GRANDE PAROISSE

Integrated production of Nitric Acid and Ammonium Nitrate: GP experience

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Vilnius, Lithuania,
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ifa International Fertilizer Industry Association

TOTAL

- 1. INTRODUCTION
- 2. GP NITRIC ACID PROCESS DESCRIPTION
- 3. GP AMMONIUM NITRATE PROCESS DESCRIPTION
- 4. INTEGRATION
- 5. CONCLUSION.

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

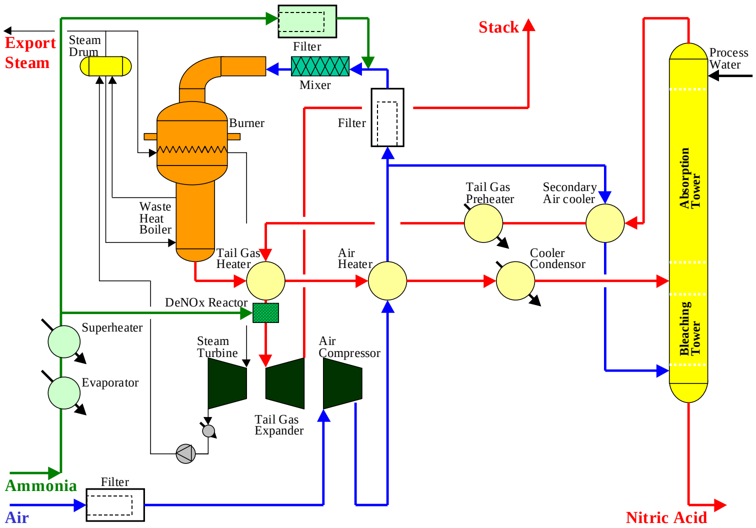
2. GP NITRIC ACID PROCESS DESCRIPTION

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

- 72 plants have been designed

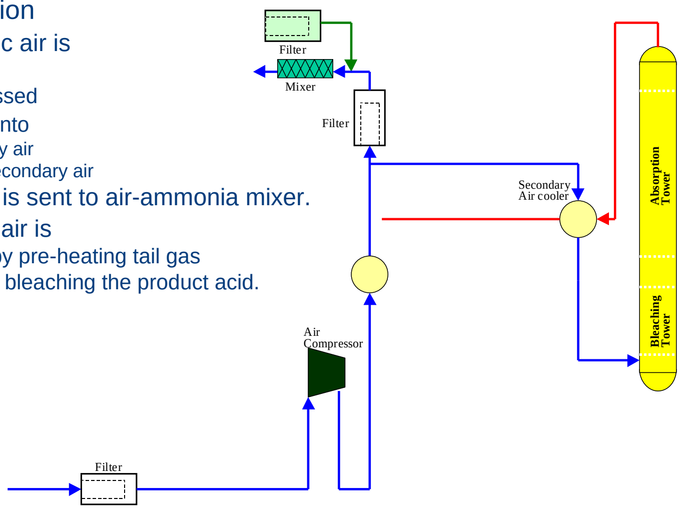
2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process



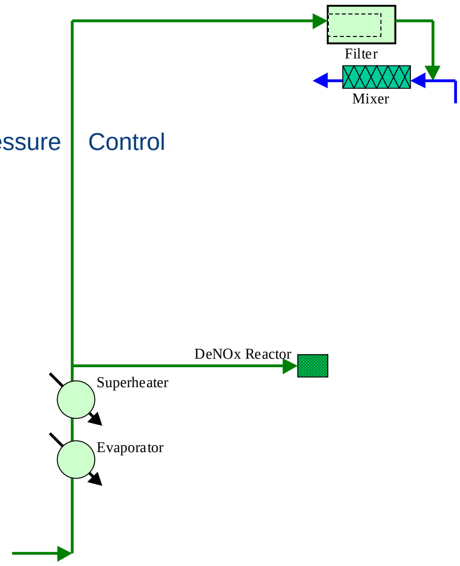
2. GP NITRIC ACID PROCESS DESCRIPTION

- 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.



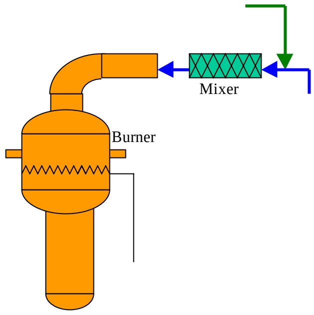
2. GP NITRIC ACID PROCESS DESCRIPTION

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



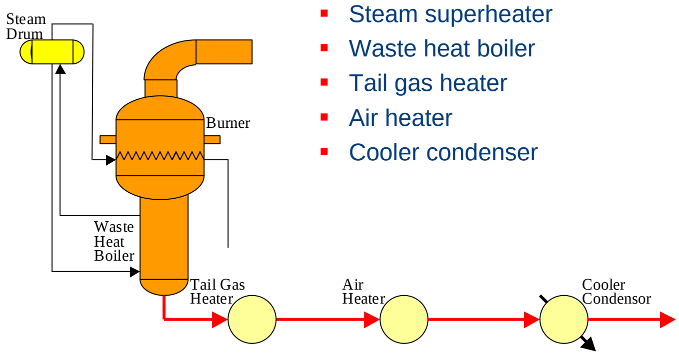
2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process
- Air Compression
- Ammonia supply
- 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 N_2O abatement technology in its design.



2. GP NITRIC ACID PROCESS DESCRIPTION

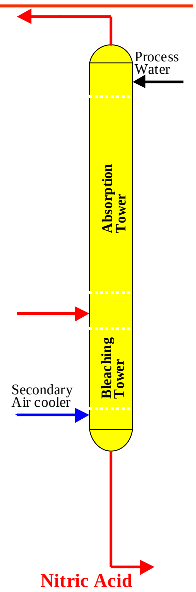
- Mono Pressure Process
- Air Compression
- Ammonia supply
- Ammonia Oxidation
- Heat Recovery on NO_x Gas



  - Steam superheater
  - Waste heat boiler
  - Tail gas heater
  - Air heater
  - Cooler condenser

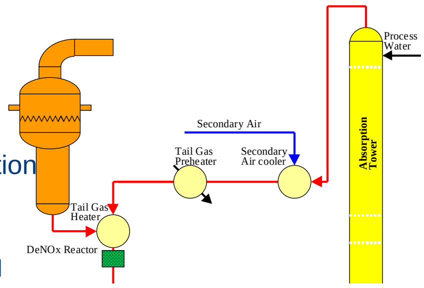
2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process
- Air Compression
- Ammonia supply
- Ammonia Oxidation
- Heat Recovery on NO_x Gas
- Acid Production by NO_x Gas Absorption
  - Process water is fed on the upper tray of absorber.
  - NO_x content in tail gas is lower than 600 ppm.
  - The nitric add 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



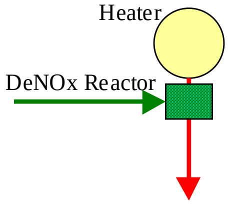
2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process
- Air Compression
- Ammonia supply
- Ammonia Oxidation
- Heat Recovery on NO_x Gas
- Acid Production by NO_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 NOx Gas from the boiler / convector.



2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process
- Air Compression
- Ammonia supply
- Ammonia Oxidation
- Heat Recovery on NO_x Gas
- Acid Production by NO_x Gas Absorption
- Tail Gas Heating
- Selective Catalytic Reduction
  - Hot tail gas is injected into a NO_x abatement reactor
  - At the outlet, NO_x content < 150 ppm.
  - With special design and operating conditions < 50 ppm achieved



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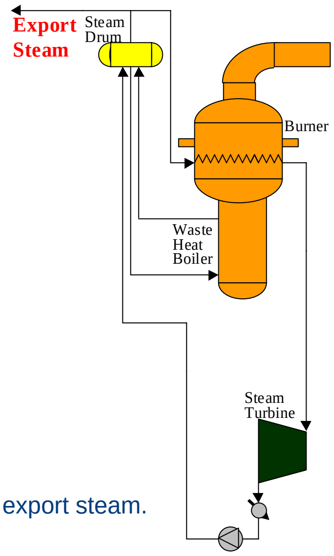
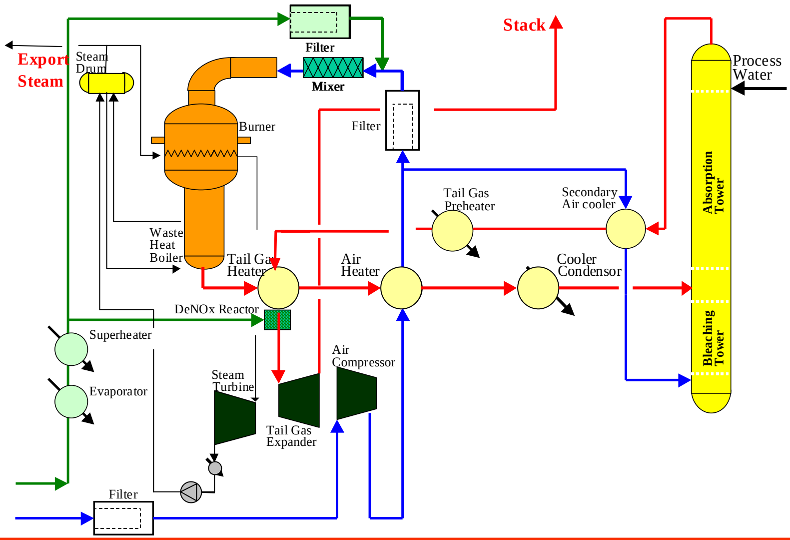
- Mono Pressure Process
- Air Compression
- Ammonia supply
- Ammonia Oxidation
- Heat Recovery on NO_x Gas
- Acid Production by NO_x Gas Absorption
- Tail Gas Heating
- Selective Catalytic Reduction
- Tail Gas Expander
- High Pressure (HP) steam
  - produced in waste heat boiler system.
  - A part is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



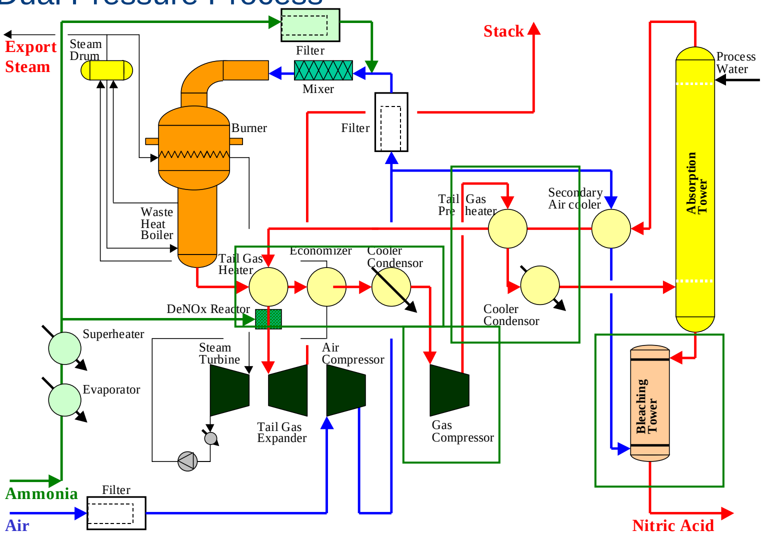
2. GP NITRIC ACID PROCESS DESCRIPTION

- Mono Pressure Process



2. GP NITRIC ACID PROCESS DESCRIPTION

- Dual Pressure Process



3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

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

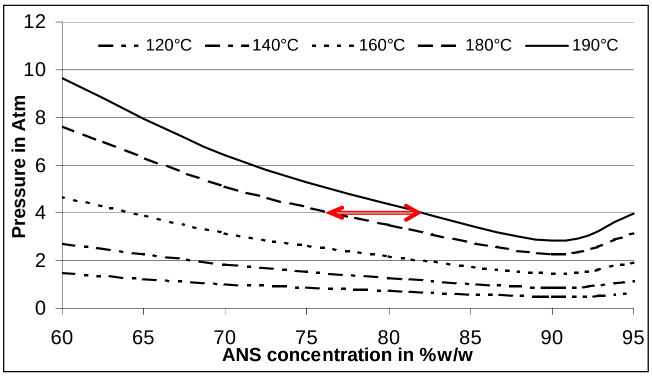
- Capacity range
  - The first Pipe Reactor was installed in a Grande Paroisse plant at Mazingarbe with a capacity of **250 MTPD.**
  - The largest one installed in 1993 in DSM Geleen (The Netherlands) has a present capacity of **2000 MTPD.**

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

3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

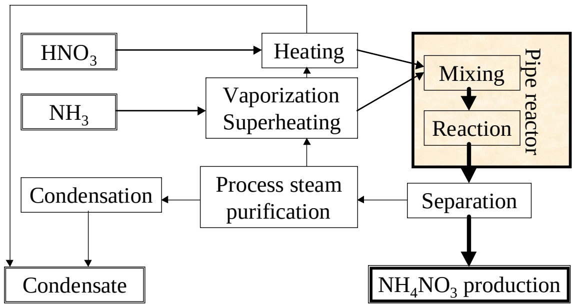
Difficulties with conventional processes:

- Operating conditions of the neutralizer (P, T, ANS Concentration) are dependant on boiling properties of the ANS



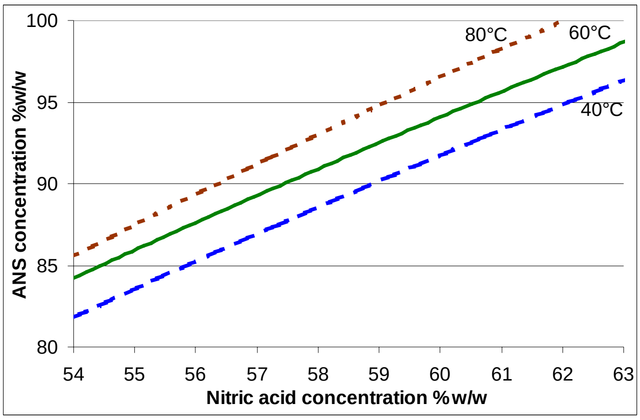
3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

GP Pipe Reactor process:



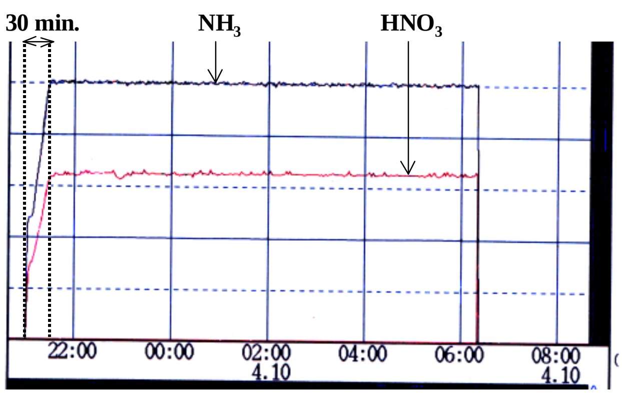
3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

- **GP Pipe Reactor process**:



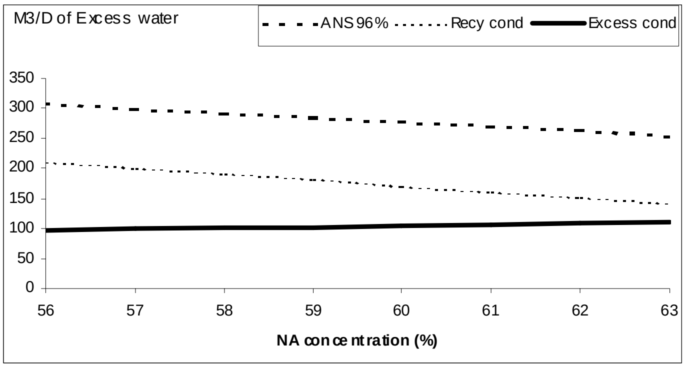
3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

- **GP Pipe Reactor process**:



3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

Water balance issue



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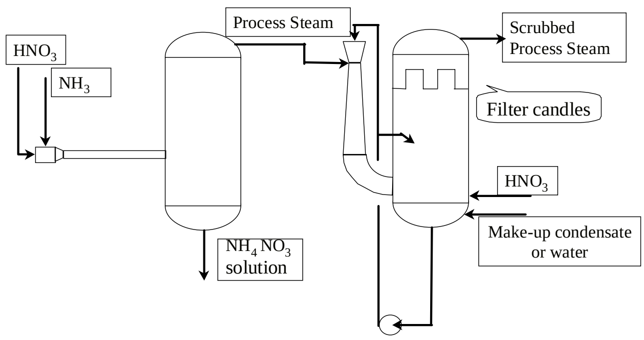
23

3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

Possible treatments of the process steam

- Filter candles
- Scrubbing column



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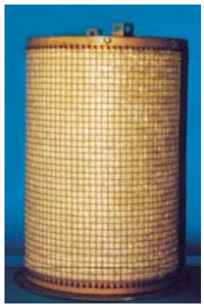
24

3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

Possible treatments of the process steam

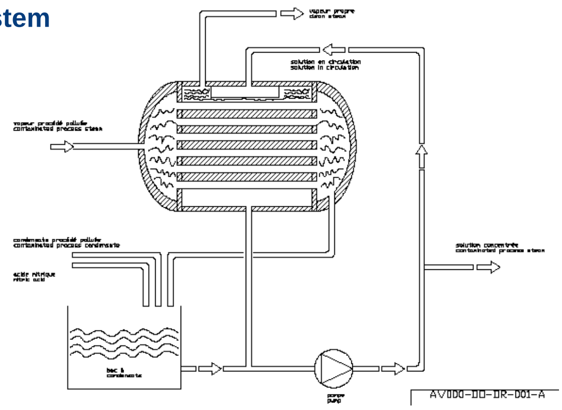
- Filter candles
  - First treatment
  - low velocity (1 m/s)
  - PTFE fibers



3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

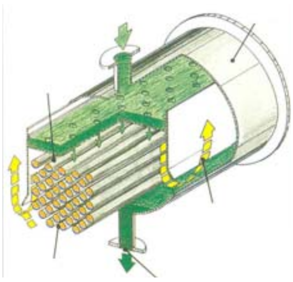
Possible treatments of the process steam

- Filter candles
- Scrubbing column
- Entropie® System



3. GP AMMONIUM NITRATE PROCESS DESCRIPTION

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



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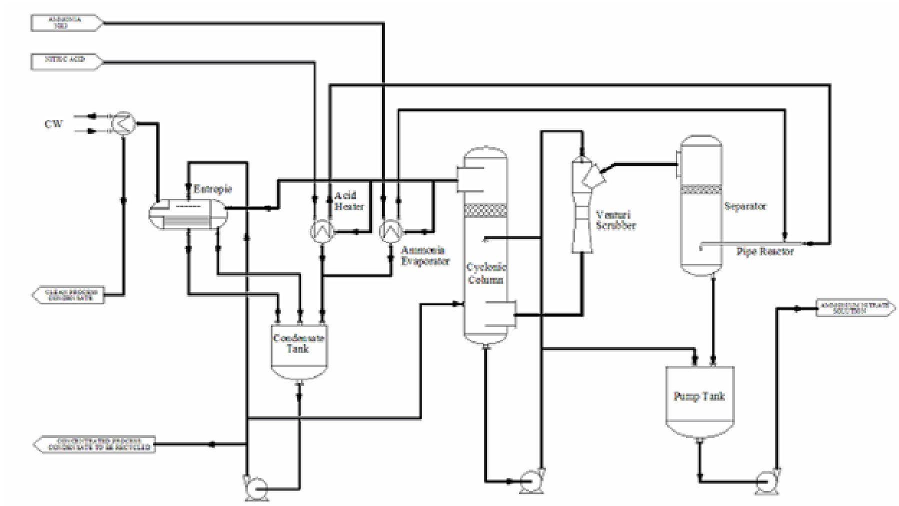


AMMONIUM NITRATE SOLUTION

- 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

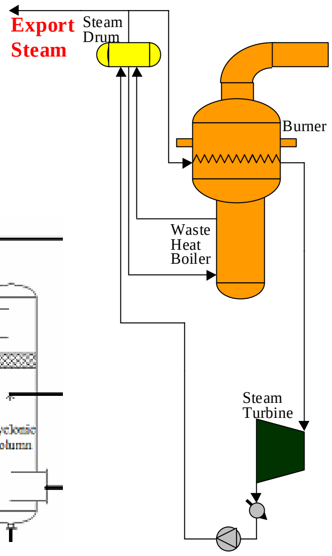
Reduction of investment cost

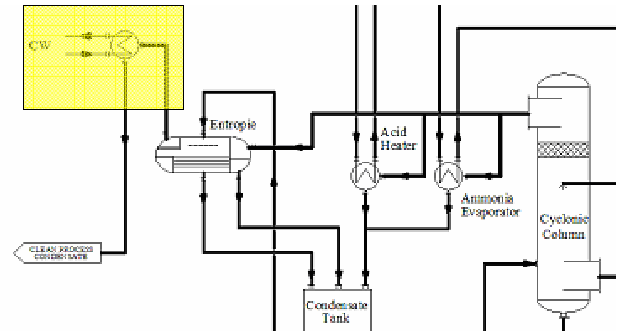
Reduction of steam consumption by 1.5 MTPH

4. INTEGRATION

Boiling feed water heating

- Temp. of condensate exiting steam turbine is ~ 43°C
- Process steam has to be condensed in ANS Plant

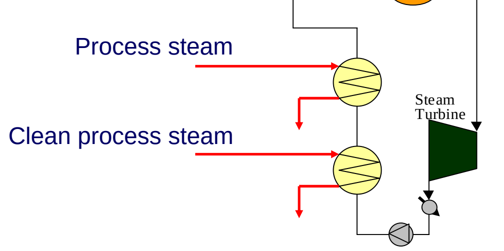




4. INTEGRATION

Boiling Feed Water heating

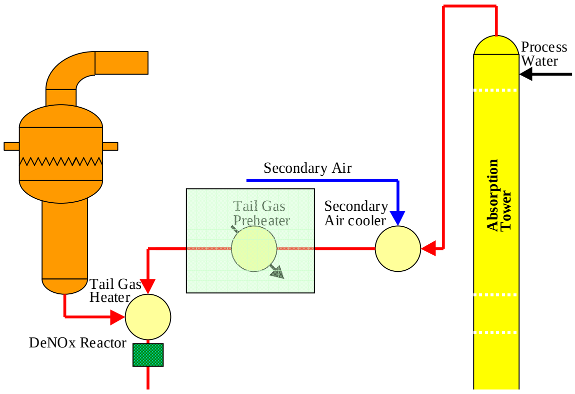
- BFW is heated up to ~ 100°C through
  - one exchanger fed with clean process steam
  - one exchanger fed with process steam



Reduction of steam consumption by 4.6 MTPH

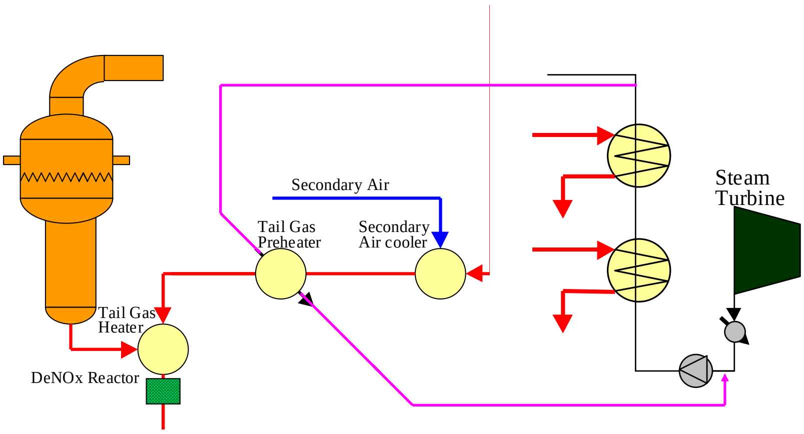
4. INTEGRATION

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



4. INTEGRATION

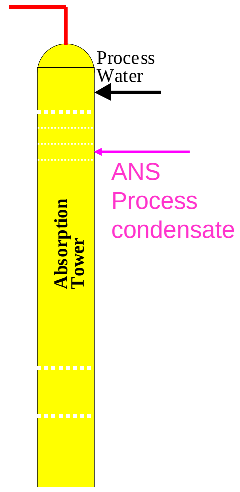
- Tail gas preheater
  - BFW can be used to preheat tail gas



Reduction of steam consumption by 2.6 MTPH

4. INTEGRATION

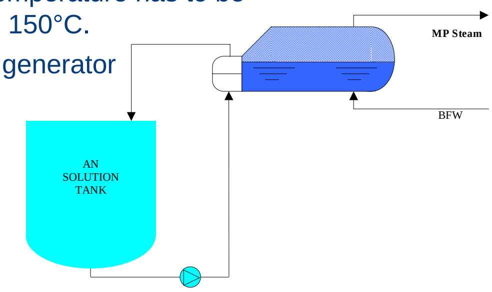
- Process condensate recycle
  - Process water is needed on NA absorption tower
  - Acidic contaminated condensate is available in ANS
  - Process condensate can partly replace process water



Reduction of Demin water consumption by 10 M^3/H

4. INTEGRATION

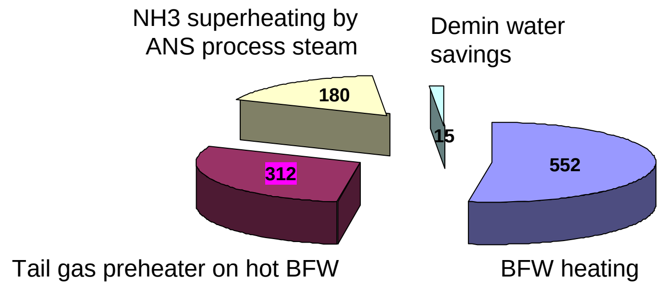
- ANS cooling
  - Ammonium Nitrate Solution
    - 97% concentration,
    - boiling temperature ~ 190°C
    - crystallization temperature ~ 135°C
  - For downstream process, temperature has to be decreased down to about 150°C.
  - GP designed an MP steam generator



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.

5. CONCLUSION

- 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