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Operational Experience of Catalyst of Secondary Reformer in IFFCO Aonla Unit

Speaker:

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Chief Manager (Process),
IFFCO Aonla Unit

IFFCO IN BRIEF

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KALOL UNIT

Year of Commissioning - 1975
Annual Ammonia Capacity - 3.63 Lakh MT
Annual Urea Capacity - 5.45 Lakh MT

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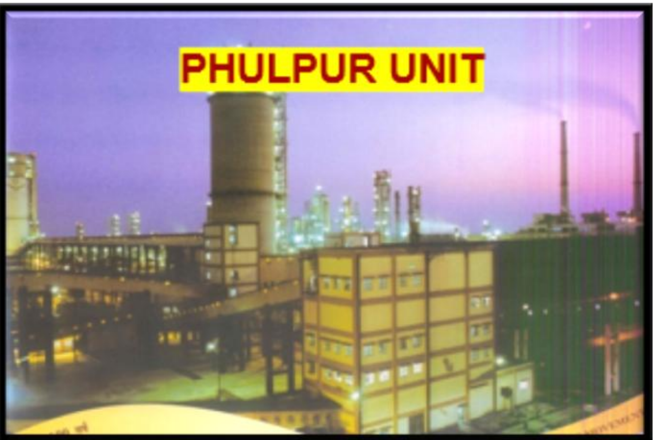
CORPORATE OFFICE
NEW DELHI

PHULPUR UNIT



Year of Commissioning - 1981/1997
Annual Ammonia Capacity – 9.75 Lakh MT
Annual Urea Capacity - 16.98 Lakh MT

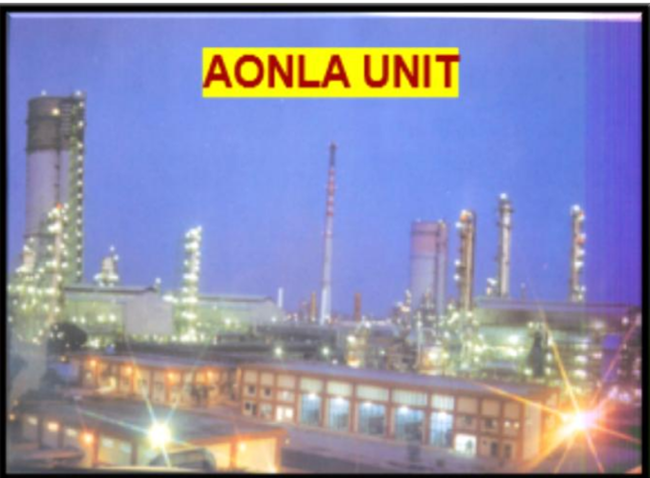
KANDLA UNIT

Year of Commissioning - 1975
Annual NPK/DAP Capacity - 24.15Lakh MT

PARADEEP UNIT

Year of Acquiring - SEP-2005
Annual Capacity - 19.20 Lakh MT (DAP + COMPLEX)

AONLA UNIT



Year of Commissioning - 1988/1996
Annual Ammonia Capacity - 11.48 Lakh MT
Annual Urea Capacity - 20.00 Lakh MT

AMMONIA-UREA MANUFACTURING COMPLEX FLOW DIAGRAM

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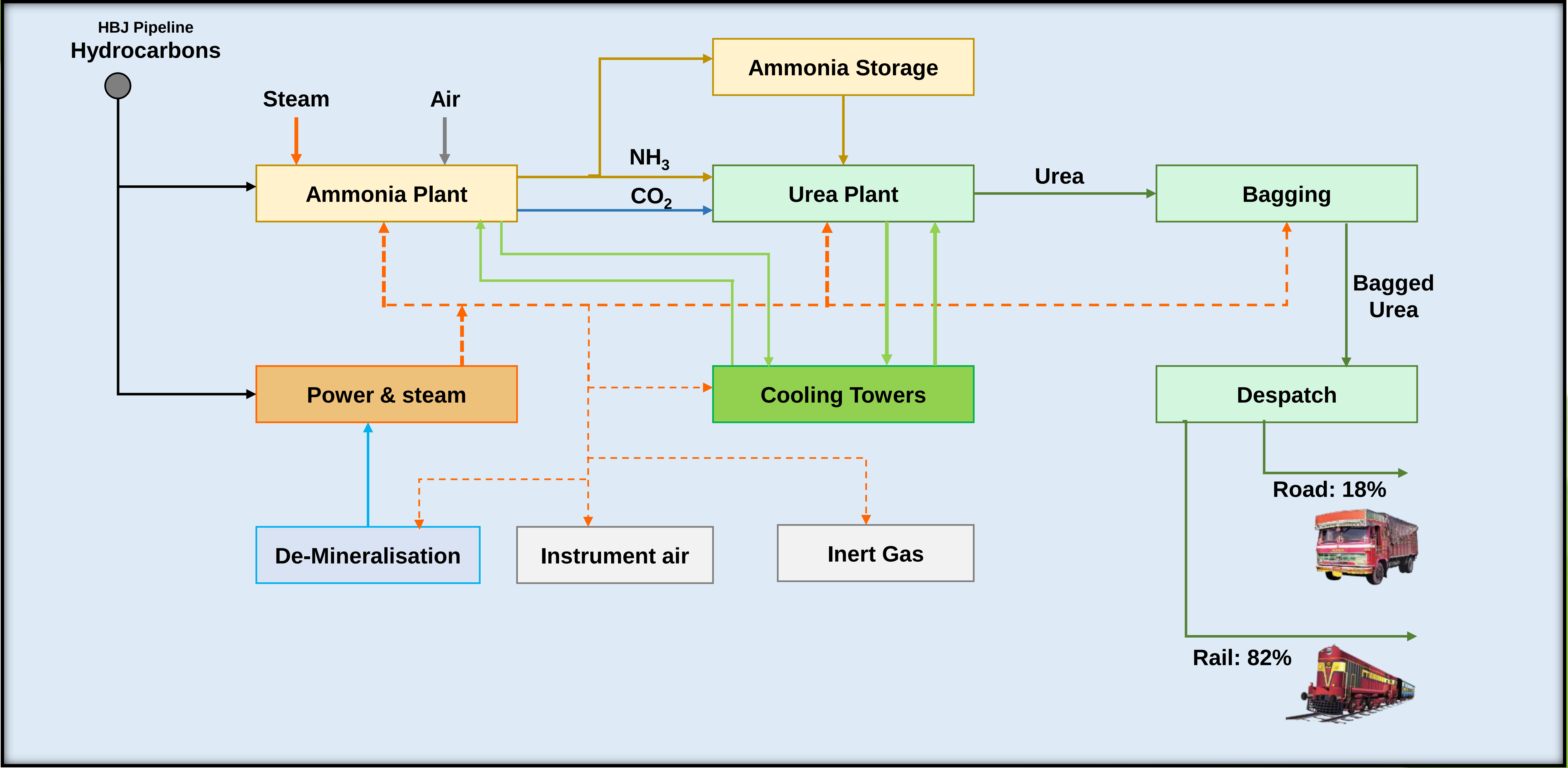

PROCESS FLOW DIAGRAM OF AMMONIA PLANT

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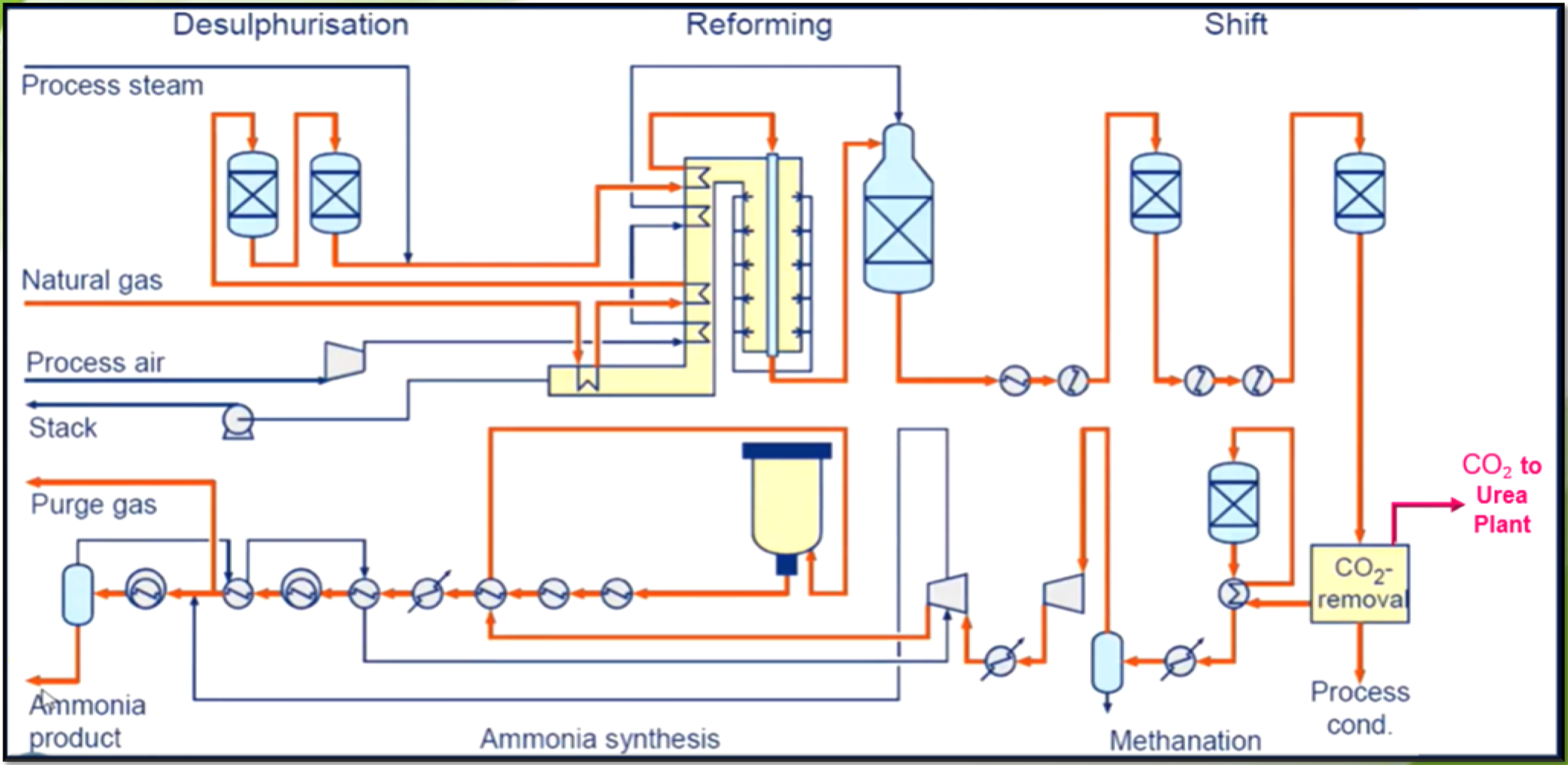

DETAILS OF SECONDARY REFORMER

DETAILS OF SECONDARY REFORMER (AONLA UNIT)

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- **Make:** M/s L&T
- **Reaction Involved:**

Combustion Reaction: $2H_2 + O_2 \Leftrightarrow 2H_2O + \text{Heat}$

Steam Reforming Reaction: $CH_4 + H_2O \Leftrightarrow CO + 3H_2 - \text{Heat}$

Water Shift Reaction: $CO + H_2O \Leftrightarrow CO_2 + H_2 + \text{Heat}$

- **Operating Conditions:**

Process gas inlet pressure, temperature & CH4%: 32 kg/cm2g, 770-780 degC, 13.5%

Inlet Process Air temperature: 550 degC

Outlet gas temperature & Methane Slip: 950 degC & 0.5%

- **Material of Construction:**

Shell, Toricone, Ellipsoidal dished end: Low alloy steel SA 204 Gr-B (1/2 Mo)

Top head unit material: Incoloy 800 H (Cr 19-23%, Ni 30-35%)

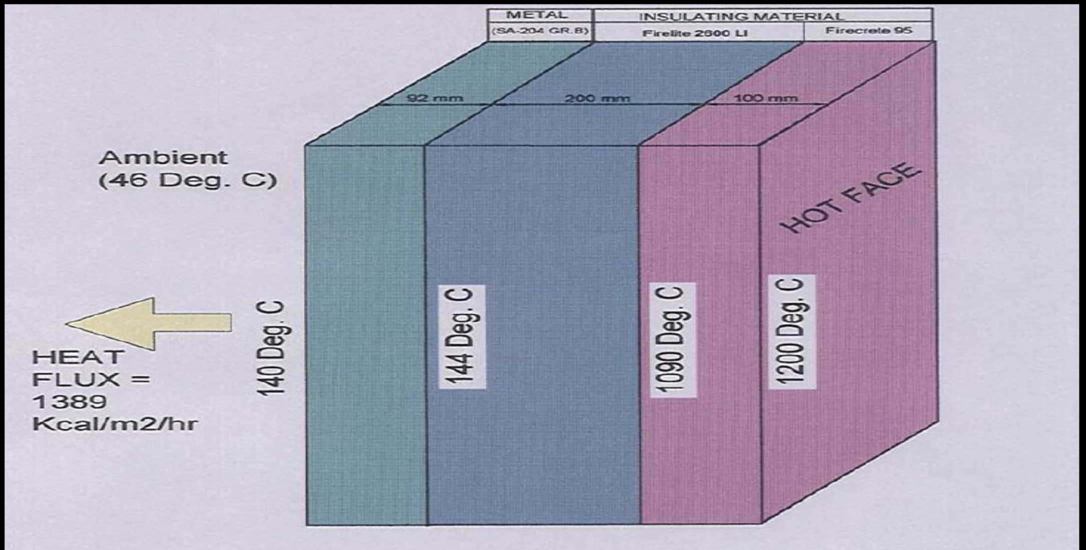
DETAILS OF SECONDARY REFORMER (AONLA UNIT)

- **Refractory Lining:**

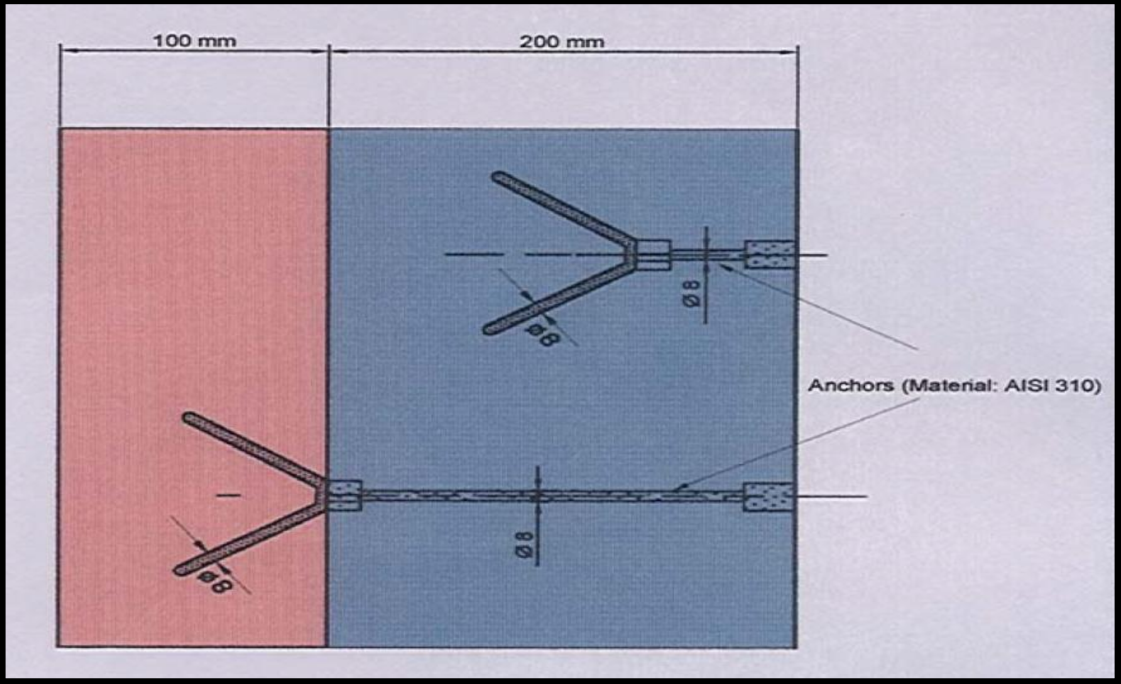
First Layer: 200 mm thick insulating castable Firelite-2600 refractory (50-60% alumina, Maximum Service temperature 1430 degC, Thermal conductivity 0.39 W/m-degK

Second Layer: 100 mm thick alumina castable Firecrete 95 refractory (94% alumina, Maximum Service temperature 1800 degC, Thermal conductivity 1.44 W/m-degK)

All these refractories are held together by stainless steel anchors.



FIRECRETE 95	High Alumina Castable refractory Material: Al_2O_3: 94.1%, SiO_2< 0.1%, Fe_2O_3: 0.1 %
FIRELITE 2600 LI	Insulating Castable refractory Material: Al_2O_3: 58 %, SiO_2: 31.4 %, Fe_2O_3: 0.7%



DETAILS OF SECONDARY REFORMER (AONLA UNIT)

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- **Thermo Indicative Paint as Shell Coating:**

  Original Colour: Green
  Green colour range: Upto 200 degC
  Blue colour range: 200-315 degC
  White colour range: 315-500 degC

- **Air Mixer Burner:**

  Central Air distributor: In Aonla-I, Single row having 6 number of nozzles. In Aonla-II, Single row having 15 number of nozzles.

  External ring: In Aonla-I, Two rows of nozzles with inner row contains 39 number of nozzles and outer row contains 54 number of nozzles. In Aonla-II, Two rows of nozzles with inner row contains 30 number of nozzles and outer row contains 45 number of nozzles.

Ammonia-I Burner | Ammonia-II Burner

DETAILS OF SECONDARY REFORMER (AONLA UNIT)

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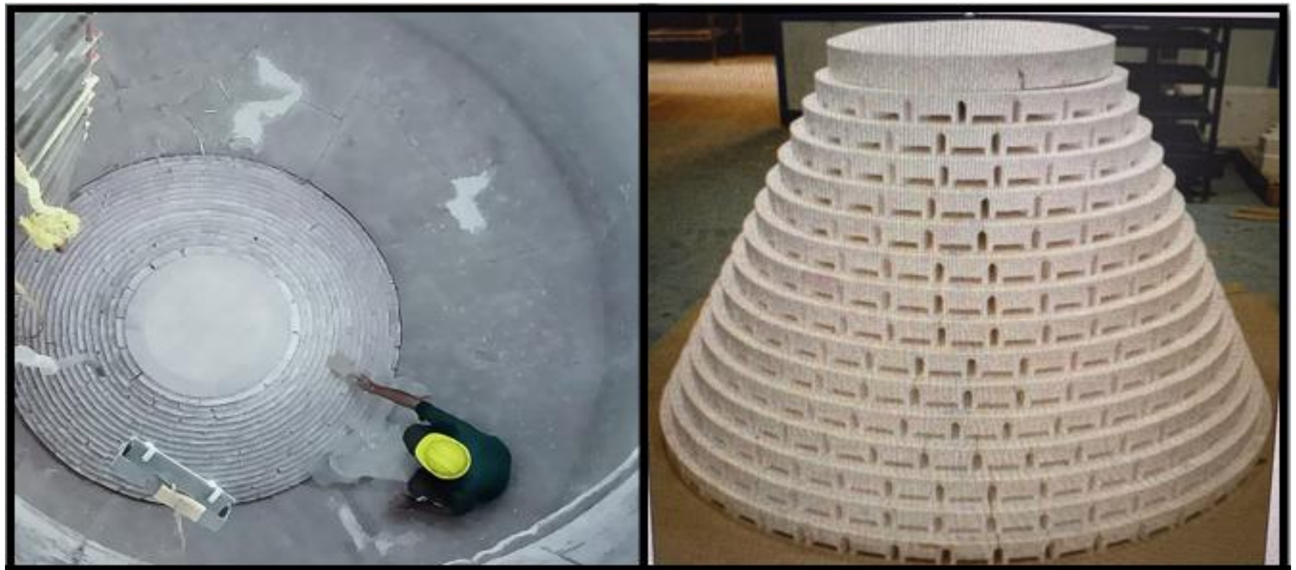
- **Catalyst Support:**

  High alumina fire brick Diffuser Cone. Constructed with 19 rows of bricks arranged in such a way so as to give 1.489 m2 of clear flow area through bricks. On the top of brick work a circular slab is placed



Catalyst Bed Support

- **Packing below Catalyst:**

  Around diffuser cone, first alumina lump of size ranging from 100-200 mm and then 50-100 mm are placed. In Ammonia-I, it has been replaced by alumina balls of size 50 mm.

  Above this, earlier, alumina lumps of 25-50 mm were charged to a height of 300 mm. This has been replaced by C-14-GG catalyst which works as bottom active support layer as well as an active catalyst.

DETAILS OF SECONDARY REFORMER (AONLA UNIT)

- **Main Catalyst:**

  C-14-2 LDP (M/s Sud-Chemie make) catalyst (Ni based catalyst having 12% NiO, Carrier CaAl12O19) is charged.

  Cylindrical type with seven holes, 20 mm diameter and 18 mm height.

  Height of catalyst bed: 2800 mm, Volume: 39 M3.


Main Catalyst

- **Packing above Main Catalyst:**

  Above the catalyst, earlier, alumina lumps of 25-50 mm size were charged upto 250 mm height. This has been replaced by C-14-GG catalyst which works as an active heat shield as well as an active catalyst.

  GG catalyst: 6 holed ring and consists of 9% NiO with carrier α-Al2O3.


GG Catalyst

DETAILS OF SECONDARY REFORMER (AONLA UNIT)

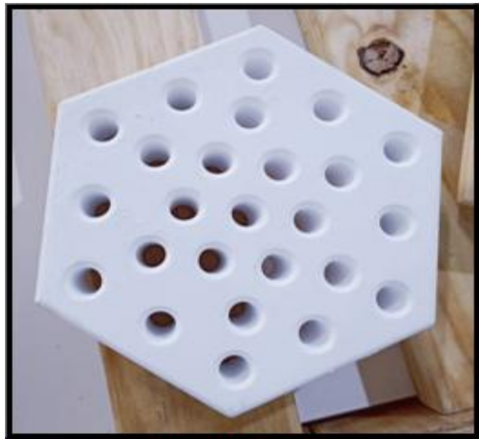
➢ Distribution Tiles:

On the top of GG catalyst, earlier, there was **50-mm** thick **hexagonal refractory alumina tiles** to distribute the gases. In the middle of this arrangement of tiles, 37 hexagonal tiles were without holes. Around this, were arranged 1150 pieces of hexagonal tiles with nine hole. On the periphery tiles were arranged depending on the space left after arranging the hexagonal tiles.

In both Ammonia plants, these tiles having 51 mm thickness have been replaced with **Jumbo Tiles having 25 holes and 64 mm thickness**.

➢ Circle Bricks:

Around this set of tiles, **60 standard circle bricks** are placed. The circle bricks are fitted tightly against the reformer lining.


Jumbo Tiles


Hexagonal Tiles


Jumbo Tiles & Circular Bricks

INTERNAL DETAILS OF SECONDARY REFORMER

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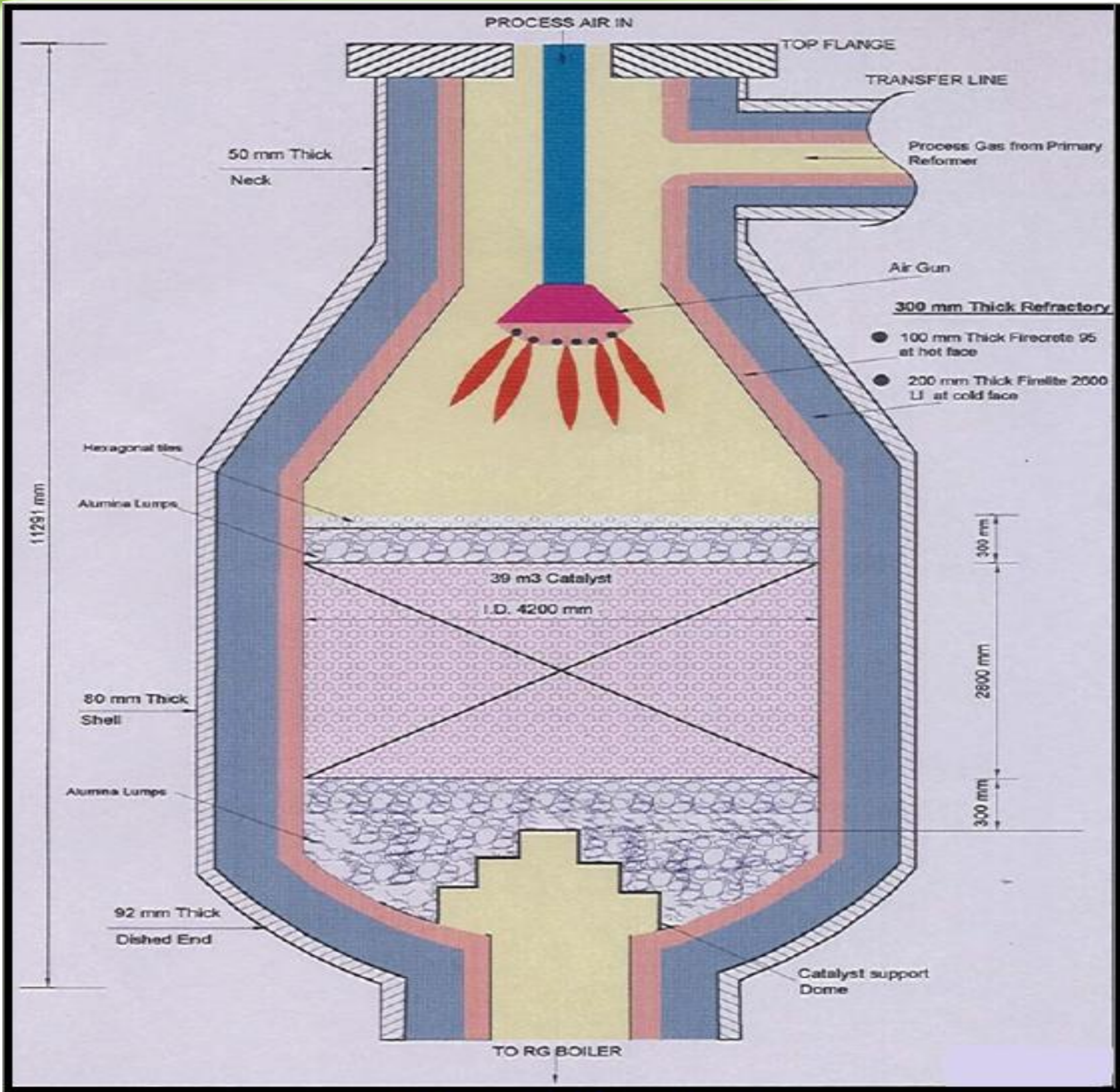
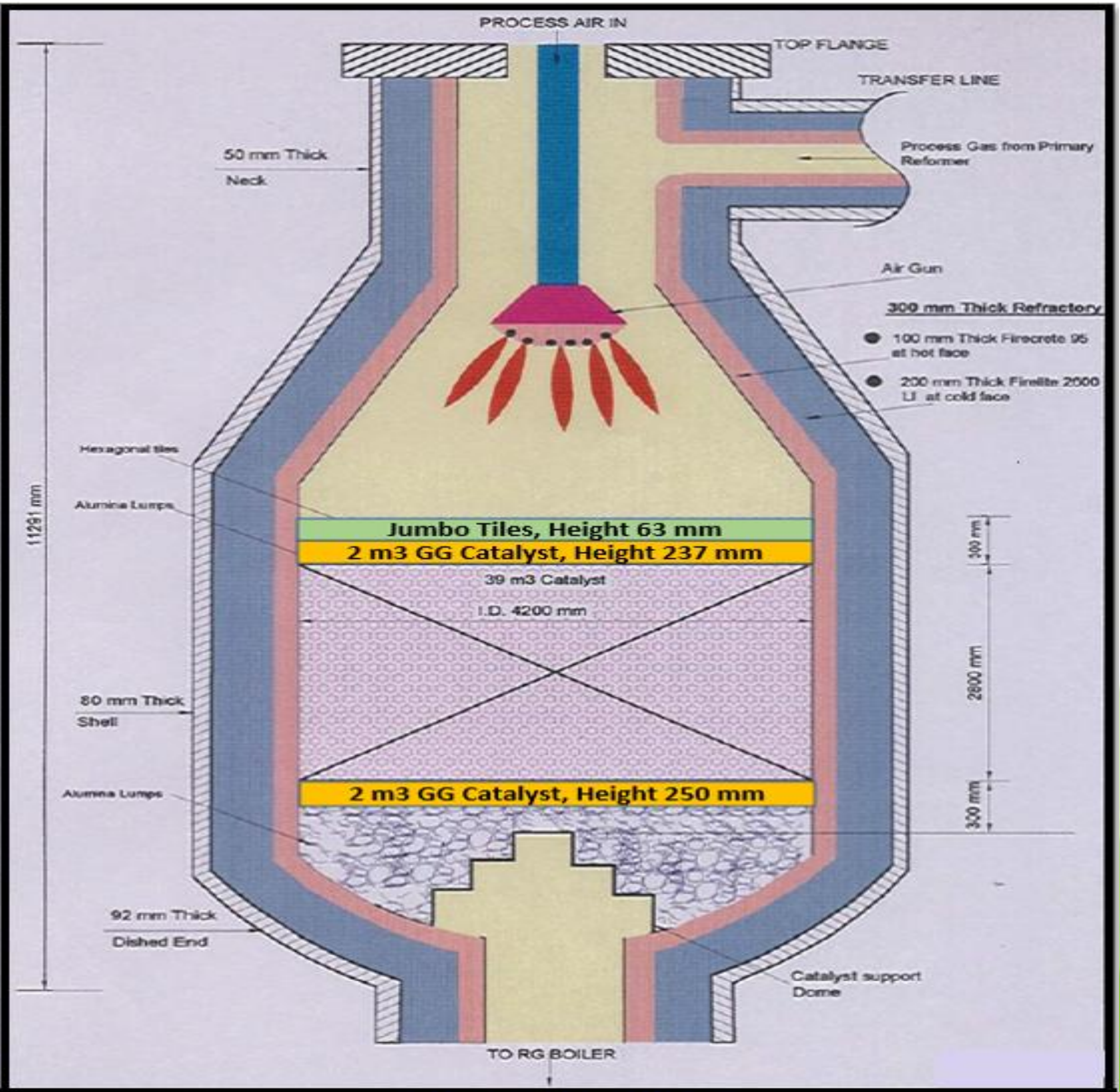


Before Changes



After Changes

OPERATIONAL EXPERIENCE OF SECONDARY REFORMER

OPERATIONAL EXPERIENCE OF SECONDARY REFORMER

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Design of Burner:

Nozzles are provided in the burner, with the number and size to produce required air velocity at the nozzle tip for good fluid mixing and to permit a uniform adiabatic flame temperature above the Reforming catalyst bed.

Reason for Burner failure: Careless handling of burner while inspecting during shutdown, Normal wear and tear, Loss of metal due to metal dusting or high temperature operation.

Burner failure can lead to the damage of wall refractory and the loss of vessel containment.

Mixing Zone Performance:

Temperature in the hottest zone inside the flame can exceed 2000 degC. Process gas temperature at the inlet of catalyst bed is desired in the order of 1200-1400 degC. So, good mixing of hot gas with the cooling gas from surrounding is desired.

Poor mixing are due to poor burner design, insufficient mixing volume and the failure of burner gun.

OPERATIONAL EXPERIENCE OF SECONDARY REFORMER

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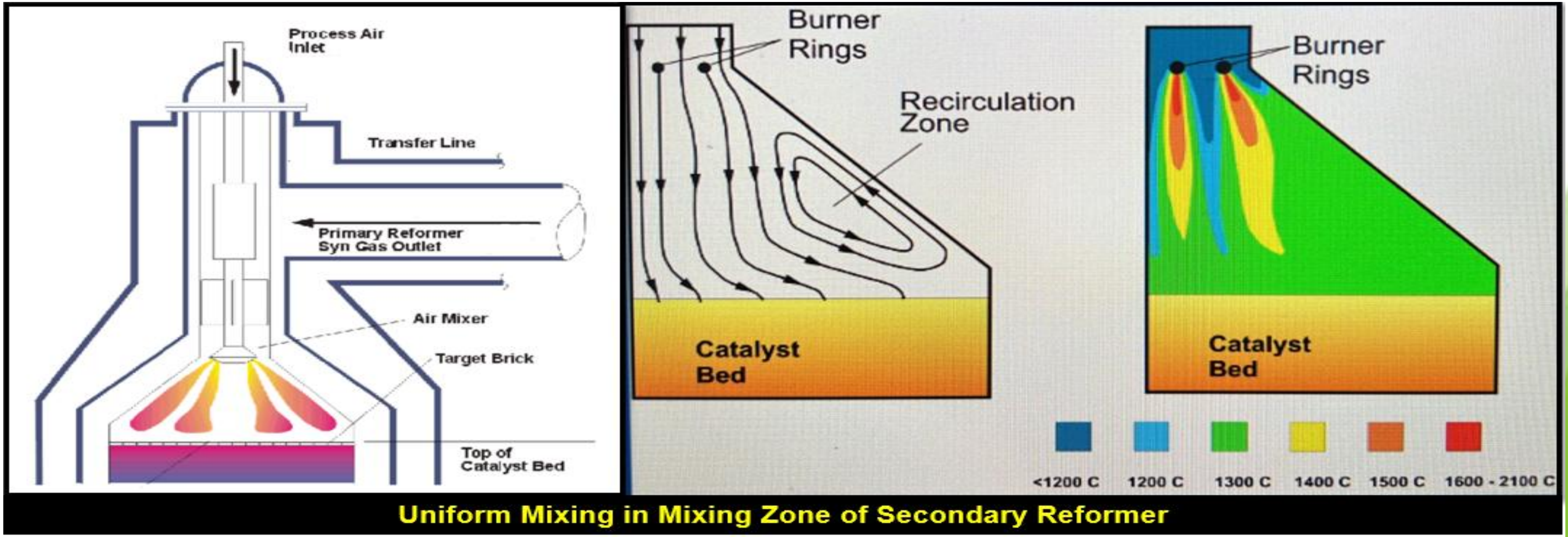
- **Mixing Zone Performance:**

Poor mixing in mixing zone will cause sintering of top layer of catalyst, increase in . Approach to Equilibrium (ATE), reduction in catalyst activity and increase in methane slip.



OPERATIONAL EXPERIENCE OF SECONDARY REFORMER

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- **Hold-down materials performance:**

Above the catalyst material, hold-down materials like target tiles (Hexagonal tiles, Jumbo tiles), alumina lumps, alumina balls, etc., are placed. Target tiles are preferred against alumina balls due to the following reasons:

- **It is much easier for a ball to be disturbed by the horizontal component of gas velocity at the surface of the bed than a tile.**
- **The thickness of the layer of tiles is much less than the thickness of the layer of balls. This will allow for some more mixing space above the catalyst.**

- **Preference of GG catalyst against 25-50 mm alumina lumps located at above & below catalyst bed:**

Above catalyst bed, GG catalyst works as an active heat shield as well as an active catalyst. Below catalyst bed, GG catalyst works as bottom active support layer as well as an active catalyst.

6 holed ring and consists of 9% NiO with carrier α-Al2O3.

OPERATIONAL EXPERIENCE OF SECONDARY REFORMER

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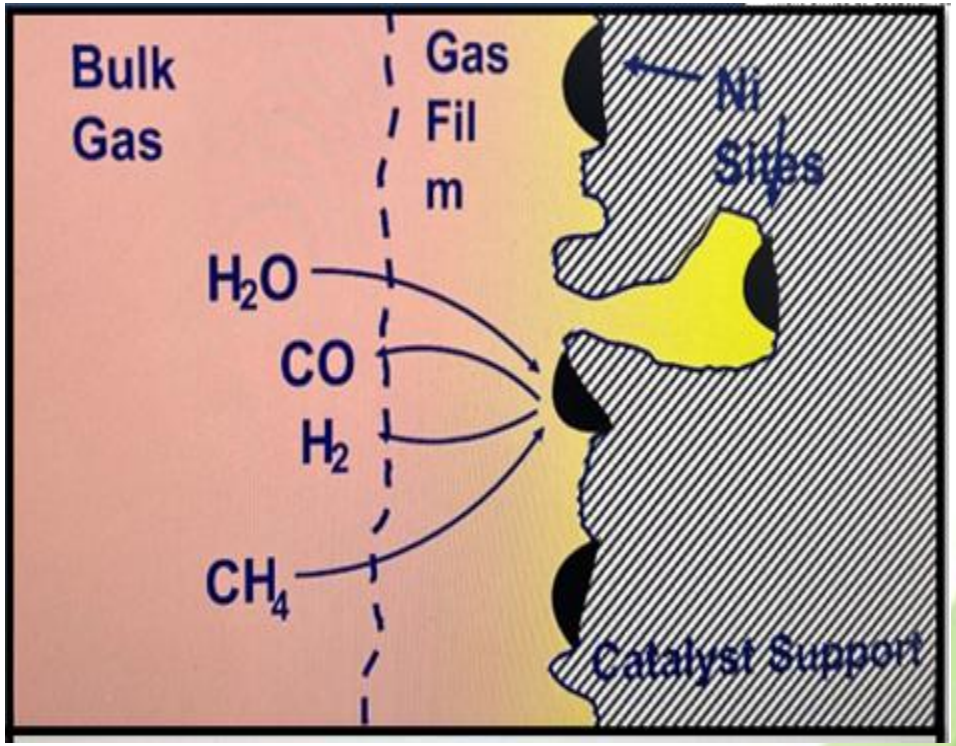
Main Catalyst:

- Catalyst must be designed to continuously operate in very high temperature conditions without thermal attrition or deformation. This requires a highly refractory catalyst support material.
- Nickel has been found to be the most cost-effective active species for Reforming catalysts, although other elements can work and are more active, including Cobalt, Lanthanum, Platinum, Palladium, Iridium, Rhodium and Ruthenium.
- Nickel is combined with various support materials including alpha-Alumina, Calcium-Aluminate, Magnesia-Alumina through proprietary means.
- Catalyst performance is directly related to catalyst size and shape. Geometric surface area is improved by optimizing passages through the catalyst structure. Void fraction and strength are simultaneously influenced by these changes. Catalyst diameter and height are adjusted to desirable pressure drop and void fraction characteristics.

OPERATIONAL EXPERIENCE OF SECONDARY REFORMER

The catalytic reaction involves :

- **Diffusion of the molecules in the bulk gas phase (fast process),**
- **Diffusion of the molecules through the gas film (slow process),**
- **Diffusion through catalyst pores (slow process),**
- **Adsorption of the molecules onto the Ni sites (fast process),**
- **Chemical reaction (fast process), and**
- **Diffusion of products from surface into gas phase (slow process)**



Reaction rate is mainly controlled by film diffusion rather than pore diffusion. Most of the reaction takes place on the catalyst surface. So, the catalysts with higher Geometric Surface Area (GSA) per unit volume of catalyst will have a higher activity. Pore size/distribution is not significant for most commercial grades of reforming catalyst.

OPERATIONAL EXPERIENCE OF SECONDARY REFORMER

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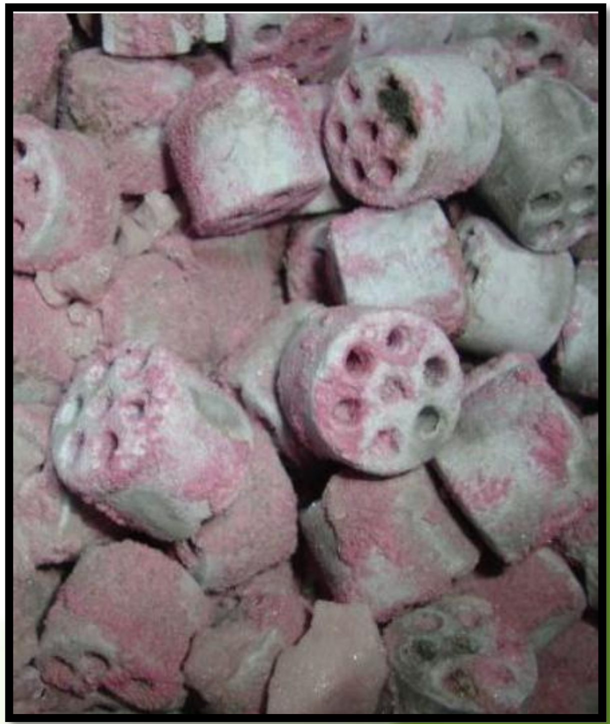
The healthiness of catalyst can be assessed with the following information:

- White color indicates loss of nickel.
- Coated in white indicates alumina vaporization.
- Blue colour indicates that the catalyst has been exposed to very high temperature.
- Pink crystal indicates synthetic ruby formation.

Ruby consists of α-Al_2O_3 with a minor content of Cr_2O_3 (0.5-2%).

The mechanism of ruby formation is the evaporation of alumina from the very top of the catalyst bed and also the refractory lining of the secondary reformer with further re-condensation. If there are traces of chromium carried over from the equipment upstream of the secondary reformer or from secondary reformer neck lining, the re-condensed alumina will have a pink colour. This is called Ruby.

Ruby formation on the catalyst physically blocks Ni sites, hence, deteriorates catalyst performance.



CATLAYST HANDLING AND INSPECTION DURING SHUTDOWN

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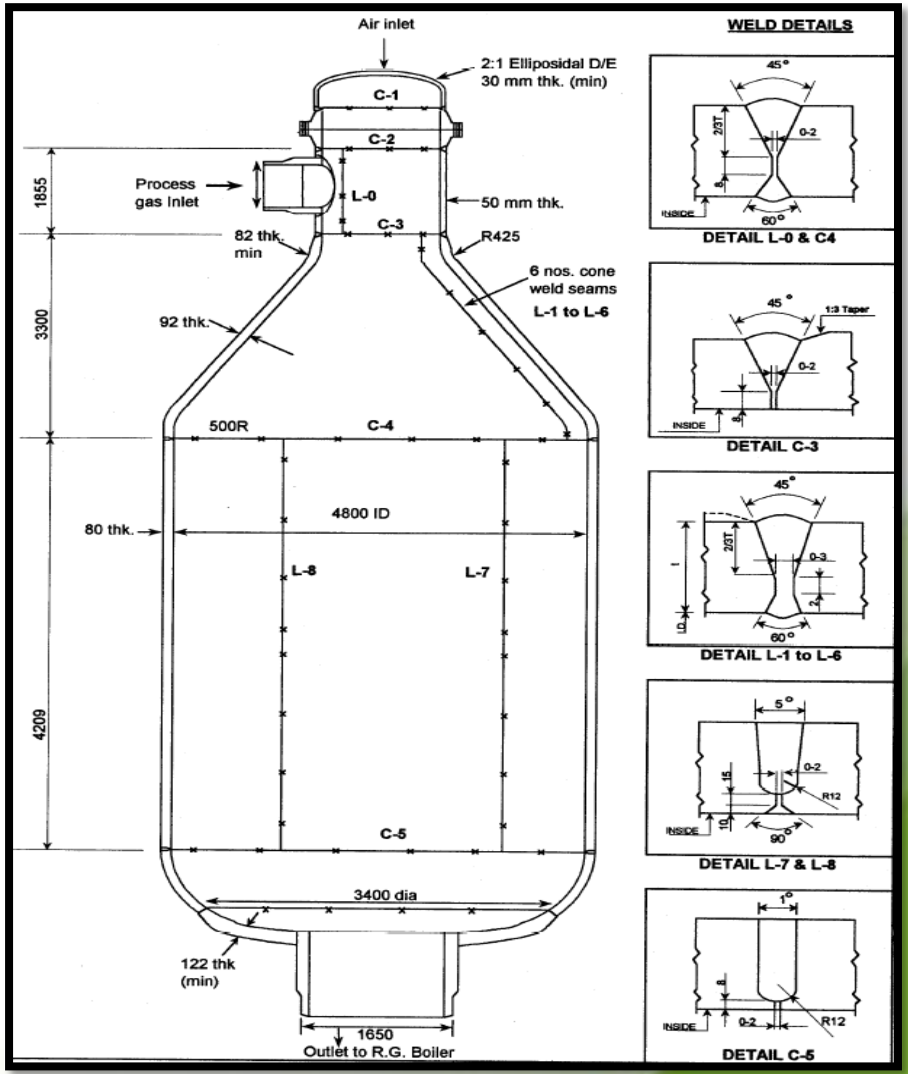
- **SOR parameters like pressures drop, methane slip, etc. are maintained to compare the performance of existing catalyst and to take decision for replacing catalyst.**

- **Before unloading of Catalyst, Reformer is cooled to the temperature of around 70 degC with the circulation of nitrogen gas. Storing, Screening and Sorting of catalyst are carried out.**
- **Visual inspection of air distribution pipes, main welds, flow straightener plates and nozzles are done. Dye Penetrant Testing of Burner nozzles & its all accessible piping are carried out. Any damage refractory found is repaired/replaced.**
- **All internals of Reactor are verified as per vessel drawings. All weld points are inspected as per the drawing through Dye Penetrant test, Ultrasonic test.**



OPERATIONAL ISSUES OF SECONDARY REFORMER

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- While inspecting during Annual Turnaround, refractory damage, nozzle damage, ruby formation on GG catalyst and main catalyst are observed. These problems are attended during Annual Turnaround.
- Due to abrasion of alumina lumps, carryover in terms of fine dusts of alumina are observed in the tubes of RG Boiler. This reduced heat transfer coefficient of the tubes which in turn reduces steam generation from RG Boiler.

  In Ammonia-I Plant having RG Boiler of Double Compartment, the problem of high temperature of mid-section of RG Boiler is found due to carryover of dust. To mitigate this problem, following actions have been taken:

  - Alumina lumps of varying sizes have been replaced by regular 50 mm size of alumina balls to reduce the abrasion between lumps.
  - Descaling operation of RG Boiler is carried out to remove dust particles from RG Boiler. During descaling operation, venting is first done from the vent valve located at upstream of Syn Gas Compressor and then the venting is shifted to the vent valve located at the inlet of HTS.

PERFORMANCE MONITORING OF SECONDARY REFORMER CATALYST

PERFORMANCE OF SECONDARY REFORMER CATALYST

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In addition to pressure drop across catalyst, Approach to Equilibrium of the catalyst is also calculated to assess the performance of the catalyst. The calculation involves following:

- **Material balance**
- **Reaction kinetics**

Methane Reforming reaction

$LN((n_{H2})^3 \times (n_{CO}) \times (P)^2 \times (n_{Total})^2) / (n_{CH4} \times n_{H2O}) = (30.53 - 4.8486 \times 10^4/T - 2.421748 \times 10^6/(T^2) + 2.49 \times 10^9/T^3)$

Water Shift reaction

$LN((n_{CO2}) \times (n_{H2})/((n_{CO}) \times (n_{H2O}))) = (-2.93062 + 3606.211/T + 5.0424 \times 10^6/T^2 - 1.815388 \times 10^9 / (T^3))$

Secondary Reformer outlet dry gas analysis and ATE if outlet methane slip is known.

Particulars	Units	Values	
SR outlet pressure	kg/cm2g	34.0	
CH4% in SR outlet dry gas	%	0.52	
SR outlet temp	degK	1228.15	
Eqlm temp for methane reforming	degK	1226.49	
	degR	2207.68	
Eqlm temp for water shift reaction	degK	1226.49	
	degR	2207.68	
Outlet dry stream flow from SR	NM3/hr	240483	
Methane reacted as reforming	moles/hr	420718	
CO reacted	moles/hr	94960.58592	
SR pressure	atm	33.911944	
Methane reforming rxn (set it to 0)		0.000000000	
Water shift rxn (set it to 0)		0.000000000	Run solver
From total material balance (set it to 0)		0.000000000	
		0.000000000	
ATE	degK	1.7	

Species	Secondary Reforme inlet stream		Steam	Process air inlet to Secondary		Secondary Reformer outlet stream		
	V (Nm^3/h)	n(mol/hr)	NM3/hr	V (Nm^3/h)	n(mol/hr)	V (Nm^3/h)	wet mol%	dry mol%
C1	21060	939606.4699				1260	0.35	0.52
$H_2O(g)$	110592	4934057.335	0	594	26496	120367	33.36	
CO_2	16244	724732.5368		22	992	18395	5.10	7.65
H_2	100581	4487399.419				130999	36.30	54.47
CO	13143	586381.474				30815	8.54	12.81
N_2	481	21447.11384		57832	2580191	58313	16.16	24.25
O2				15555	693980	0	0.00	0.00
Ar	4	191.7627599		697	31079	701	0.19	0.29
Total	262105.2		0.00	74700	3332738	360850	100.00	100.00

PROCESS SENSITIVITY TO OUTLET TEMPERATURE OF REACTOR

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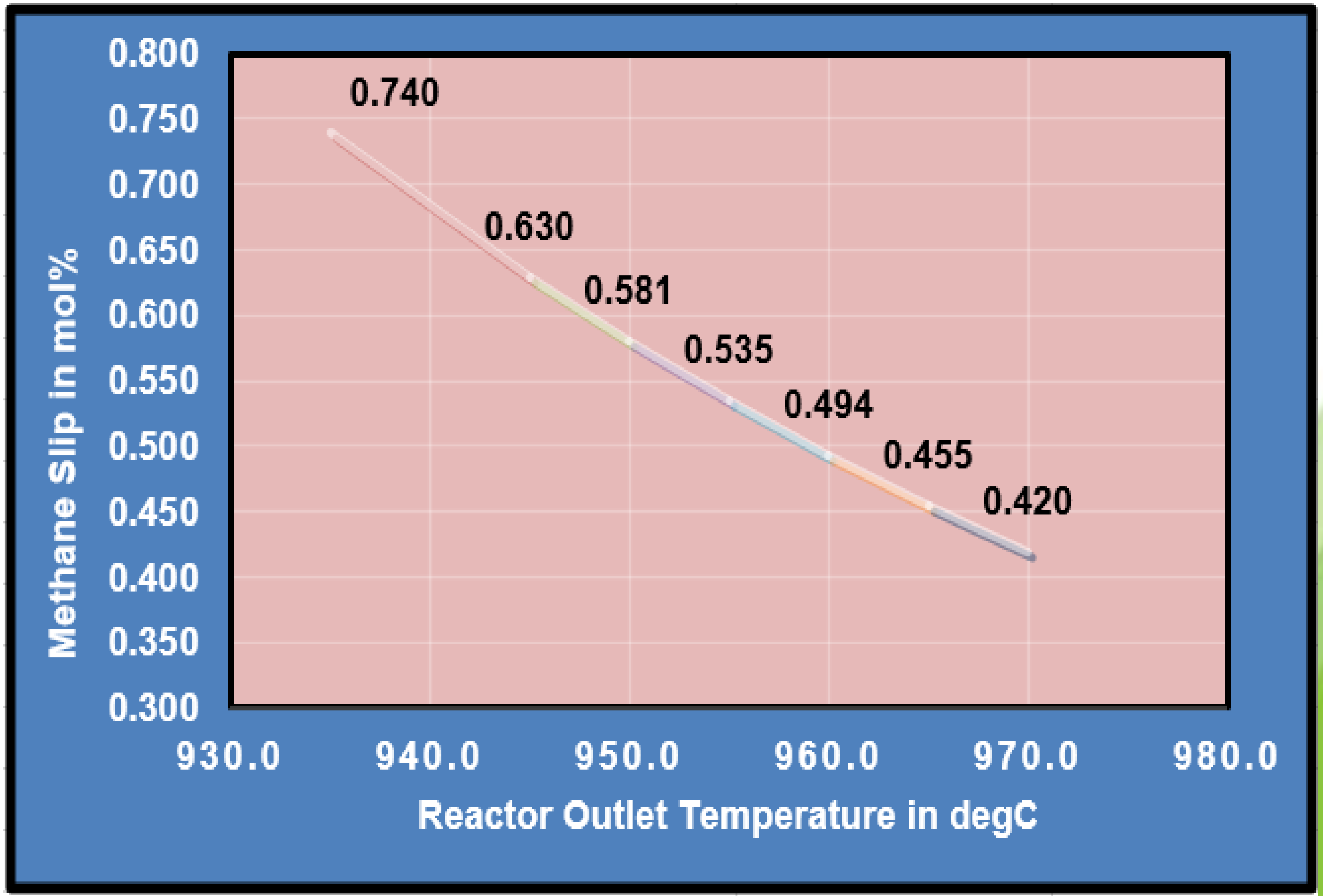
Reforming process favors high temperatures as it shifts the reforming reaction equilibrium towards the production of hydrogen and reduces methane slip.

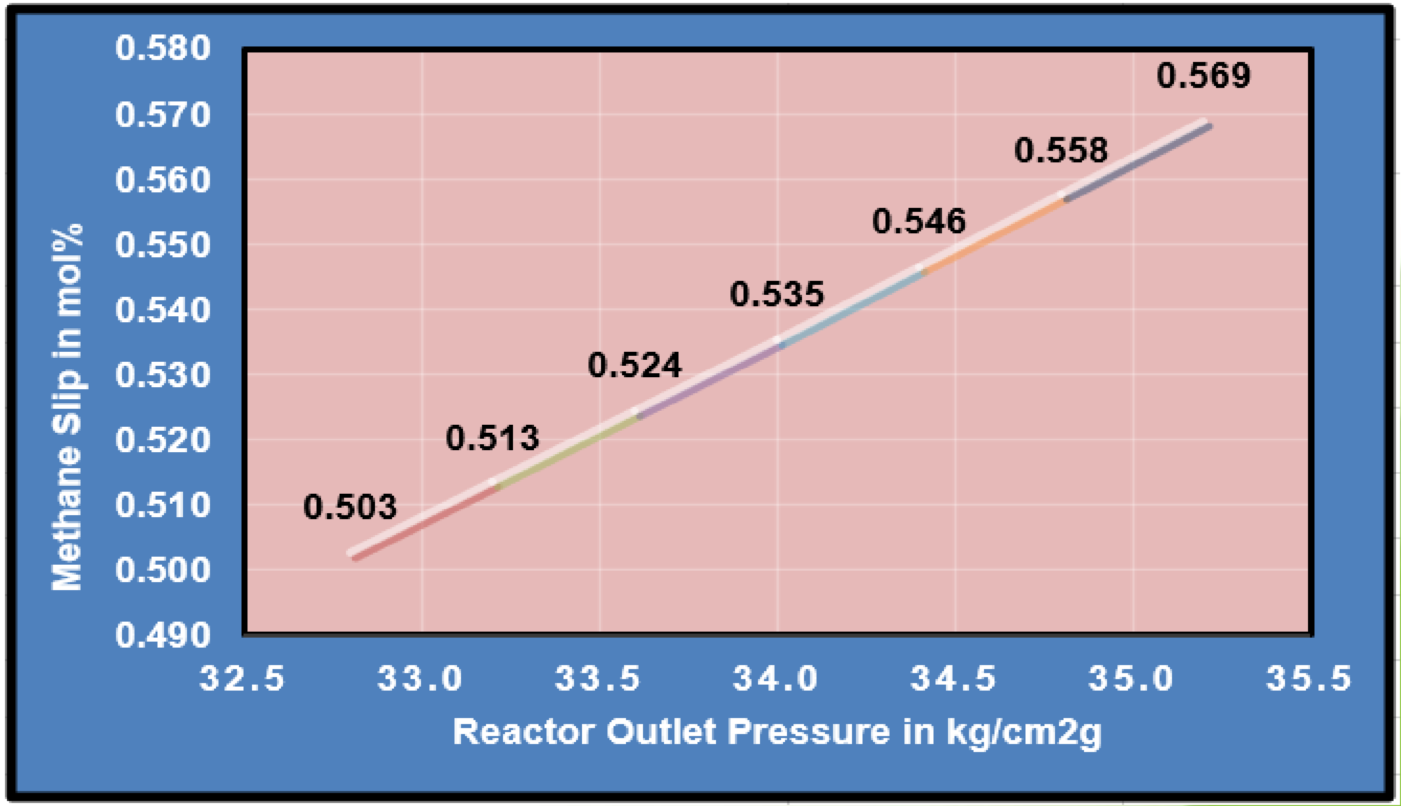
The operational philosophy is to run the Reformer at such an elevated temperature which is based on thermal stability limit of Refractory & the internals of the Reformer and to maximize H2 production. Based on this, the outlet temperature of secondary Reformer is maintained around 950 degC.



PROCESS SENSITIVITY TO PRESSURE OF REACTOR

The reforming process favors low pressure as it shifts the reforming reaction equilibrium towards the production of hydrogen and reduces methane slip. However, operating the reformers at lower pressure causes increase in power consumption in Syn Gas Compressor.

Considering these factors and the supply of NG pressure from Gas Supplier, the optimum pressure for the reforming section is decided.



PROCESS SENSITIVITY TO STEAM TO GAS RATIO AT INLET

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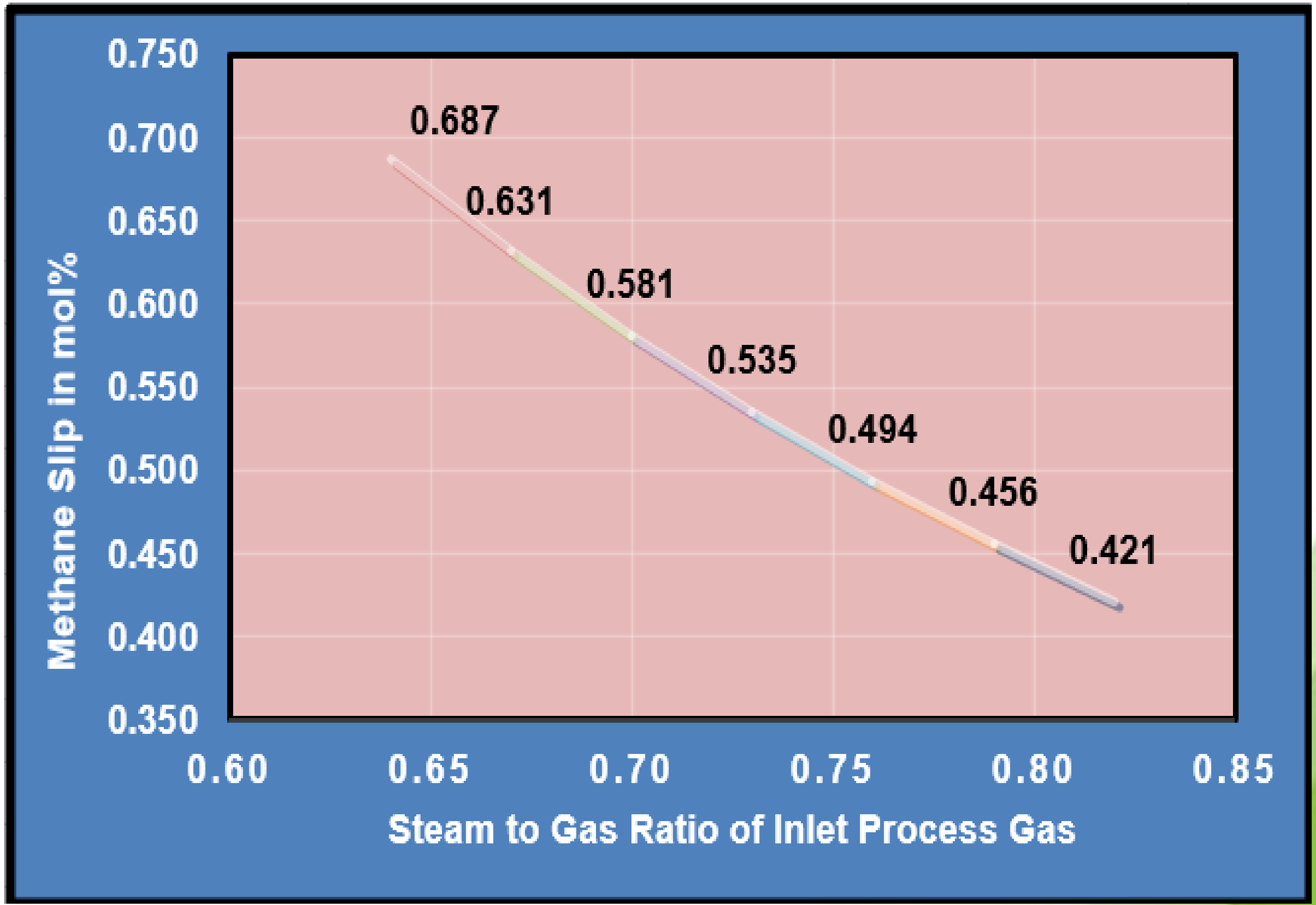
Higher steam to gas ratio of inlet process gas to Secondary Reformer favors the products in the reforming reaction equilibrium. It lowers the amount of unreacted methane and increase the production of hydrogen.



CONCLUSION

- The optimization in Secondary reformer is essential to introduce the nitrogen required for ammonia synthesis and to meet out the balance reforming reaction.
- The combustion of hydrocarbons in air provides the heat input required for the reforming reaction, but it also leads to a relatively high temperature. These conditions necessitate careful design to achieve reliable, stable and safe operation.
- Proper and efficient mixing of air and process gas in the top of the secondary reformer is critical for the performance of the secondary reformer.
- The optimized burner maintains a controlled flame in the combustion zone and a uniform gas flow into the catalyst bed, both of which are essential for proper mixing.
- The refractory lining ensures that the heat generated is used to promote the reforming reaction and it protects the pressure shell from excessive temperature.
- Target tiles are used at the top of the catalyst bed as heat shield for the catalyst.
- The catalyst should be optimally designed to ensure conversion to chemical equilibrium as well as a low and stable pressure drop through Secondary Reformer.

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THANK YOU