



# GAS ANALYTICAL SOLUTIONS FOR FERTILIZER INDUSTRY





### **FERTILIZER**

### UREA AMMONIA (Non-Nitrate Based)

Nitrate Based (NPK DAP PAP)

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### Ammonia

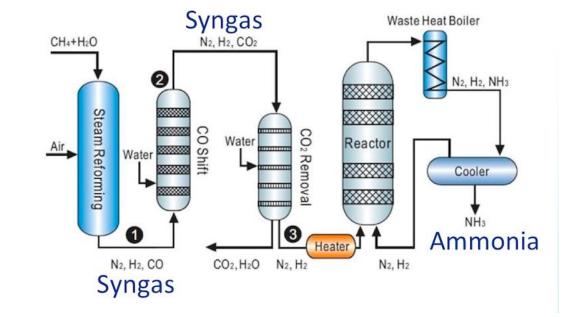
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Ammonia, a chemical compound of nitrogen and hydrogen is produced using RLNG, steam and air. Feedstock RLNG is the source for hydrogen and atmospheric air for nitrogen.

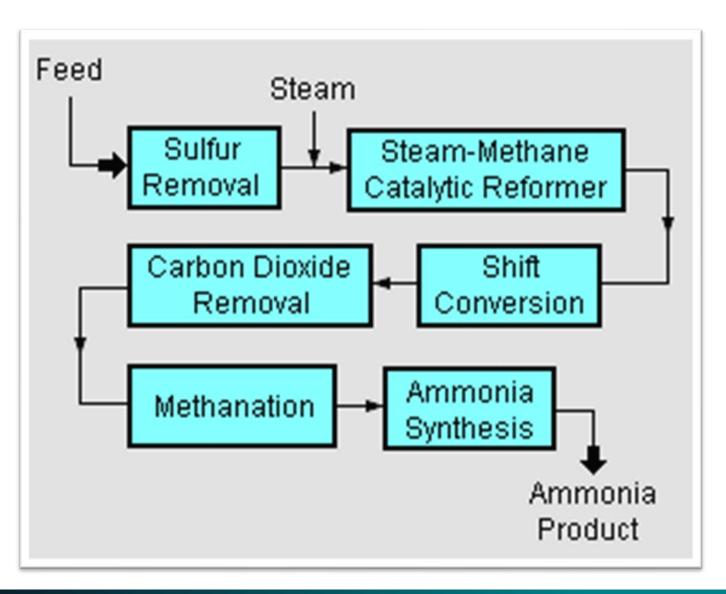
The process feed RLNG (hydrocarbon) is reformed together with steam and air to raw synthesis gas in the reforming section. The reforming section consists of Pre-reformer, Primary Reformer and Secondary Reformer. Air is introduced in the Secondary Reformer. Reformed gas containing H2, N2, CO and CO2 and traces of unconverted methane (CH4) is sent to the CO conversion section where CO is converted into CO2 in two steps in shift conversion units. CO2 is absorbed using Methyl Di-ethanol Amine.

CO2 from MDEA section sent to Urea Plant as one of the raw materials for Urea production. The remaining CO and CO2 from the process gas are converted to CH4 in the Methanator. The processed synthesis gas is compressed and sent to the catalytic converters (S 200 and S 50) where Ammonia is produced by the catalytic action. Synthesized Ammonia is separated and sent to Urea Plant as raw material and the remaining quantity is refrigerated and sent to cylindrical storage tanks.









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### The process..... Ammonia Plant

#### • Ammonia plant

An ammonia plant has several key sections:

- Primary reformer
- Secondary reformer
- Carbon dioxide absorber
- Ammonia convertor





### **Raw materials**

The raw materials needed are air, natural gas (or other hydrocarbons) and steam.

Removal of sulfur from feedstock, e.g. natural gas, involves these chemical reactions:

 $R-SH + H_2 \rightarrow H_2S + RH$ 

 $H_2S + ZnO \rightarrow ZnS + H_2O$ 





### Primary reformer The chemistry

After the removal of sulfur compounds, the gas is mixed with superheated steam and fed into a primary reformer.

The mixture is heated to 770 °C in the presence of a nickel catalyst and these reversible reactions occur:

 $CH_4 + H_2O \rightleftharpoons CO + 3H_2$   $\Delta H^{\circ}_{298} = +206 \text{ kJ mol}^{-1}$ 

 $CO + H_2O \rightleftharpoons CO_2 + H_2$   $\Delta H^{\circ}_{298} = -41 \text{ kJ mol}^{-1}$ 

Overall reaction:

 $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$   $\Delta H^{\circ}_{298} = +165 \text{ kJ mol}^{-1}$ 

The overall reaction (methane and steam to carbon dioxide and hydrogen) is highly endothermic.

Therefore, maintaining a high reaction temperature moves the position of equilibrium to the right.

The mixture that emerges is called synthesis gas.

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### Secondary reformer

### Reforming

Only 30-40% of the hydrocarbon is reformed in the primary reformer because of the equilibrium reactions. The synthesis gas is cooled slightly to 735 oC, mixed with air and passed into the secondary reformer. Highly exothermic reactions happen such as:

CH4 + 2O2 2 2H2O + CO2 ΔHo298 = -82 kJ mol-1

With the energy released and further heating a temperature of about 1000 oC is reached and up to 99% conversion to methane to hydrogen achieved. Nitrogen (from the air) is used later in the synthesis of ammonia.

#### Shift conversion

Any remaining carbon monoxide in the gas mixture is converted to carbon dioxide in the shift section of the process:

 $CO + H2O \rightleftharpoons CO2 + H2$   $\Delta Ho298 = -41 \text{ kJ mol}-1$ 

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### The shift conversion happens in two stages:

- High temperature shift (iron oxide/chromium oxide catalyst at about 400 oC) that lowers the carbon monoxide content from 12-15% to about 3%.
- Low temperature shift (copper oxide/zinc oxide-based catalyst at about 200-220 oC) which lowers the carbon monoxide content further to about 0.2-0.4%.



### **Ammonia Synthesis**

#### Removal of water and carbon dioxide

The gas mixture now consists of mainly hydrogen, nitrogen, carbon dioxide and steam. Cooling the gas causes steam to condense and be removed as liquid water.

Carbon dioxide is removed by chemical or physical absorption. It is used for the manufacture of urea.

#### **Methanation**

Any remaining amounts of carbon monoxide and carbon dioxide must be removed before the ammonia synthesis stage as they would poison the catalyst. This is done by reacting them with hydrogen at 300 °C over a nickel-containing catalyst.

 $CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H^{\circ}_{298} = -206 \text{ kJ mol}^{-1}$ 

 $CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$   $\Delta H^{\circ}_{298} = -165 \text{ kJ mol}^{-1}$ 

The emerging gas must be completely dry and so water produced in these reactions is removed by condensation.



#### **Ammonia synthesis**

- High temperature shift (iron oxide/chromium oxide catalyst at about 400 oC) that lowers the carbon monoxide content from 12-15% to about 3%.
- Low temperature shift (copper oxide/zinc oxidebased catalyst at about 200-220 oC) which lowers the carbon monoxide content further to about 0.2-0.4%.



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### Urea

Urea is produced by reacting Ammonia with carbon di oxide (obtained from Ammonia Plant) in stainless steel lined reactors at 215-220 kg/cm2g pressure, using the technology of UTI total heat recycle Process. The high efficiency Reactor has a conversion of CO2 to Urea of about 76% per pass. After flashing and decomposition at medium pressure, an additional Carbon-di-oxide is injected into the Medium Pressure System followed by flashing and decomposition at low pressure and then concentration of urea solution at vacuum. Further concentration takes place at evaporators at the top of Prill Tower.

Here the hot Urea solution sprayed down in a 210' cylindrical concrete Prill Tower, counter current to a stream of cold air with a free fall height of prills for 170'. The Urea solidifies into small white Urea prills. The prills are then passed through a Fluidized Bed Cooler (Prills Cooling System) to reduce temperature and fines thereby improving the quality of the product.

The entire off gas is absorbed in a bubble cap tray absorber and then recycled to the reactors. The chloride-free effluent is treated in a Hydrolyser Stripper and the contents are recycled fully. The treated water is used for demister washing.

The product is sent through a system of conveyors and elevators to bagging streams. There it is bagged and shipped as Urea product.







### NPK / DAP / PAP

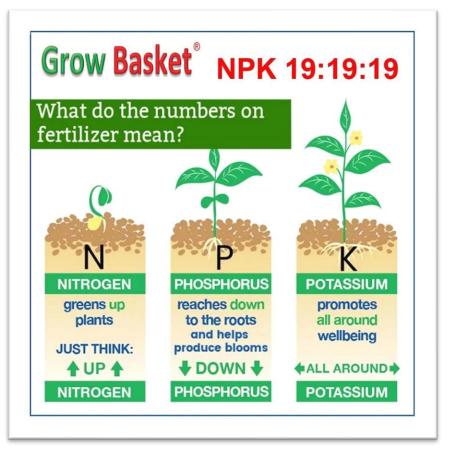
The basic steps for NPK manufacture are:

Reaction of liquid Ammonia and Phosphoric Acid to form slurry of mono and di ammonium phosphates in Pre-neutralizer.

Mixing of the slurry with other feed materials: Liquid Ammonia, Urea, Muriate of Potash, Filler and re cycled NPK granules. Solid raw materials are fed to the system through the modern J&N Weigh Feeders (with Programmable Logic Control device) which maintain accuracy according the set load. Mixing is done in the `Blunger units where the fertilizer granules are formed.

Drying of the granulated material in a rotary dryer.

Separation of granule produced by screening followed by cooling, coating & polishing of the granules and product bagging.







### **APPLICATIONS:**

- Measurement of CH4 at gas Generator Outlet
- Measurement of CO at LT & HT Shift Convertor
- Measurement if H2 at Inlet of Shift Convertor
- Measurement of CO2 at inlet of Methanator
- Measurement of H2, CO, CO2, & CH4 at Methanator Exit
- Measurement of H2 in CO2 to Urea
- Measurement of H2 & CH4 at Inlet of NH3 Convertor
- Measurement of H2 in at Inlet of N2 receiver
- Measurement of CO,CO2,CH4,H2 & NH3 in Syn Gas.
- Measurement if N2 & H2 for Ratio Control
- Measurement of NH3 at Prill Tower Outlet
- Gas Chromatography for NG measurement at Feed
- Measurement of Total Sulfur in NG and after H2S Removal
- O2+Coe at Reformer Heater Outlets
- CEMS at Reformer Stacks (SO2,Nox.PM)
- CEMS at DAP/NPK Stacks (NH3 & HF)





### **Analyser Used:**

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- SIEMENS ULTRAMAT 23, ULTRAMAT 6 FOR CO, CO2, CH4, NH3(dry)
- **SIEMENS CALOMAT 6 FOR H2 & N2**
- **VALMET GAS CHROMATOGRAPHY**
- **PROCESS INSIGHTS TOTAL SULFUR**
- **SIEMENS TLDS 6 FOR NH3 & HF**
- **SIEMENS ULTRAMAT 23 FOR CEMS**
- **EXTREL (PI) MASS SPECTROMETRY** ٠













### **NH3 Measurement in a DAP/NPK Stack HF Measurement in a PAPStack** State of the art Laser FAST, ACCURATE. Of course **RELIABLE, CONTINUOUS,** Analyzers reduced NH3 **REAL TIME HF** Measurement with Laser emissions Analyzers considerably Reduced consumption of NH3 Increased efficiency of **Scrubbers** .....may give you information **Saves Cost & Energy** on feed rate consumption of raw material

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### **NH3 Measurement in Prill Towers**





For the very first time we had the opportunity to measure NH3 in the Prill Towers accurately, continuously, real time and quickly THANKS TO THE UNIQUE TECHNOLOGY OF LASER ANALYZERS

For sure it will tell us something of the Urea consumption of the air consumption

FOR SURE IT WILL HELP US TO OPTIMISE THE PROCESS

IT WILL HELP US ULTIMATELY TO SAVE SOME COST & ENERGY

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# AKAI

SUCCESSFUL INSTALLATION & OPERATION FOR APPLICATION (Urea Prill Tower) FOR NH<sub>3</sub> MEASUREMENT IN MCFL, Mangalore SINCE August 2015





SUCCESSFUL INSTALLATION & OPERATION FOR APPLICATION (DAP Stack) FOR NH<sub>3</sub> and HF MEASUREMENT IN MCFL, Mangalore SINCE August 2015

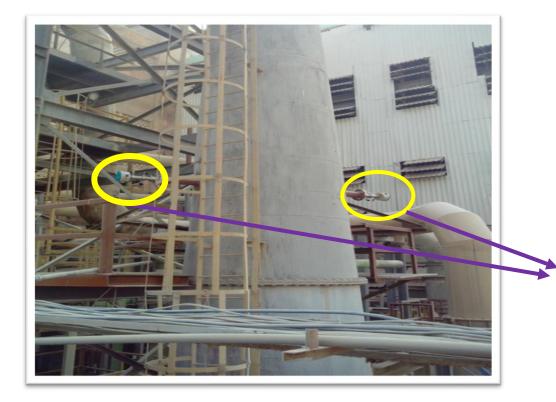
Transmitter and receiver units being installed at the Dap Stack for HF and NH<sub>3</sub>

Analyzer Shelter equipped Central Unit installed at the Bottom of Dap Stack for HF and NH<sub>3</sub>





### SUCCESSFUL INSTALLATION & OPERATION FOR APPLICATION (NPK/DAP) FOR NH<sub>3</sub> MEASUREMENT IN RCF CHEMBUR, MUMBAI SINCE FEBRUARY 2014



INDIA'S 1<sup>ST</sup> TDLS ANALYSER INSTALLED IN A FERTILISER PLANT

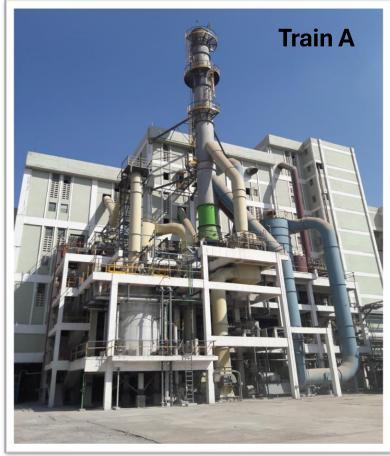
Transmitter and Receiver units being installed at the NPK/DAP Stack For the Measurement Of NH<sub>3</sub>





#### SUCCESSFUL INSTALLATION & OPERATION FOR APPLICATION

(DAP /SAP/NPK Stack) in TRAIN A, Train B and Train C FOR NH<sub>3</sub> MEASUREMENT IN GSFC, Sikka SINCE December 2015











### SUCCESSFUL INSTALLATION & OPERATION FOR APPLICATION in 16 Stacks FOR NH<sub>3</sub> MEASUREMENT IN GSFC, Baroda SINCE November 2015



**CEP** Lactum



**SO2 Scrubber** 



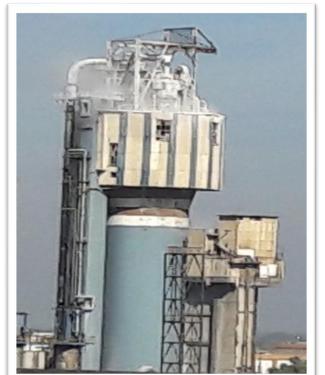
**De NOx** 



Melamine



Urea Melamine ECS



**Urea Prill Tower** 





### SUCCESSFUL INSTALLATION & OPERATION FOR APPLICATION (Urea Prill Tower) FOR NH<sub>3</sub> MEASUREMENT IN CHAMBAL FERTILIZERS AND CHEMICALS LIMITED, KOTA, RAJASTHAN



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### GAS CHROMATOGRAPH AND TOTAL SULFUR INSTALLED IN A FERTILISER PLANT WITH INTEGRATED SHELTER AND HVAC



## **THANK YOU**

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