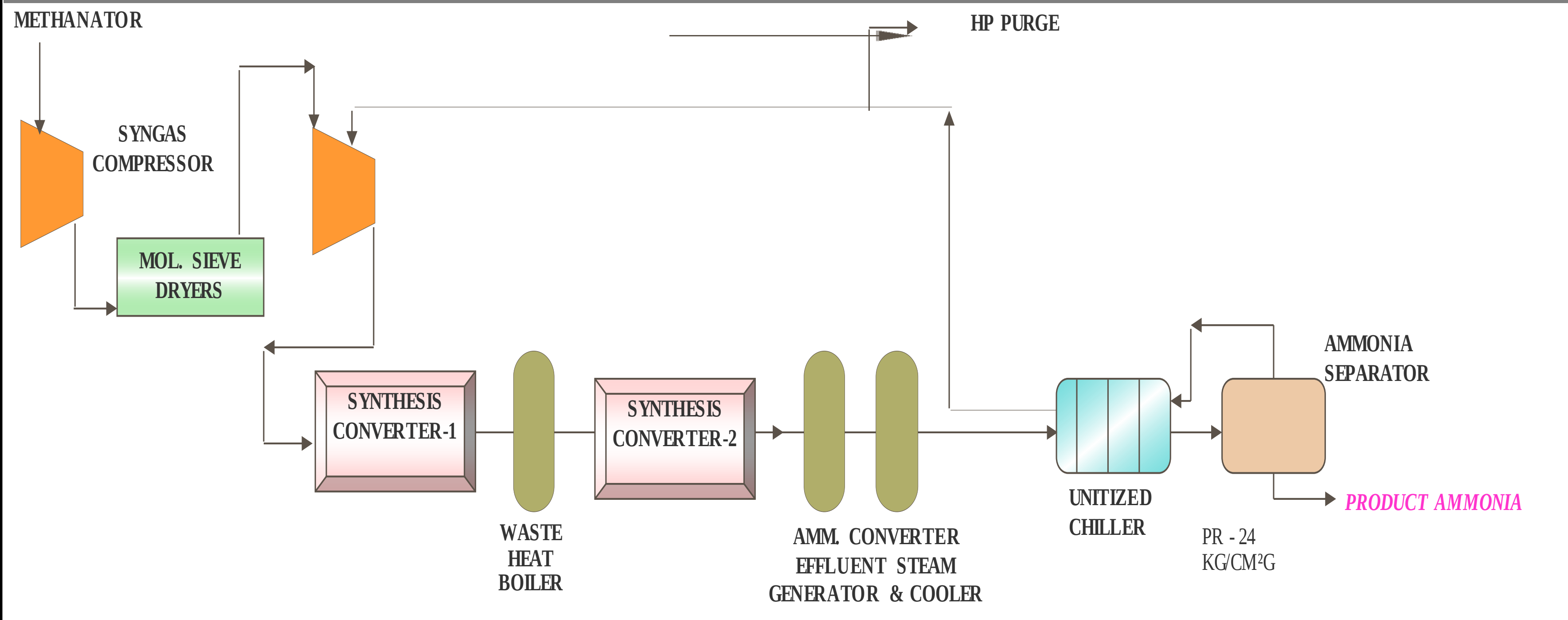
DE-ACTIVATION OF AMMONIA SYNTHESIS CATALYST- A CASE STUDY

Case Study- De-activation of Ammonia Synthesis catalyst

NORMAL OPERATION

- Methanator outlet synthesis gas is compressed in a turbine driven Compressor & discharge of the compressor is directed to the Ammonia Converter.
- After 2nd stage discharge of Synthesis Gas Compressor, the syn gas passes through the Molecular Sieve Dryers to remove remaining moisture
- The syn gas, which has hydrogen & nitrogen in a volumetric ratio of 3:1 and some inerts, is compressed and introduced into the synthesis loop for producing Ammonia.

AMMONIA - 2 PROCESS FLOW BLOCK DIAGRAMS
(KELLOGG PROCESS)



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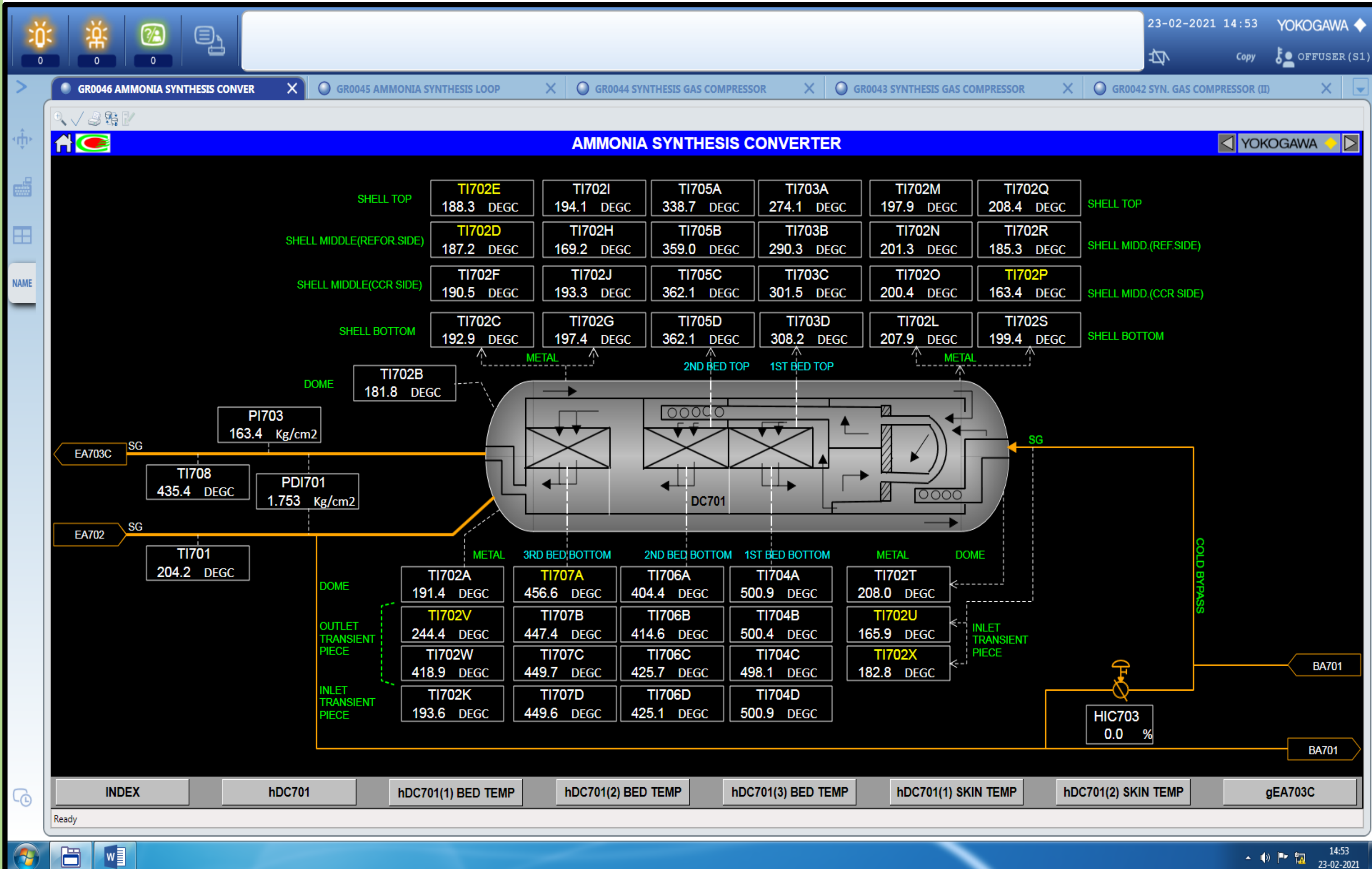
KELLOGG'S HORIZONTAL CONVERTOR



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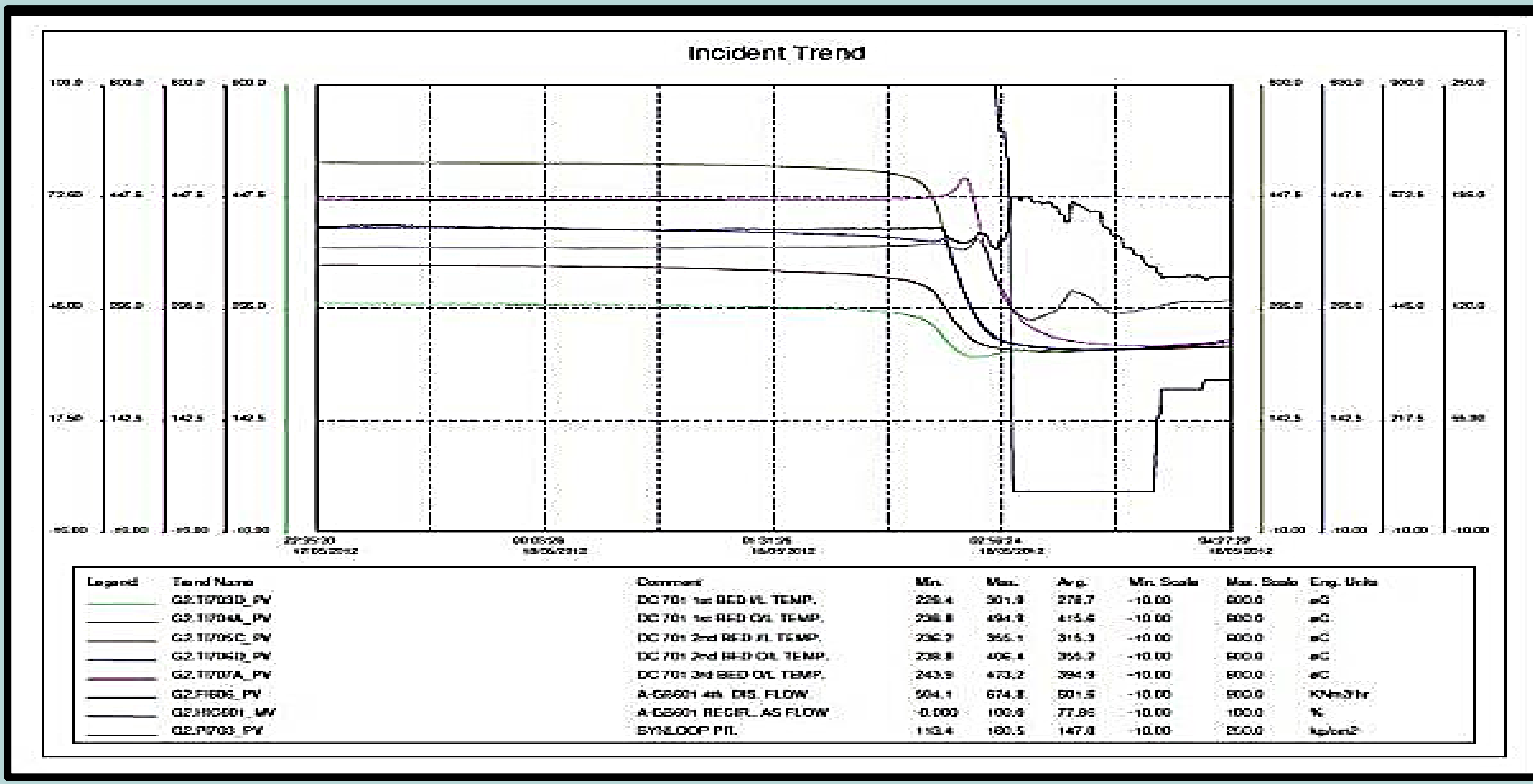
OBSERVATIONS IN 2012

- Ammonia synthesis converter bed temperatures started dropping sharply to the extent of reactor quench.



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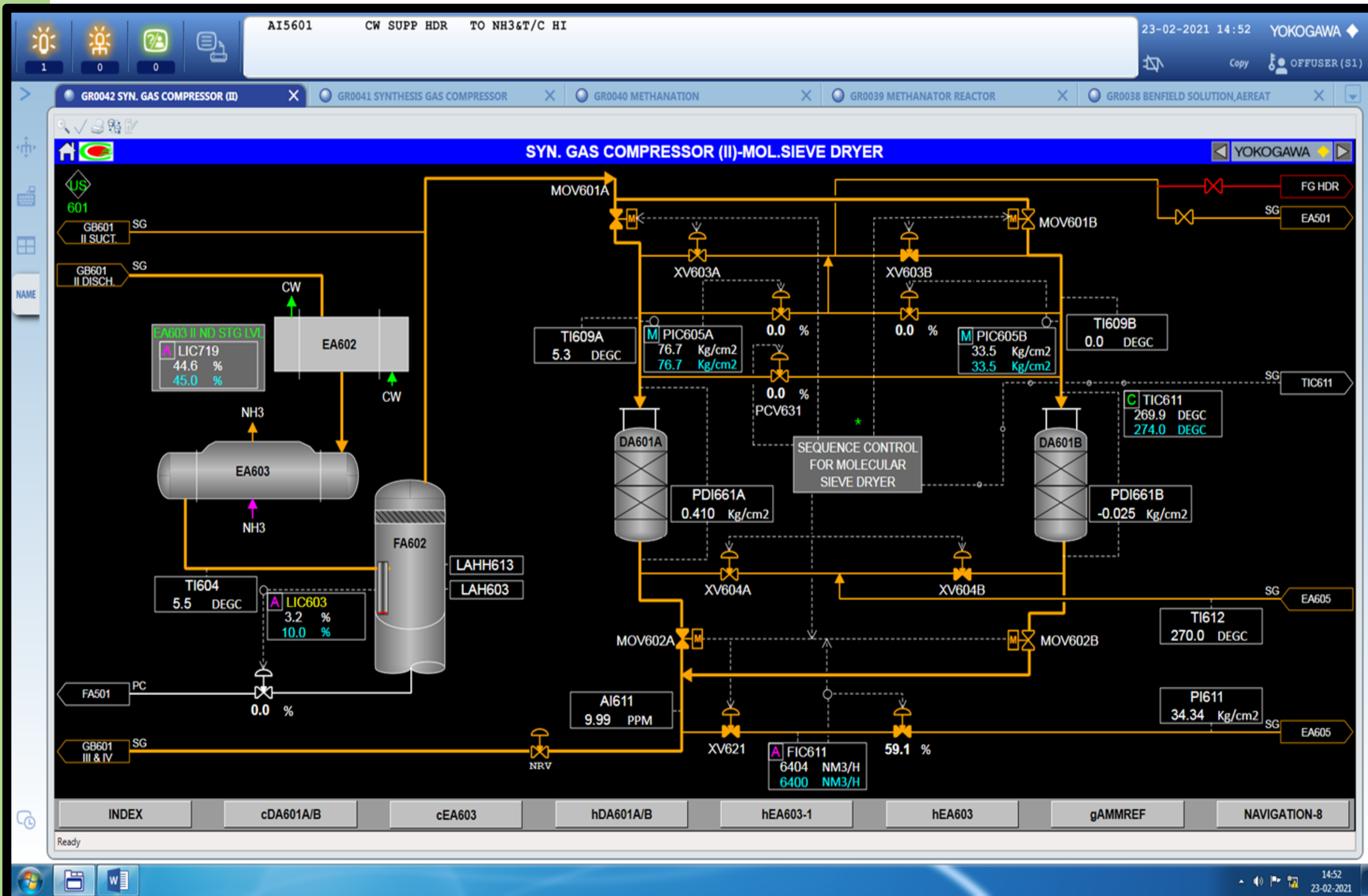

Amm-2 Molecular Sieve Dryers schematic

How did it happen

- Two Molecular Sieve Dryers (DA601A,B) provide continuous drying of the syn gas.
- Each drier is in service while other is being regenerated.
- Problem in Molecular sieve drier (A Drier) outlet valve occurred, so B drier was in line for ~60 Hrs against 12 hrs.
- CO+CO2+H2O might have slipped and oxidized/Deactivated the ammonia convertor catalyst and reaction started seizing
- As part of the catalyst got oxidized, kinetics of the reaction changed and amount of heat from exothermic reaction came down.
- Decrease in bed temp was drastic and couldn't be controlled and finally reaction was completely seized and back end was tripped.

Root Cause Analysis

Two most probable reasons for Ammonia reaction seized :

- Molecular sieve drier (Drier B) was in continuous operation for ~ 60 Hrs against normal period of 12 Hrs.
- CO+CO2+H2O slip from molecular sieve drier and which in-turn oxidized the catalyst.
- Converter was running at lower inlet temperature after 2009 revamp. So there was no margin in the inlet temperature increase.
- After MOV maintenance, Molecular Sieve Dryer Inlet and Outlet MOV was put on auto mode and sequence was normalized.
- Post plant start up, the catalyst performance was deemed satisfactory.

Thanks