GRANDE PAROISSE

Integrated production of Nitric Acid and Ammonium Nitrate: GP experience
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1. INTRODUCTION

GP developed in the 1950’s the technology of Nitric Acid production by dual pressure process and later on by mono pressure process.

Continuous improvements have concerned:
- efficiency (both regarding Ammonia consumption and energy)
- environment,
- safety.

1. INTRODUCTION

GP developed in the 1980’s the technology of Pipe Reactor for ANS production.

Continuous improvements have concerned:
- flexibility of operation,
- environment,
- safety.
1. INTRODUCTION

GP made more than 10 years ago some developments in both processes in order to
- minimize investment cost
- maximize energy recovery
- minimize emissions

through process integration.

Capacity of the case:
- Nitric Acid plant 500 MTPD
- Ammonium Nitrate solution plant 635 MTPD

2. GP NITRIC ACID PROCESS DESCRIPTION

Capacity range
- First Nitric Acid plant designed by GP (1958) Frais Marais (France) capacity 160 MTPD.
- Largest one (1986) Yara Sluiskil site (The Netherlands) 2000 MTPD.

72 plants have been designed
2. GP NITRIC ACID PROCESS DESCRIPTION

Mono Pressure Process

Air Compression
- Atmospheric air is
  - filtered
  - compressed
  - divided into primary air and secondary air
- Primary air is sent to air-ammonia mixer.
- Secondary air is
  - cooled by pre-heating tail gas
  - used for bleaching the product acid.

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2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process
- Air Compression
- Ammonia supply
  - Ammonia Evaporation and Pressure Control
  - Ammonia Superheating
  - Air-Ammonia Ratio Control

Ammonia Oxidation
- Air-ammonia mixture is introduced into the ammonia burner
- Ammonia combustion temperature is about 900°C
- Main reaction produces NO
- Side reactions also take place
- GP is integrating N₂O abatement technology in its design.
2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process
- Air Compression
- Ammonia supply
- Ammonia Oxidation
- Heat Recovery on NO\textsubscript{x} Gas
- Acid Production by NO\textsubscript{x} Gas Absorption
  - Process water is fed on the upper tray of absorber.
  - NO\textsubscript{x} content in tail gas is lower than 600 ppm.
  - The nitric acid produced in the absorber contains a large amount of NOx gases in solution that colors the acid.
  - The secondary air eliminates dissolved NOx gases by stripping in the bleacher
2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process
- Air Compression
- Ammonia supply
- Ammonia Oxidation
- Heat Recovery on NO\textsubscript{x} Gas
- Acid Production by NO\textsubscript{x} Gas Absorption
- Tail Gas Heating
  - To maximize recovery of energy through tail gas expander is heated in the following exchangers:
    - Secondary air cooler
    - Tail gas preheater by cross exchange with LP steam.
    - Tail gas heater by cross exchange with NO\textsubscript{x} Gas from the boiler / conveter.

Selective Catalytic Reduction
- Hot tail gas is injected into a NO\textsubscript{x} abatement reactor
- At the outlet, NO\textsubscript{x} content < 150 ppm.
- With special design and operating conditions < 50 ppm achieved
2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process
- Air Compression
- Ammonia supply
- Ammonia Oxidation
- Heat Recovery on NOx Gas
- Acid Production by NOx Gas Absorption
- Tail Gas Heating
- Selective Catalytic Reduction
- Tail Gas Expander
- High Pressure (HP) steam
  - produced in waste heat boiler system.
  - A part is superheated in superheater and sent to the steam turbine.
  - The remainder is sent to battery limits as export steam.

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2. GP NITRIC ACID PROCESS DESCRIPTION

Dual Pressure Process

- Water
- Superheater
- Steam Drum
- Burner
- Mixer
- Filter
- Waste Heat Boiler
- Filter
- Tail Gas Preheater
- Secondary Air Cooler
- Tail Gas Heater
- Condenser
- Expander
- Air Compressor
- DeNOx Reactor
- Absorption Tower
- Bleaching Tower
- Ammonia
- Air Nitric Acid
- Stack
- Export Steam

3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

GP developed in the 1980’s the technology of Pipe Reactor for ANS production.

Capacity range

- The first Pipe Reactor was installed in a Grande Paroisse plant at Mazingarbe with a capacity of 250 MTPD.
- The largest one installed in 1993 in DSM Geleen (The Netherlands) has a present capacity of 2000 MTPD.

Continuous improvements have concerned

- flexibility of operation,
- environment,
- safety.
3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

Difficulties with conventional processes:
- Operating conditions of the neutralizer (P, T, ANS Concentration) are dependant on boiling properties of the ANS

![Graph showing pressure in atm as a function of ANS concentration in %w/w at different temperatures (60°C, 120°C, 140°C, 160°C, 180°C, 190°C).]

3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

GP Pipe Reactor process:
- HNO₃
- NH₃
- Condensation
- Process steam purification
- Mixing
- Heating
- Vaporization Superheating
- Reaction
- Separation
- Condensate
- NH₄NO₃ production
3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

GP Pipe Reactor process:

![Graph showing ANS concentration %w/w as a function of Nitric acid concentration %w/w at 40°C, 60°C, and 80°C.](image)

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3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

GP Pipe Reactor process:

![Graph showing NH₃ and HNO₃ concentration over time.](image)
3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

Water balance issue

Possible treatments of the process steam
- Filter candles
- Scrubbing column
3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

Possible treatments of the process steam
- Filter candles
  - First treatment
  - low velocity (1 m/s)
  - PTFE fibers
3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

Possible treatments of the process steam
- Filter candles
- Scrubbing column
- Entropie® System

3. GP AMMONIUM NITRATE PROCESS DESCRIPTION
4. INTEGRATION

Integration logic:
- Gaseous Ammonia is a common raw material
- Low pressure steam is available in ANS plant
- Process water is needed for absorption in NA plant and excess water is available in ANS plant

Gaseous Ammonia
- Ammonia for NA is
  - vaporized to cool down chilled water
  - superheated by MP Steam
- Ammonia for ANS is vaporized by Process steam.

- Having a common vaporizer
  - Doubles the available chilled water for the NA plant and save some Process steam
- Having a common super-heater
  - increases the condensation of Process steam in ANS plant
  - reduces the consumption of MP Steam in NA plant

Reduction of investment cost
Reduction of steam consumption by 1.5 MTPH
4. INTEGRATION

Boiling Feed Water heating
- BFW is heated up to ~ 100°C through
  - one exchanger fed with clean process steam
  - one exchanger fed with process steam

Reduction of steam consumption by 4.6 MTPH
4. INTEGRATION

Tail gas preheater
- Preheating performed by MP steam
- BFW is hot

Tail gas preheater
- BFW can be used to preheat tail gas

Reduction of steam consumption by 2.6 MTPH
4. INTEGRATION

Process condensate recycle
- Process water is needed on NA absorption tower
- Acidic contaminated condensate is available in ANS
- Process condensate can partly replace process water

Reduction of Demin water consumption by 10 M³/H

4. INTEGRATION

ANS cooling
- Ammonium Nitrate Solution
  - 97% concentration,
  - boiling temperature ~ 190°C
  - crystallization temperature ~ 135°C
- For downstream process, temperature has to be decreased down to about 150°C.
- GP designed an MP steam generator

MP Steam Production is about 0.5 MTPH
5. CONCLUSION

SAVINGS

- investment cost => common equipment for both plants
- operation cost => much better energy efficiency
  high reduction of the demin.water demand

Resulting benefit in operating cost is more than 1000 k€/year.

LOW EMISSION:

- Recycling of contaminated process condensate to the absorption
  - not only reduces the consumption of demineralized water
  - but also provide a reduction of Nitrogen emissions
- Thus making the plants more environment friendly.
- Nitrogen emission to waste water treatment ~ 3 kg/day.
5. CONCLUSION

- Today, those two plants have been running for many years without any problem.

- The integration has been proven as reliable and efficient for the entire period.

Thank you for your attention