Developments in Ammonia Production Technology

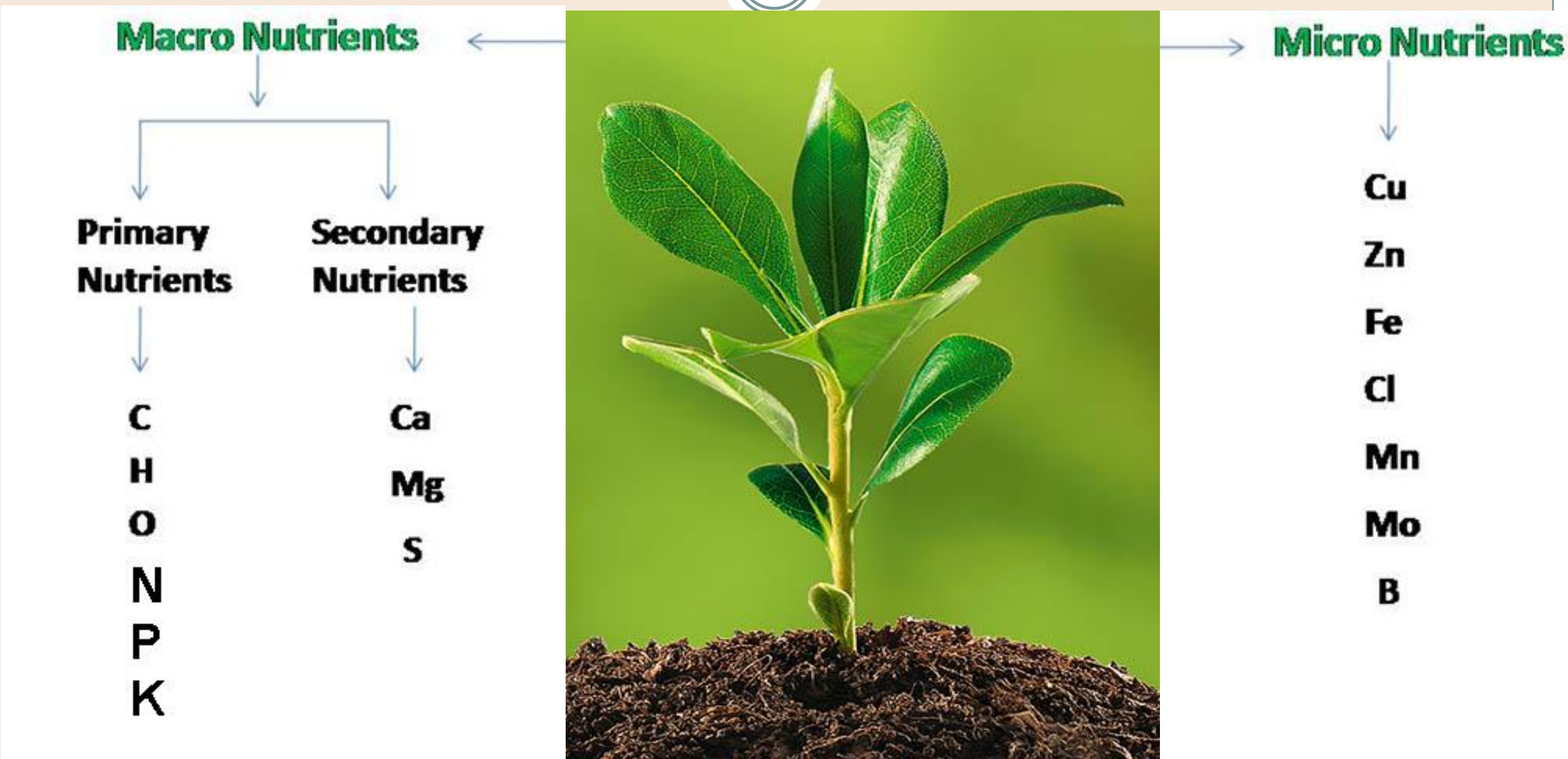
Dr. S. Nand
Deputy Director General

ENSURING FOOD SECURITY

FERTILISER ASSOCIATION OF INDIA
FAI HOUSE, 10, SAHAEED JIT SINGH, MARG, NEW DELHI
Email: tech@faidelhi.org

Presented at : IIChE NRC, New Delhi 13.07.2019

Plant Nutrients



Type of Fertilizers

Straight Fertilizers

- Containing only one of the primary nutrients

  E.g. Urea (N), SSP, TSP (P), MOP (KCl-K)

- Complex or Compound Fertilizers

  Containing two or all three primary nutrients

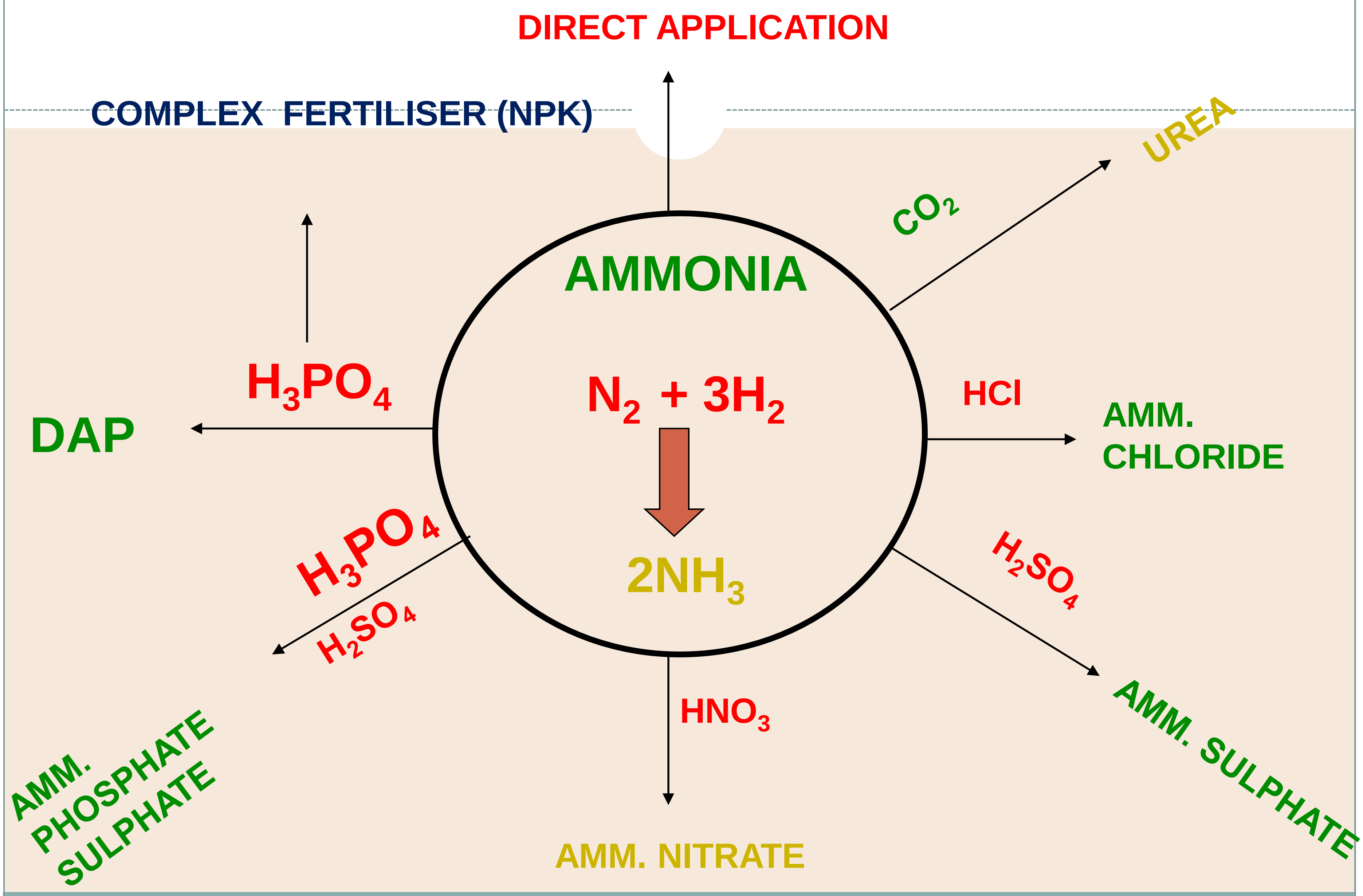
  E.g. Di-ammonium phosphate (DAP - N&P)

  Ammonium Phosphate + KCl (N, P & K)

Nitrogenous Fertilizers – Containing N

Phosphatic Fertilizers – Containing P

Potassic Fertilizers – Containing K

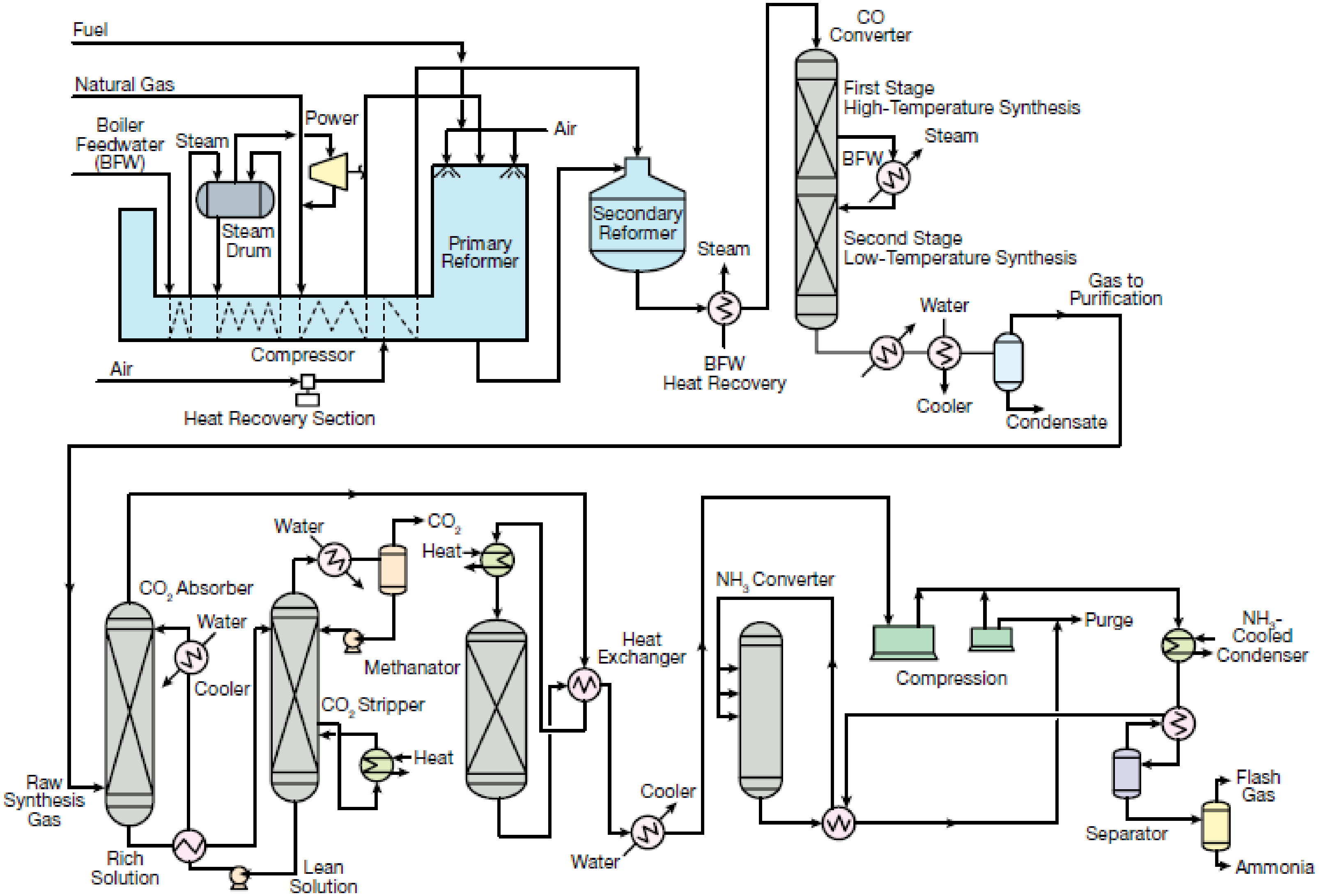


DIRECT APPLICATION
COMPLEX FERTILISER (NPK)
UREA
CO2
AMMONIA
N2 + 3H2
2NH3
H3PO4
DAP
HCl
AMM. CHLORIDE
H3PO4
H2SO4
H2SO4
AMM. PHOSPHATE SULPHATE
HNO3
AMM. SULPHATE
AMM. NITRATE

Feedstock and Processes for Ammonia

Feedstock	Process
Natural Gas	Steam Reforming
Naphtha	Steam Reforming
Fuel Oil	Partial Oxidation
Coal	Gasification
Water	Electrolysis

A Typical Ammonia Process Flow Diagram



Feed Treatment

Hydro-desulphurisation/Desulphurisation

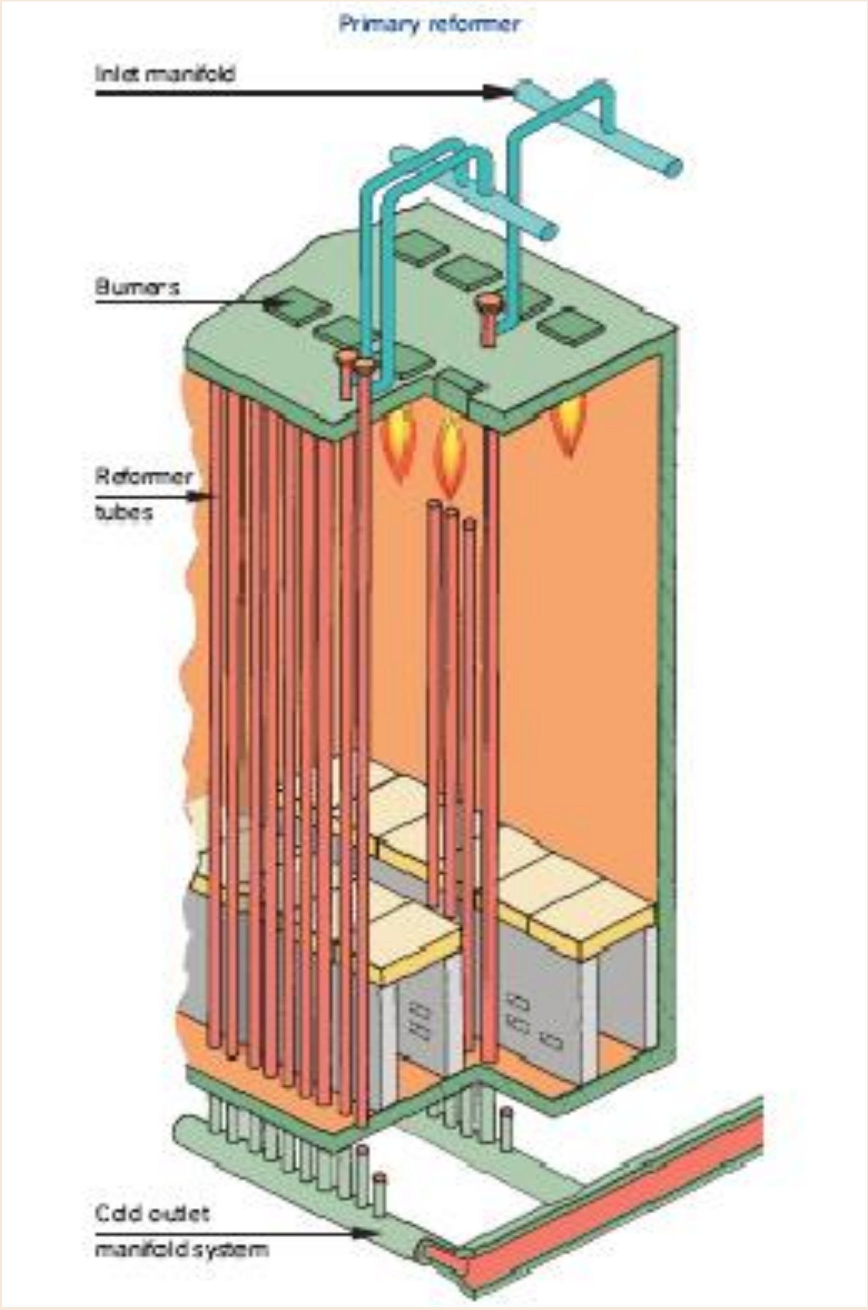
350-400 °C

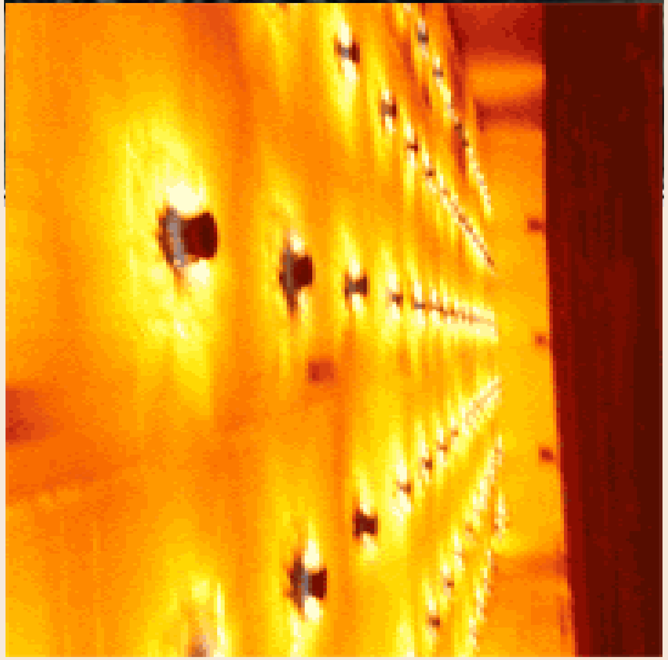
Co-Mo catalyst

7

$$1/2H_2 + RSH \rightarrow H_2S + RH$$

$$H_2S + ZnO \rightarrow ZnS + H_2O$$


Primary reformer
Inlet manifold
Burners
Reformer tubes
Cold outlet manifold system



Synthesis Gas Production

Primary Reforming

750-830 °C

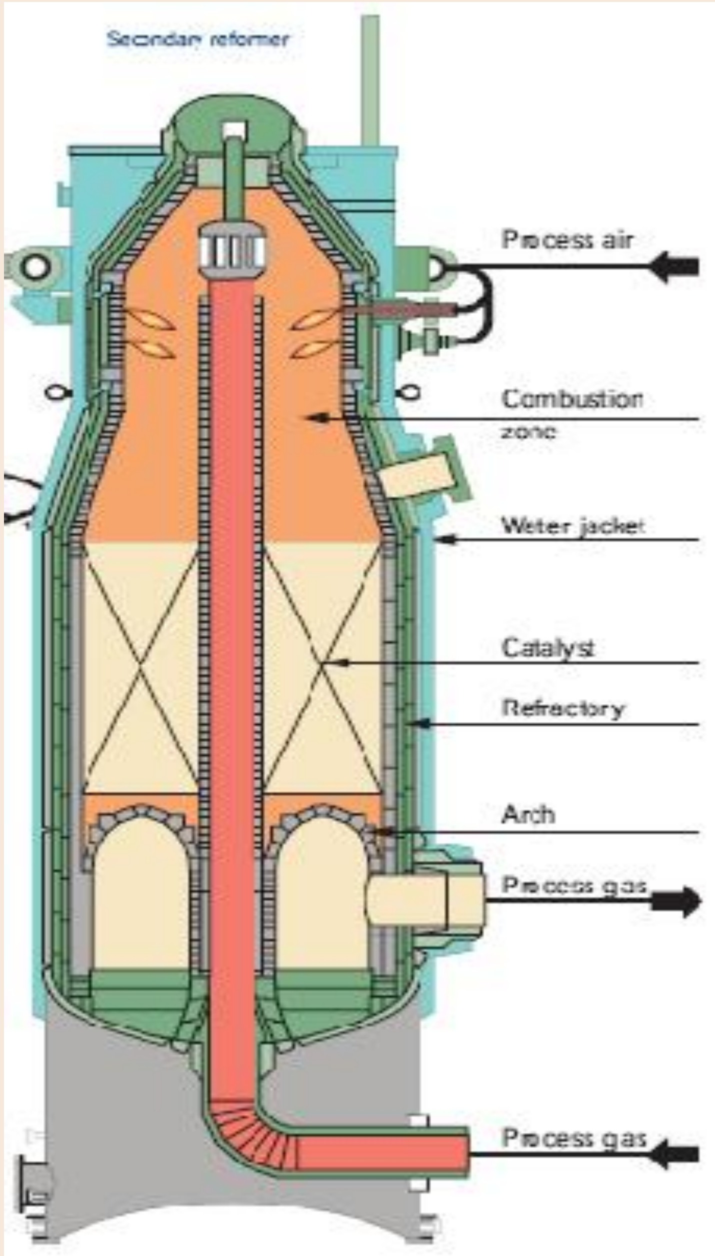
endothermic

$CH_4 + H_2O \xrightleftharpoons{NiO\text{-}Al_2O_3} 3H_2 + CO$ (1)

1. Δ H=+206 kJ/mol (49.2 kcal/mol)

$CO + H_2O \rightleftharpoons H_2 + CO_2$ (2)

2. Δ H=-41 kJ/mol


Secondary reformer
Process air
Combustion zone
Water jacket
Catalyst
Refractory
Arch
Process gas
Process gas

Synthesis Gas Production

Secondary reforming

950-1000 ºC

exothermic

Air $(O_2 + N_2)$

$$CH_4 + H_2O \xrightarrow[NiO-Al_2O_3]{} 3H_2 + CO$$

$$CH_4 + 2O_2 \text{ (air)} \leftrightarrow CO_2 + 2H_2O$$

$$CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2$$

Synthesis Gas Production

exothermic

High Temp CO Shift

320-350 °C

$$CO + H_2O \xrightarrow[Fe_2O_3\text{-}Cr_2O_3\text{-}CuO]{320\text{-}350\ ^{o}C} CO_2 + H_2$$

1. Δ H= -41 kJ/mol)

exothermic

Low Temp CO Shift

200-220 °C

$$CO + H_2O \xrightarrow[CuO\text{-}ZnO\text{-}Al_2O_3]{200\text{-}220\ ^{o}C} CO_2 + H_2$$

1. Δ H= -41 kJ/mol)

Synthesis Gas Purification

CO_2 removal

70-75 °C

$$K_2CO_3 + H_2O + CO_2 \leftrightarrow 2KHCO_3$$

$$2KHCO_3 \leftrightarrow K_2CO_3 + 2H_2O + CO_2$$

Carbon dioxide removal	
Chemical	Physical
Amines like MEA or MDEA or aMDEA	Rectisol (Methanol)
Hot Potasium carbonate like Benefied or GV	Selexol (propylene glycol dimethyl ether)

Carbon dioxide Removal Section with two-Stage regeneration

Synthesis Gas Purification

exothermic

Methanation

300 ºC

$NiO\text{-}Al_2O_3$

$CO + 3H_2 \leftrightarrow CH_{4+} H_2O$

$CO_2 + 4H_2 \leftrightarrow CH4 + H_2O$

1. Δ H= -206.1 kJ/mol)
2. Δ H= -164.9 kJ/mol

Ammonia Synthesis

exothermic

400-450 °C

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Fe_3O_4-K_2O-Al_2O_3-CaO

Δ H= -46.2 kJ/mol)

Growth in Ammonia Industry

Phases	Capacity MTPD	Feedstock	Characteristics
Phase I Plants of 60’s	200 to < 500	Coke oven gas Hydrogen, Lignite, Naphtha	Reciprocating compressors, Mainly Electric Drives
Phase II Plants of 70's	600 or 900	Naphtha, Fuel Oil	A mix of electric and turbine drives
Phase III Plants of 80’s	900 or 1350	NG, Naphtha, Fuel Oil and coal	Centrifugal Compressors Major pumps and fans on steam drive
Phase IV Plants of 90’s	1350 or more	NG, Naphtha /mixed feed	Centrifugal Compressors Major pumps and fans on steam drive

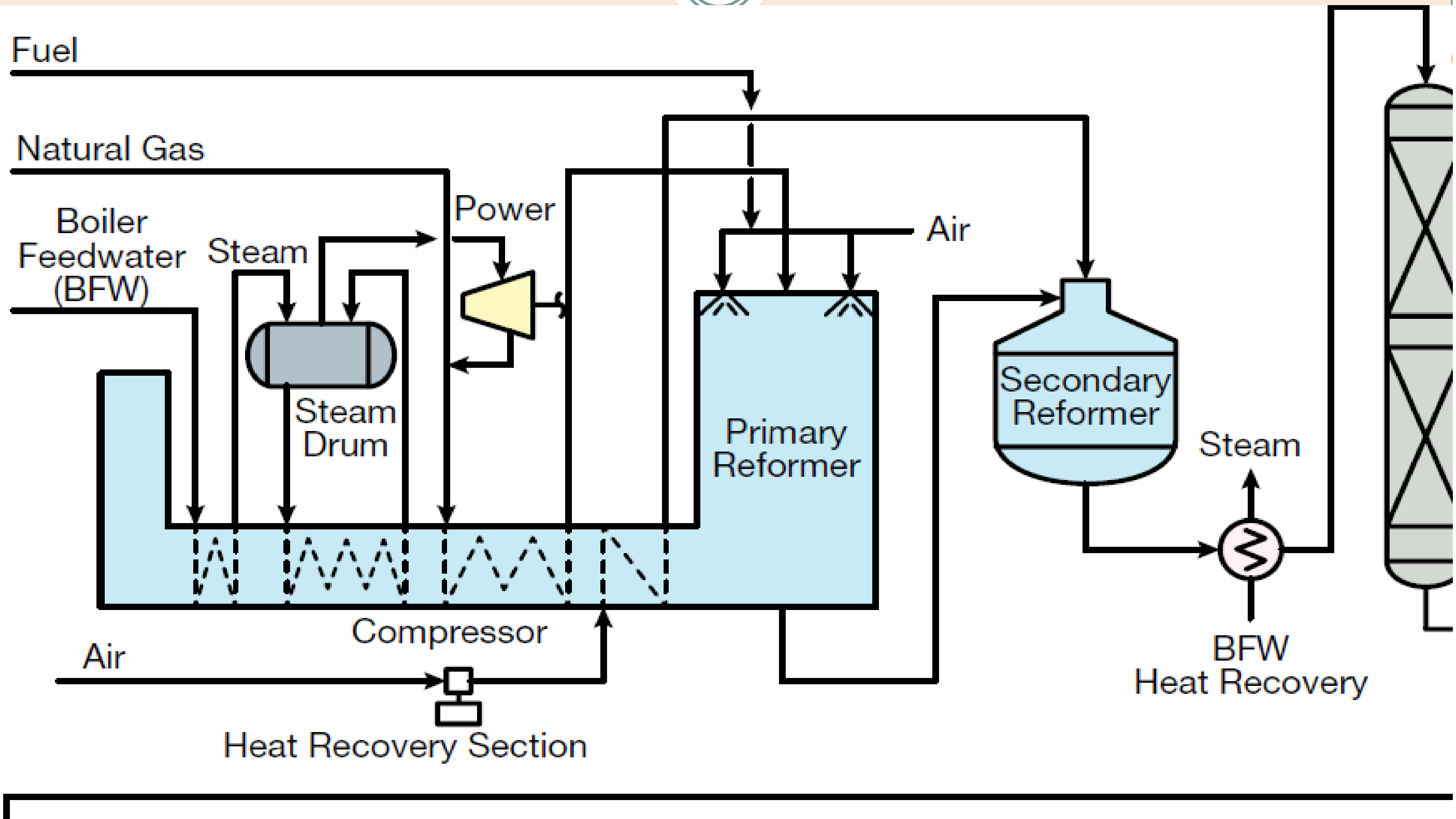
Technological Trends

- Reduce duty on primary reformer
- Heat recovery from Furnace Flue gases
- Low NOx burners
- Better catalysts
- Improved final purification
- Better materials of construction
- Improved synthesis loop efficiency
- Utilization of low grade heat
- Better design of moving machines (turbines, compressors, pumps) for higher efficiency
- Optimization of Process Parameters

Developments in Reforming Section

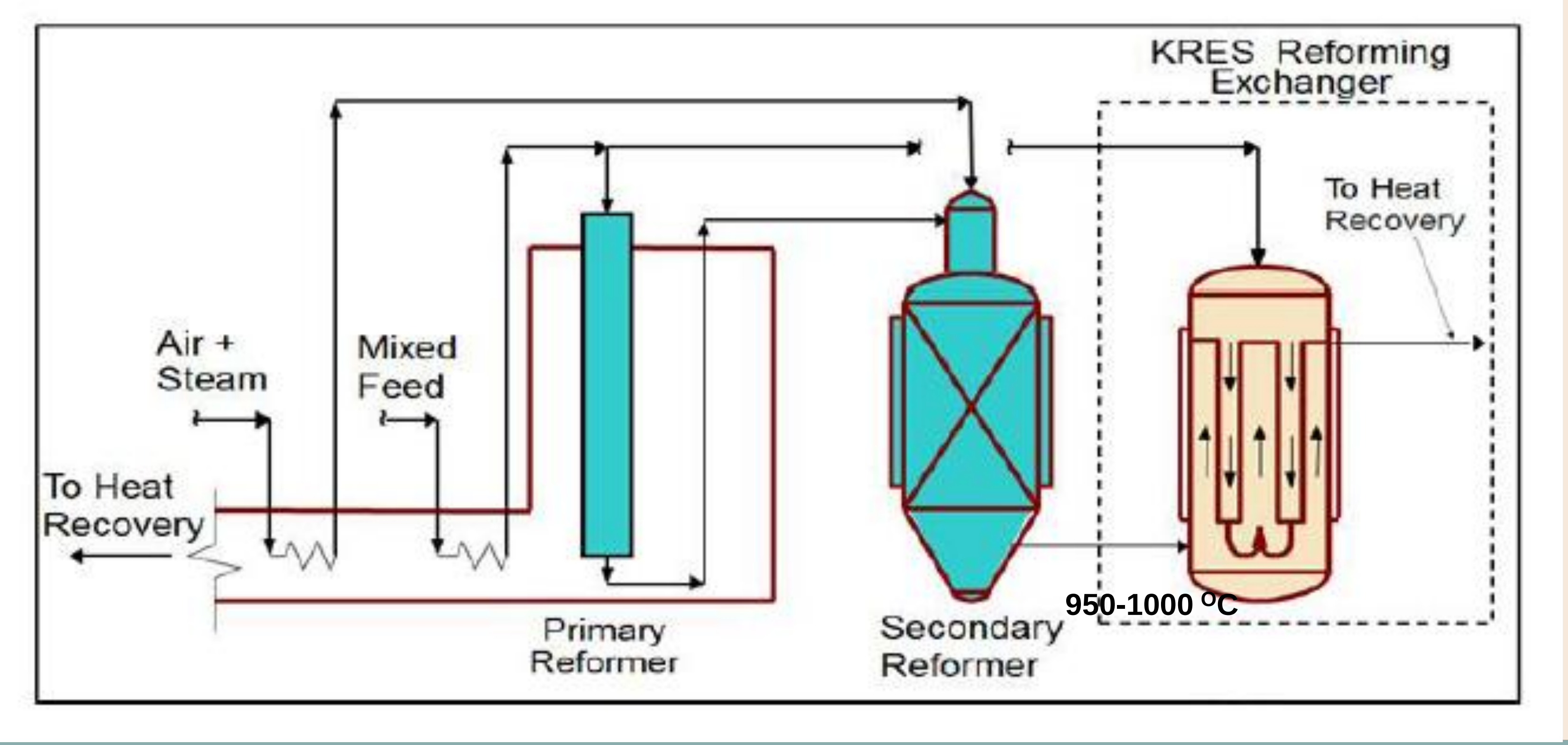
- Pre-reformer
- Flue Gas Heat Recovery
- Feed Gas Saturator
- Heat Exchanger Reformer
- Lowering S/C ratio
- Reformer Duty Shift
- Improved Tube Material
- Improved Catalysts
- Improved Insulation/Refractory
- Furnace Management

Convection Section



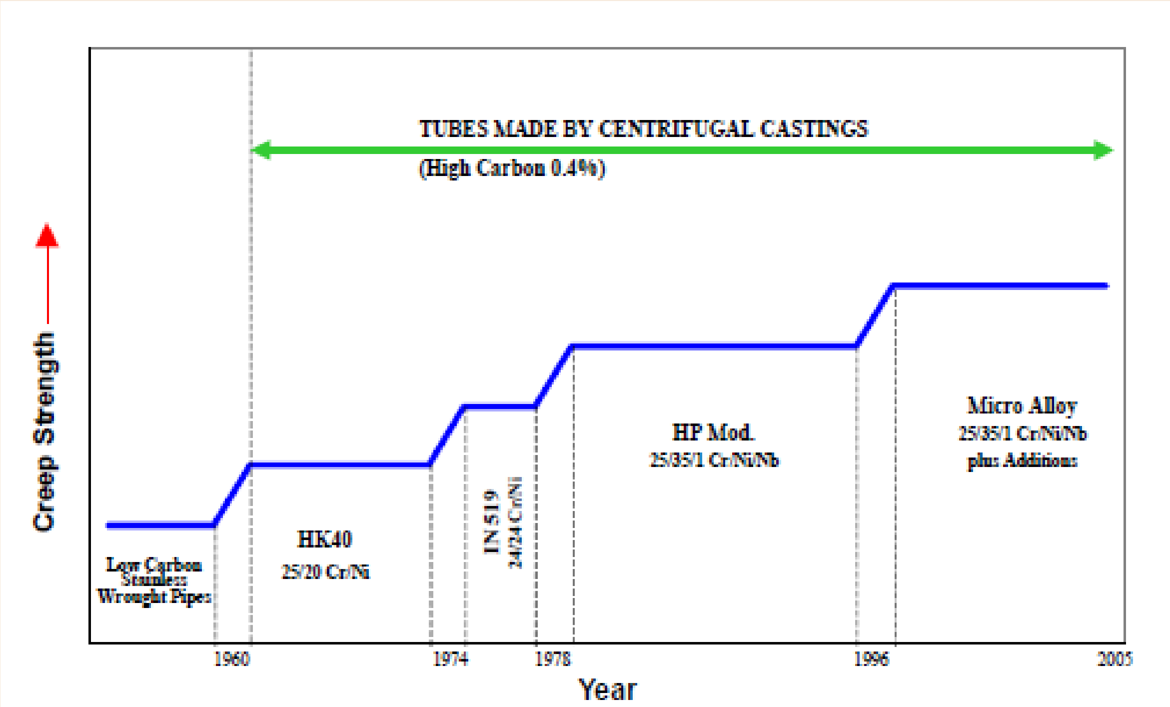
Reforming Section: Installation of Heat Exchanger Reformer

- **Utilisation of process heat of secondary reformer to reform more feed gas.**
- **Increase capacity**



Reforming Section: Improvement in Materials of Construction

- HK 40 (25% Cr, 25% Ni)
- HP Modified (25% Cr, 35% Ni, 1% Nb)
- Micro alloy (25% Cr, 35% Ni, 1% Nb, trace elements like Zr, Ti)

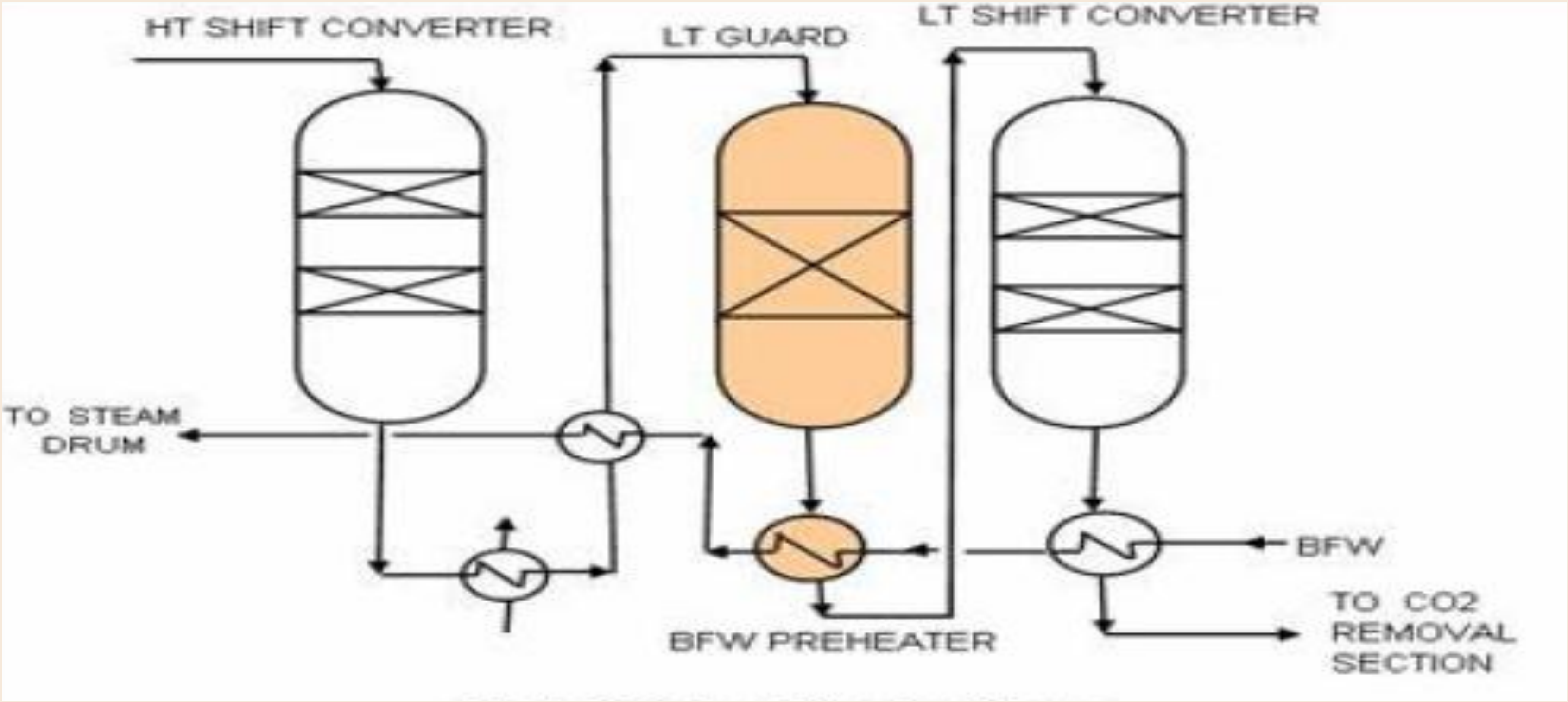


- Reduced tube thickness for same design lifetime (~100,000 hr).
- More catalyst packing
- Increase capacity of reforming section.

Developments in Purification Section

CO Shift Conversion

- Axial to Axial-radial converter
- LTS Guard With Heat Recovery



Developments in Purification Section

CO2 Removal Section

- Replacement of Solvent
  (e.g. MEA to MDEA to aMDEA or K_2CO_3 to amine based solvent)
- Hydraulic Turbine
- Single Stage to Two Stage Regeneration
- Additional Stage in existing Two stage regeneration
- Change Over of Random Packing With Structured Packing
- Modification of Internals In Towers

Cryogenic Purification

- Very low inerts (methane+argon) in make-up gas
- No purge gas requirement

Developments in Synthesis Section

Additional Purification of Synthesis Gas

- Liquid Ammonia Wash of Make Up Synthesis Gas to remove impurities of CO2 and moisture
- Drying of Synthesis Gas By Molecular Sieve

Purge Gas recovery

- Cryogenic
- Membrane Separation

Reactor Design

- Conversion of Converter flow path from Axial to Axial Radial or Radial
- Installation of Additional Converter
- Replacement of Existing Converter (Either complete or only basket retaining Shell)

Utilisation of Low Level Heat

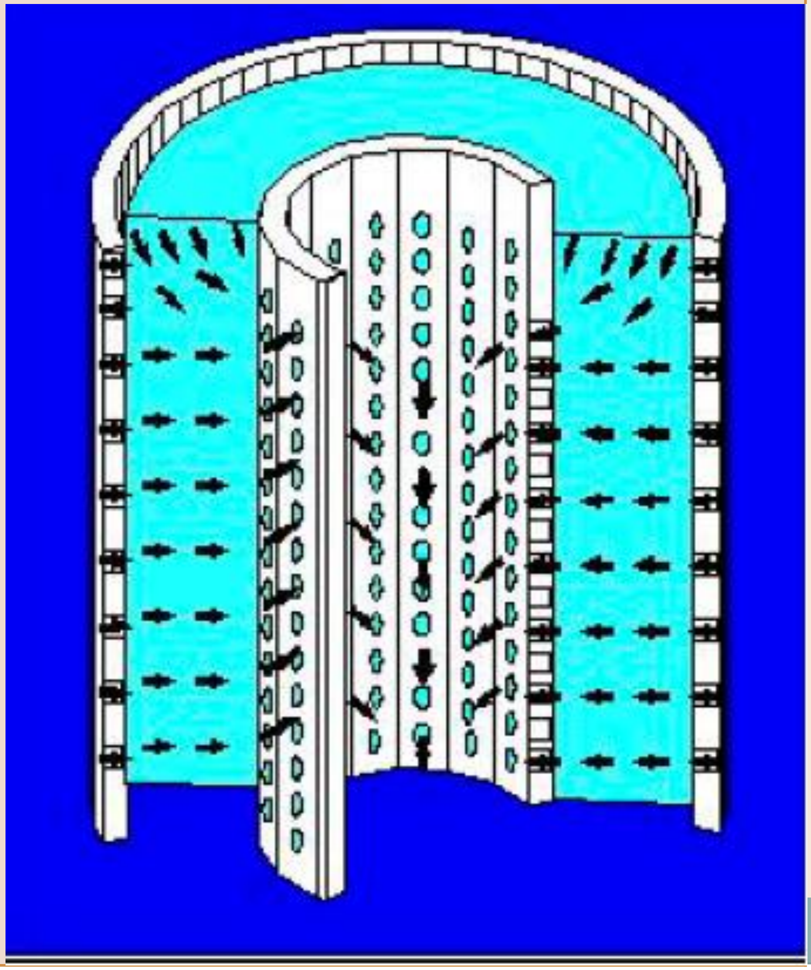
- Chilling of Make up Synthesis Gas to Save Compressor Power

Ammonia Synthesis Section
Conversion of Converter from Axial to Axial Radial

-Most gas passed through catalyst bed in radial direction

- Results in low pressure drop compared to axial flow

-Smaller particle size more active catalyst can be used.



Developments in Catalysts

Developments in Catalysts

- **Higher Activity (Higher surface area promoters)**
- **Higher Mechanical Strength**
- **Longer Life**
- **Ruthenium Catalyst for Ammonia Synthesis**
- **Nano-iron coated (~50 nm) Catalyst for Ammonia Synthesis**

Developments in Utilities

- Replacement of Turbo-Generators with GT with HRU for Captive Power Generation
- Provision of Gas Turbine for Air Compressor with HRU for Steam Generation
- VAR for cooling Process Air compressor/Carbon dioxide at inlet of Compressors
- Variable Frequency Drive for pumps
- Trimming of Pumps Impellers to Match the Load Requirement
- Change of drives of pumps and fans from steam turbine to electric motor
- FRP Blades in Cooling Tower
- Advance Process Control

Future Trends

- **Efficiency Improvements in conventional Technology**
- **Use of Renewable Energy for Ammonia Production**
- **De-carbonization of Fertilizers**
- **Use of Ammonia as Energy Carrier**

Performance of Indian Ammonia Plants

Feedstock wise Ammonia Capacity, 2018

Feedstock	Capacity (million tonnes)
Natural Gas	158.6
Coal	63.7
Fuel Oil	2.2
Naphtha	0.9
Others	2.4
Total	227.8

Source: IFA

Feedstock-wise Production for Ammonia (2017-18)

Feedstock	Production (MMT)	Percent of Total
Natural Gas	13.73	93.7
Naphtha	0.93	6.3
Total	14.66	100.0

Categorization of Ammonia Plants

Vintage	No. of plants	Feedstock	No. of plants	Size (MTPD)	No. of plants
1. 1960’s	3	Natural gas	36	<=600	7
2. 1970’s	10	Naphtha	3	>600 & <= 1000	8
3. 1980’s	12	Fuel oil	0	>1000 & <= 1520	9
4. 1990’s	12			>1520-2200	12
5. After 2000	2			>2200	2
Total	39		39		39

Technology wise Indian Ammonia Plants

Sl. No.	Technology	No. of plants
1.	KTI Selas	2
2.	Linde	1
3.	ICI	6
4.	Kellogg (KBR)	8
5.	Haldor Topsoe	22
	Total	39

Performance Evaluation of Ammonia Plants

- Production
- Energy efficiency and CO2 emission
- Forced downtime causing loss of production in ammonia and urea plants
- Safety
- Environment

Production and Energy Efficiency

- Energy consumption of ammonia and urea plants
- Benchmarking of Energy consumption of Ammonia Plants w.r.t. World Plants
- Benchmarking of Critical Process Parameters in Ammonia Plants
  - Steam/Carbon Ratio
  - Methane Slip from Primary Reformer
  - CO slip from LT Shift
  - CO_2 Slip from Absorber
  - Hydrogen loss with CO_2
  - Inerts in make up Gas
  - Inerts in recirculation Gas
  - Differential ammonia Conversion in reactor
  - Pressure drop in front end

Downtime in Ammonia Urea Plants

- Downtime due to Internal And External Factors
  - Plant Related Downtime
  - Power Problems
  - Raw Materials Shortage
  - Water Problems
  - Labour Problems
- Plant Related Problems
  - Mechanical
  - Process
  - Electrical
  - Instrumentation
  - Miscellaneous

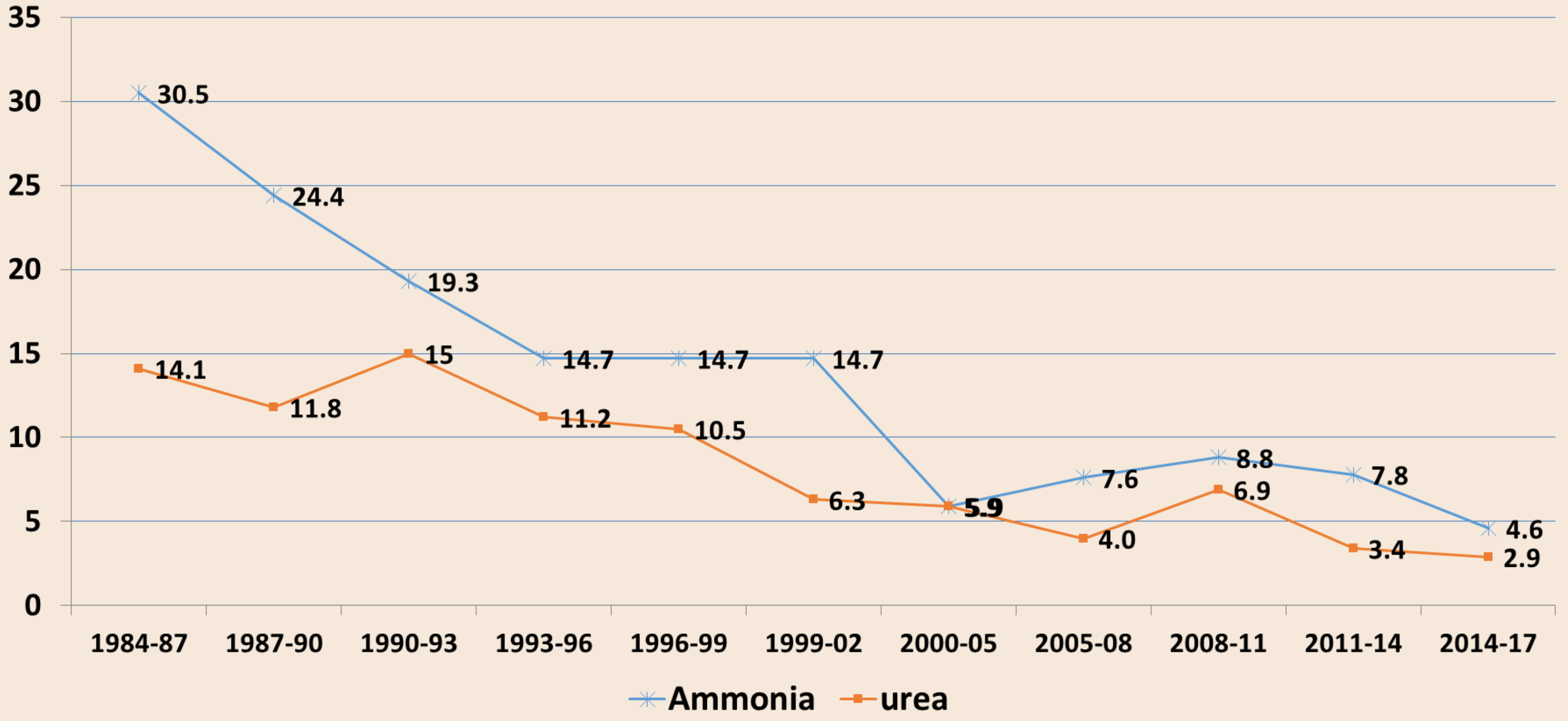
Downtime in Ammonia-Urea Plants

- Mechanical Problems in Ammonia Plants
  - De-sulphurization
  - Reforming (Pre, Primary, Secondary along with WHB)
  - Purification (Shift, CO2 Removal and Methanation and their associated eqiuipment)
  - Synthesis Section (Reactor, heat exchangers)
  - Pumps
  - Compressors (Air, Synthesis, Refrigeration)
  - Piping and valves
  - Other Miscellaneous equipment

Downtime in Ammonia-Urea Plants

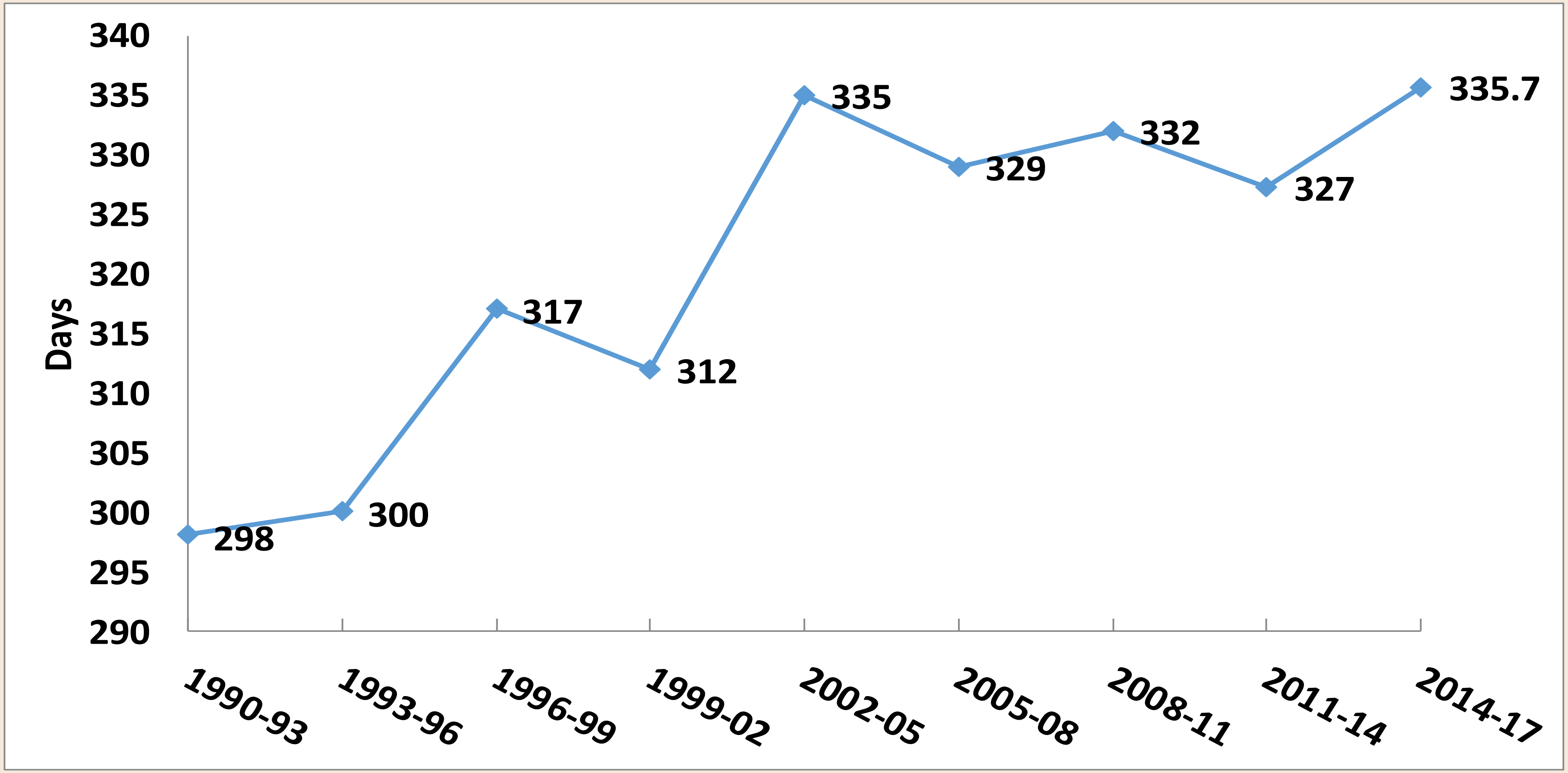
- Mechanical Problems in Urea Plants
  - Ammonia Pre-hater
  - Autoclave/Reactor
  - Stripper /Decomposer
  - Pumps (ammonia, carbamate, slurry and other)
  - CO2 Compressor
  - Heat Exchangers
  - Absorber/recovery vessels
  - Evaporator/crystallizers
  - Steam ejector/vacuum generation
  - Dryer/cooler/fans/blower
  - Conveyer/elevators
  - Prilling Tower
  - Miscellaneous

Downtime in Ammonia and Urea Plants due to Mechanical Failures (DDPY)



DDPY = Downtime in Days Per Plant Per Year

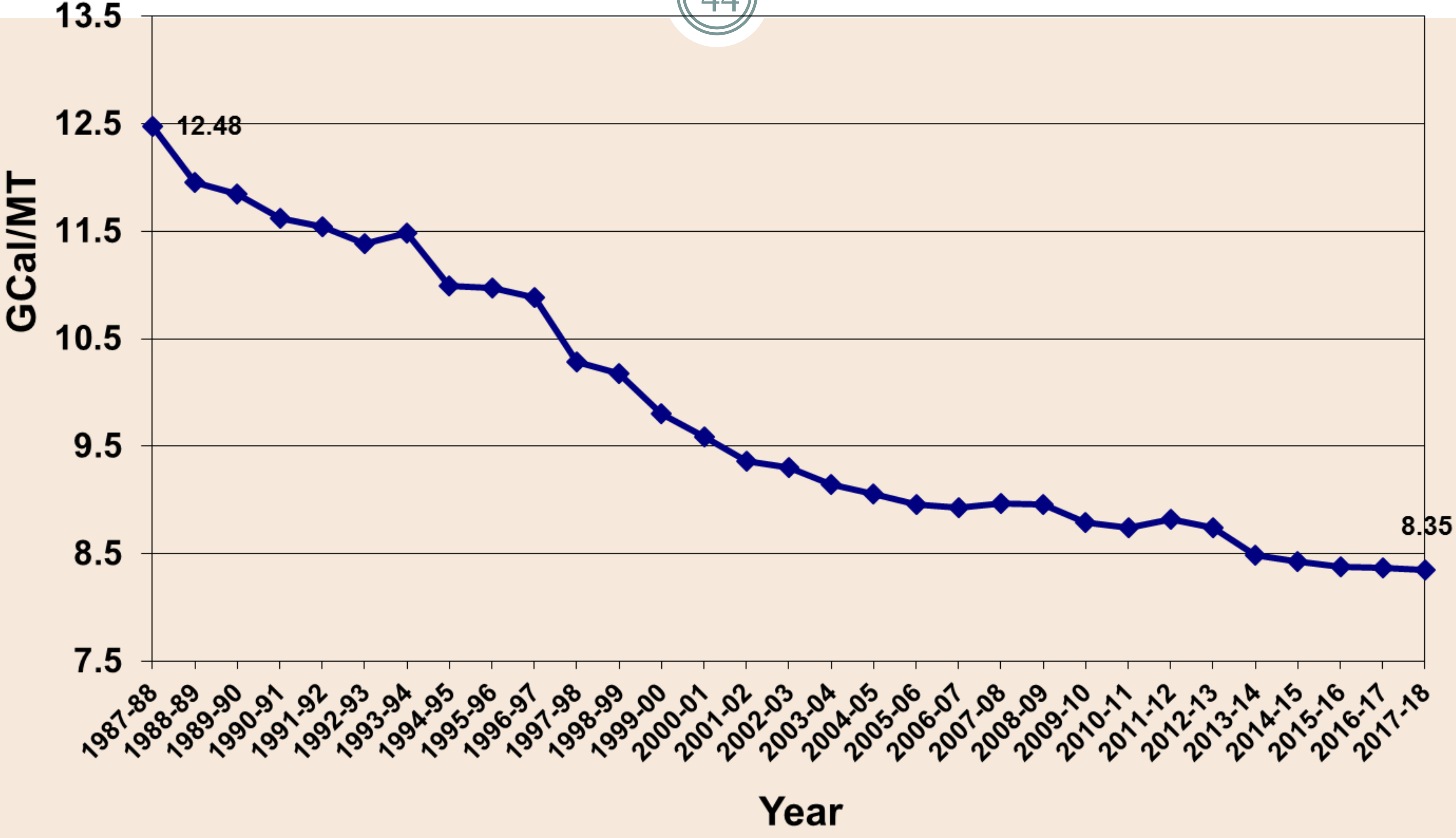
On Stream Days in Ammonia Plants



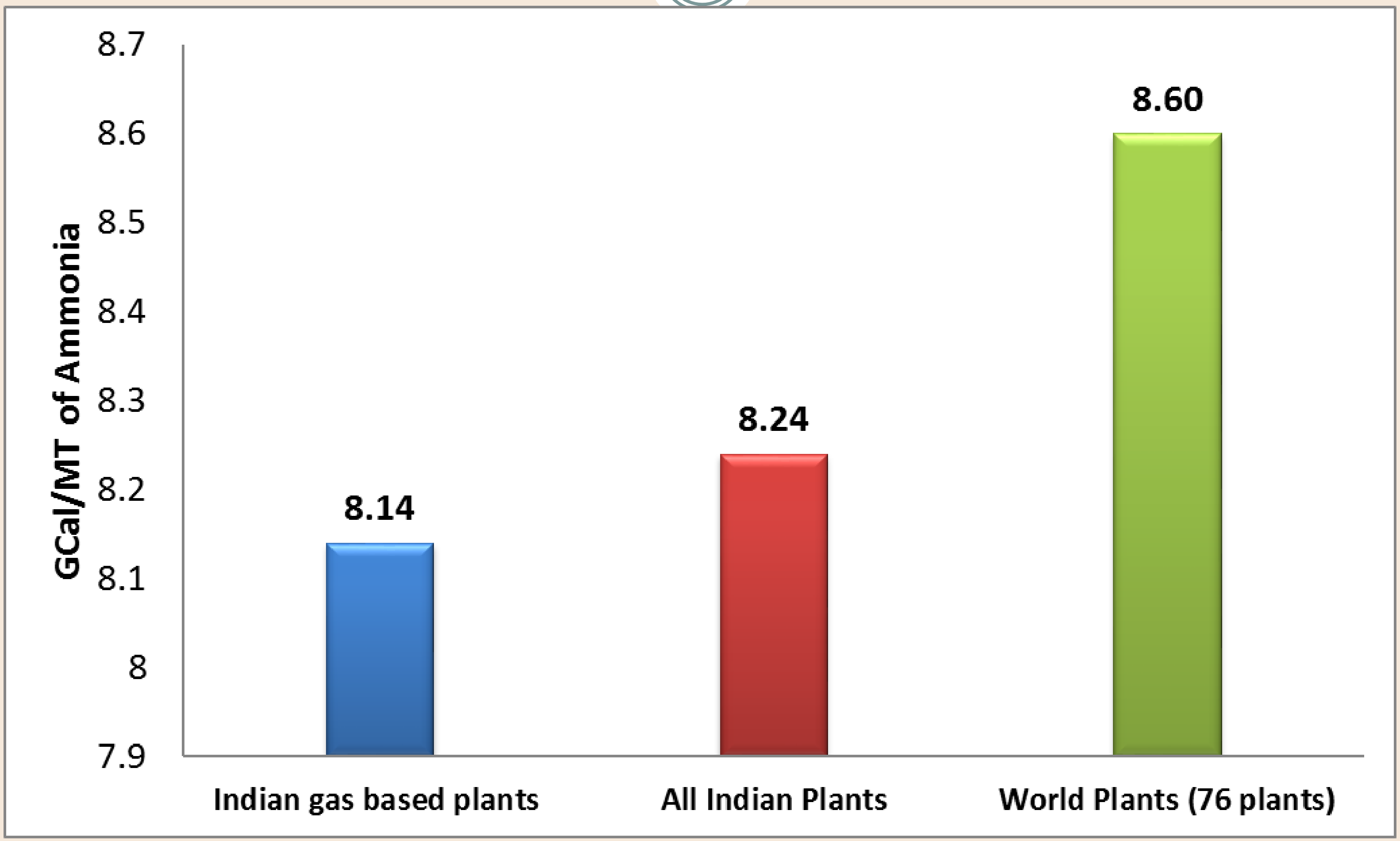
Energy Consumption in Ammonia Plant

- Energy component calculated at the battery limit of the plant
  - Feed energy
  - Fuel Energy
  - Steam at enthalpy (debit/credit)
  - Power at a conversion factor of 1kw=2520 kcal
  - Allocated share of utilities

Energy Consumption Trends in Ammonia Plants

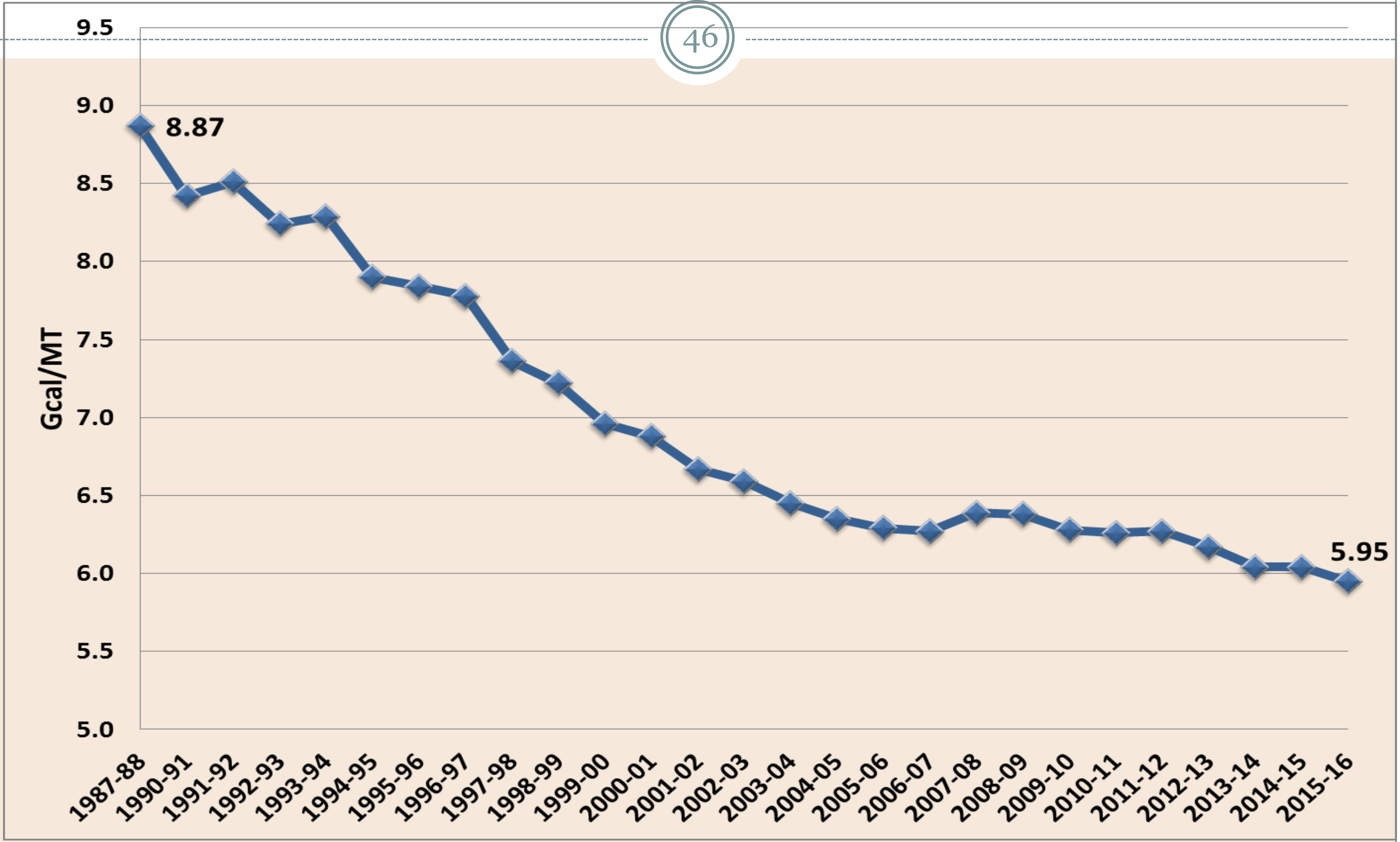


Benchmarking of Energy Efficiency of Ammonia Plants 2016



Source : FAI Data and IFA Global Technical Symposium, April 2019

Energy Consumption Trends in Urea Plants



Safety Performance

- Incidence Rate or Loss Time Injury Rate

  = number of injuries/million man hours worked

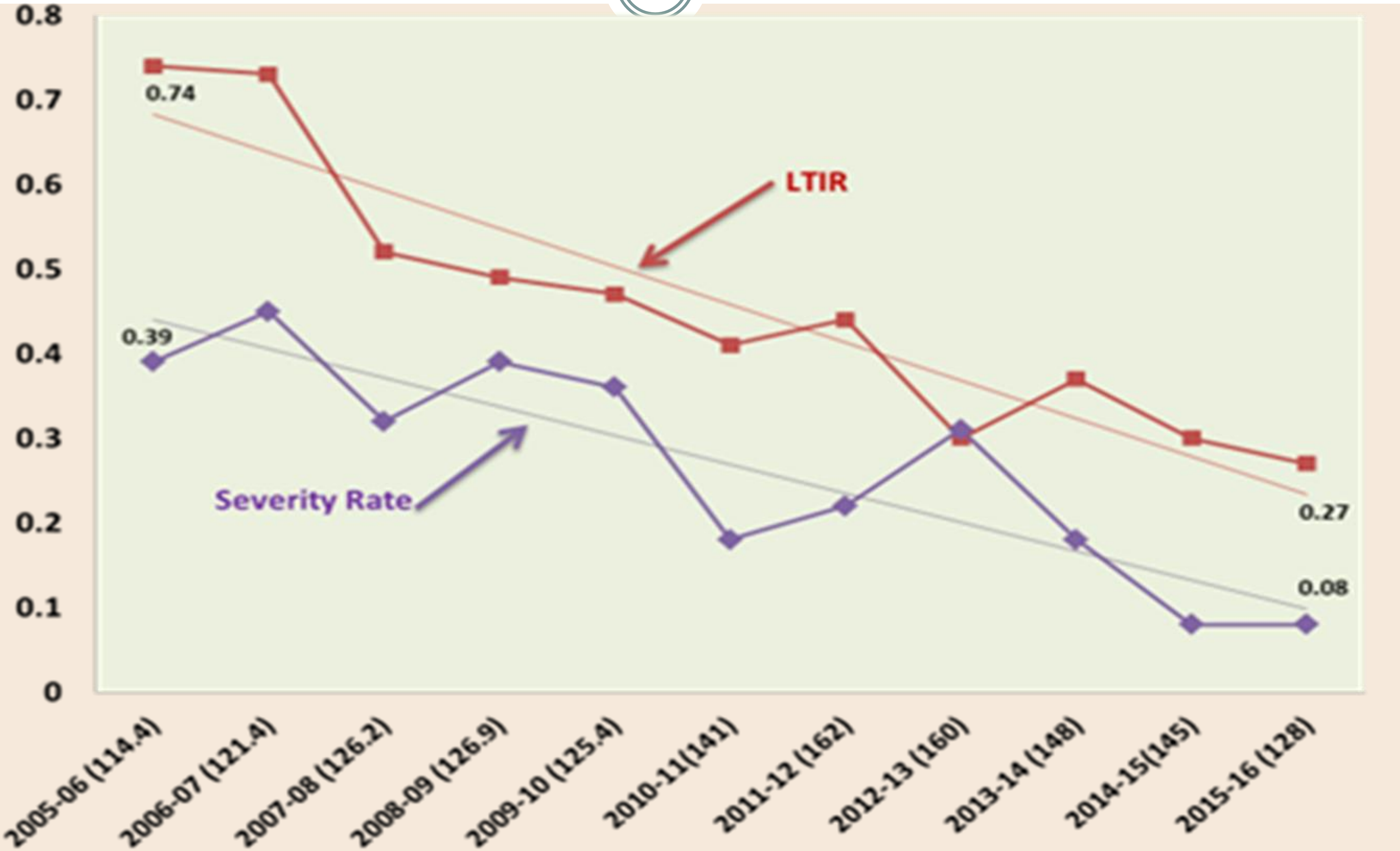
- Severity Rate

  $$= \frac{\text{number of man-hours lost X 100}}{\text{million man hours worked}}$$

- Causes of Accidents

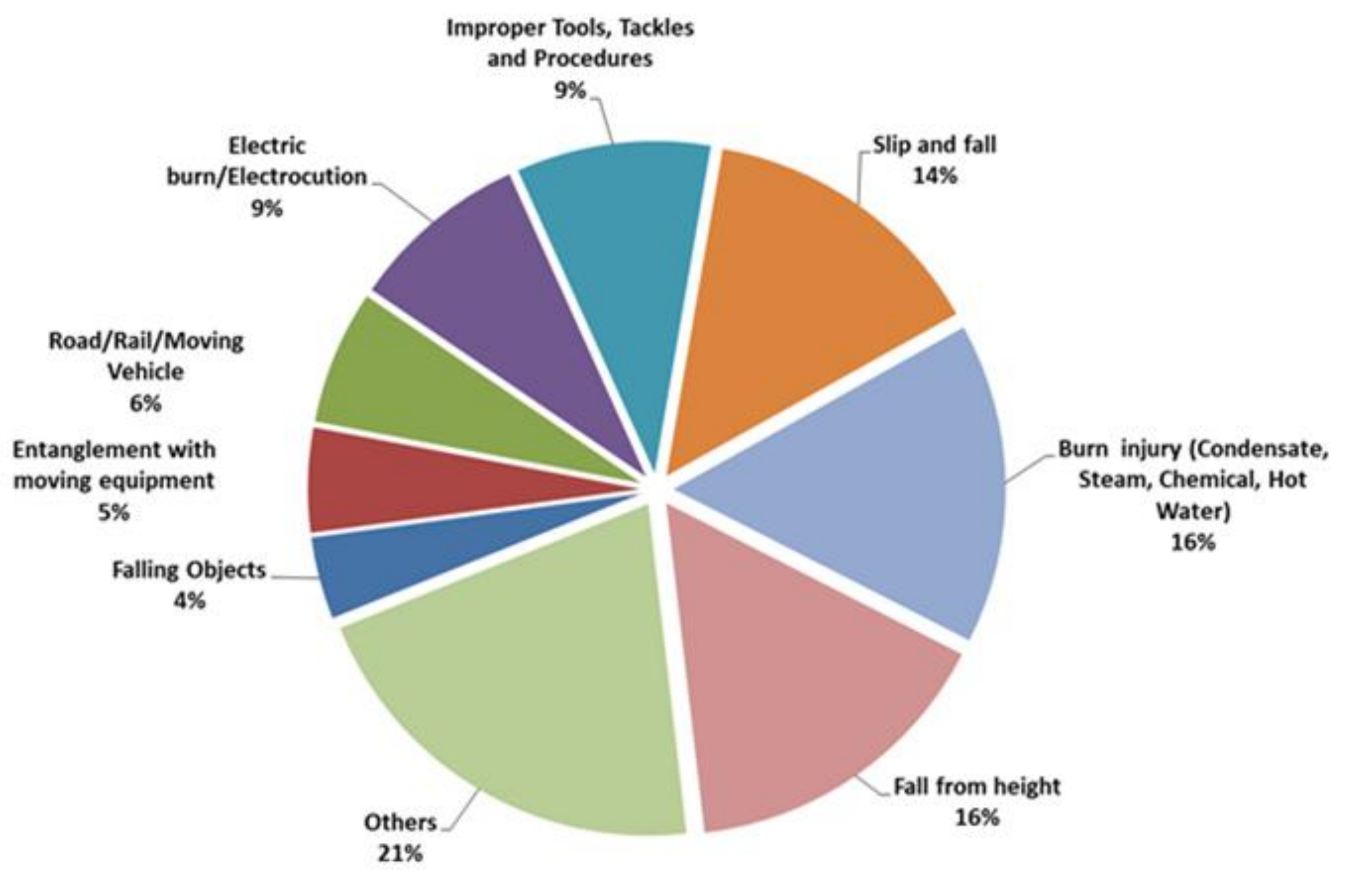
- Areas of Incidents

Incidence and Severity Rates in Fertilizer Plants



Pranthesis shows million man-hours worked

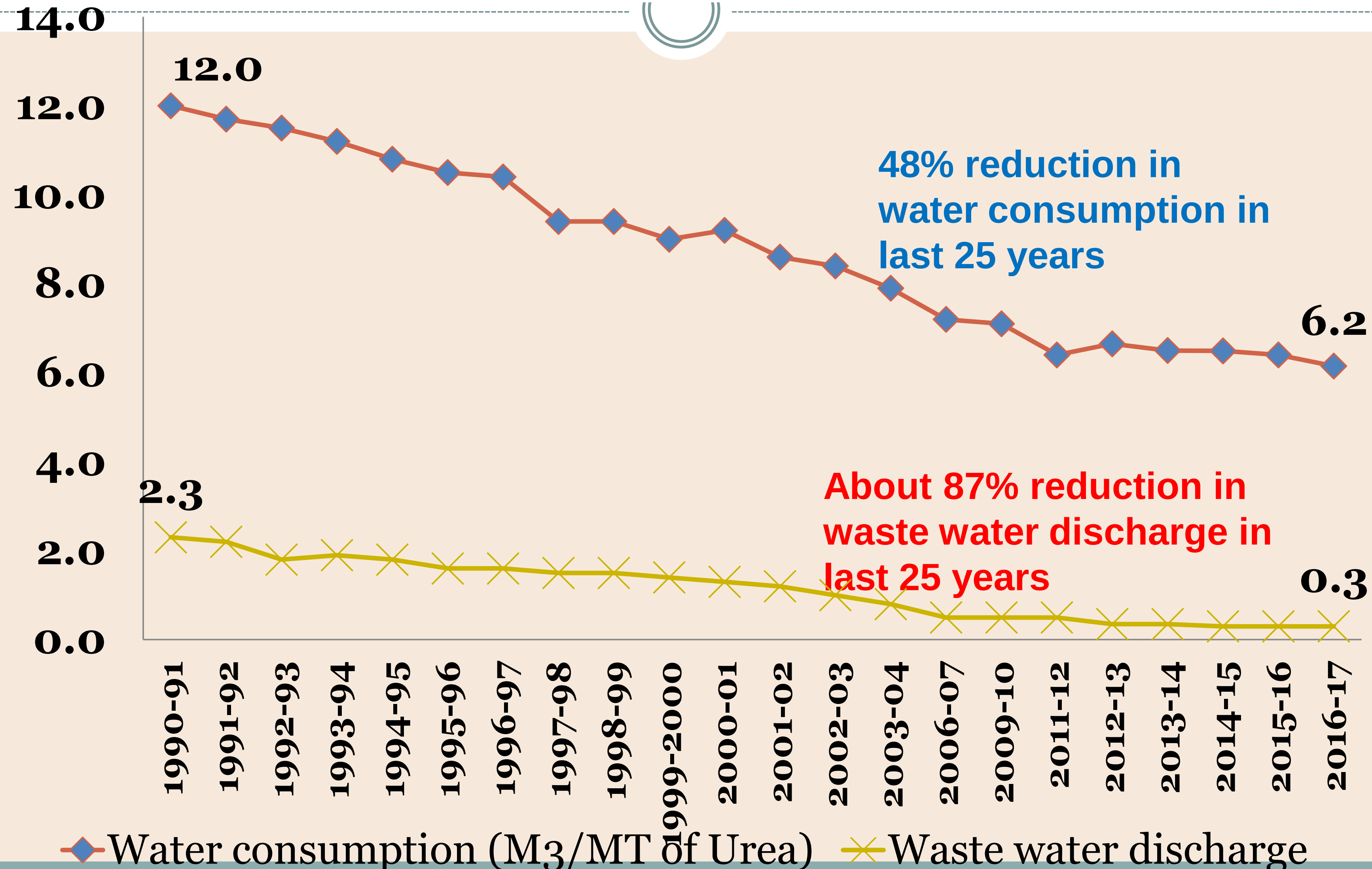
Cause-wise Analysis of accidents (2010-2015)



The Indicators of Environmental Parameters

1. Water Conservation	**-** Water consumed per MT of Product - Waste Water Discharged per MT of Product
2. Improvement in raw material Recovery Efficiency	- Specific NH_3 Consumption for Urea Production - N & P2O5 Recovery Eff. for NPK production
3. Environmental Quality Improvement	- Liquid Effluent Quality for various parameters (pH, Nitrogen, Phosphate, Fluoride) - Stack Emission (Urea Dust, Total Fluoride, Ammonia) - Total Ambient Air Quality (PM10, PM2.5, NH3, F, SOx, NOx) - Noise Level - Solid Waste Generation and its management
4. Environment Management	- Development of Greenbelt - Ground Water Monitoring - Rain water Harvesting - Use of Renewable Energy - Implementation of EMS - Voluntary Initiatives

Water Consumption and Waste Water Discharge for Urea Plants



QUESTIONS