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ENERGY OPTIMISATION OF A HIGH MONOPRESSURE NITRIC ACID PLANT[1]

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SUMMARY

A decoloration system for NOx tail gas of a **high monopressure** nitric acid plant was used in a **warm climate** site (Cartagena, Southeast Spain). This system consisted of an injection of propane in order to reduce NO_2 to NO and for energy purposes: to raise the temperature of the tail gas to the expander. For refrigeration requirements of the plant, an air-cooler system was used.

The Fertiberia Technical Department studied the case, and after **simulating the process** (chemical reactions in parallel with heat exchange and pressure drop in all equipment) **and machines**, proposed "a solution" for an energy optimisation and reduction of NOx to levels of 200 ppm or lower:

1. Substitution of the air-coolers by a cooling-tower: better yields of machines (compressor and turbine) and lower temperature for the absorption tower.
2. Installation of a gas-gas heat exchanger in a strategic place of the exchanger train in order to get the necessary temperature for the NOx abatement.
3. Installation of a NO_x selective abatement unit.
4. Installation of an innovative (no-TEMA shell split flow) tube-bundle in the first gas-gas heat exchanger below the reactor, in order to have high temperature to the expander.

RESUME

*Un système de décoloration des gaz de queue NOx d'une unité d'acide nitrique **à monopression élevée** a servi dans un site à **climat chaud** (Carthagène, sud de l'Espagne). Ce système consiste en une injection de propane afin de réduire NO_2 en NO et, dans un but énergétique, d'élever la température du gaz de queue vers le détendeur. Pour les besoins de réfrigération de l'unité, on a utilisé un système de refroidissement à l'air.*

*Le Département Technique de Fertiberia a étudié le cas, et après **simulation du procédé** (réactions chimiques en parallèle avec échange de chaleur et baisse de pression dans tout l'équipement) et **les machines**, a proposé une solution pour optimiser l'énergie et la réduction de NOx jusqu'à 200 ppm ou moins.*

1. *Substitution des refroidisseurs à air par une tour de refroidissement, meilleur rendement des machines (compresseur et turbine) et température plus basse pour la tour d'absorption*
2. *Installation d'un échangeur de chaleur gaz-gaz à un endroit stratégique du train d'échangeur afin d'obtenir la température nécessaire à l'abattement de NOx.*
3. *Installation d'un abattement sélectif de NOx.*
4. *Installation d'un faisceau de tubes innovateurs (flux divisé sans enveloppe TEMA) dans le premier échangeur gaz-gaz sous le réacteur pour atteindre une température élevée du détendeur.*

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Introduction and description of the plant

The fertiliser factory of Cartagena, at the Southeast coast of Spain, began its operation in 1969 with three units (nitric acid, AN liquor and granulation) aimed at producing ammonium nitrates, ammonium nitrosulphate and NPKs.

Lummus-Técnicas Reunidas designed the nitric acid unit with a capacity of 270 T/d. It is a single pressure plant operating at 9 bar abs. (air compressor discharge).

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[1] *Optimisation énergétique d'un atelier d'acide nitrique à mono pression élevée*

A major characteristic of the unit is the compact design with most of the heat exchangers placed one after another in a long heat exchange train where the process gas coming out of the burner is cooled by:

(1) Tail gas in the first exchanger just below the ammonia burner,
(2) Compressed air going to the ammonia-air mixer,
(3) The steam superheater,
(4) The boiler, and
(5) A tail gas preheater (2nd) from which tail gas proceeds to exchanger 1.

In between exchangers 4 and 5, a platinum filter was originally installed. Its internals were removed some years ago because the platinum recovery was too costly to be profitable and the pressure drop due to the filter was very high. Removing the filter resulted in an increase of capacity around 10%.

The process gas is further cooled with water in a closed circuit using this heat for the evaporation of ammonia, and finally by means of air coolers in the cooler condenser. The absorption tower is of the bubble-cap type.

Tail gas from the absorption tower with a NO_x content around 1500 ppm(v) passes through a separator and a 1st tail gas preheater -cooling secondary air from the compressor going to the bleaching tower (now being by-passed)- before entering exchanger 5 from which it goes to exchanger 1.

The heated tail gas mixed with propane enters a non selective catalytic reduction unit where the gas is completely decolourised, then passes through the expansion turbine and preheats boiler feedwater before being exhausted through the stack.

The compressor train, supplied by Brown Bovery, consists of: a steam turbine- using steam at 14.9 bar (a) and 300ºC which is condensed under vacuum-, two axial air compressors in series with intermediate cooling and a seven-stage expansion turbine where tail gas is expanded from 6.5 bar (a) to slightly above atmospheric pressure.

The cooling required for the condenser of the steam turbine, the compressor intermediate cooler and oil cooler, and also the absorption tower is provided by a closed circuit of water. The water is cooled in an air cooler, a solution that, as well as for the cooler condenser, was adopted due to the lack of water in the area. Absorption tower and condenser of the steam turbine are cooled in series.

To complete the description of the process, it will be mentioned that steam condensate from the turbine condenser is cooled by evaporating propane and used as process water in the absorption tower where nitric acid is produced with a concentration of up to 57%.

In 1975 the company started a second unit designed by Espindesa-Técnicas Reunidas and is similar to the first one. The main differences are:

- Ammonia was evaporated by steam although this is only used when this unit is working alone or for start up of any of the units, since all the ammonia required by both units can be supplied by the first.

- Secondary air from the compressor is cooled by preheating ammonia.

- Tail gas from the absorption tower is preheated by the expansion turbine exhaust, before going to gas-gas exchanger 1, instead of being preheated in the gas-gas exchanger 5.

- Exchanger 5 is an economiser that preheats boiler feed water with the gas to the cooler condenser.

- The steam turbine was supplied by Siemens.

- The absorption tower is of the sieve tray type.

On purpose minor details that are not relevant to the understanding of this paper are omitted.

The reasons for the modification and problems faced

Although the plant met the NOx limit set by the Spanish legislation, pressure from the local authorities led the company, in 1995, to make the decision of installing a selective catalytic reduction (SCR) unit. This was the most economic way of achieving the required level of 200 ppm(v) following the same solution already implemented in other factories.

The difference with the other projects was that the existing non selective catalytic reduction (NSCR) unit had to be removed and as a consequence:

- The energy will no longer be supplied by the propane and the energy balance of the plant modified, the steam turbine will have to compensate totally or partially this energy and the steam export of the plant will be reduced. **By how much?**
- The pressure equilibrium of the plant will also be affected:
    - The high pressure drop of the NSCR is eliminated,
    - The temperature of the gas at the inlet to the expansion turbine decreases so the actual volume per unit time will be lower which results in a depressurisation of the unit. Besides the value of the **new pressure**, other parameters had to be known like the **NO_x concentration** at the outlet of the absorption tower, the **acid concentration** and of course the **capacity** of the plant.

As for the **new SCR, where to install it?**

- In the high pressure part of the plant, upstream the expansion turbine:
    - The advantages are:
        - Smaller size of reactor and piping,
        - Reactor pressure drop has less influence in the power delivered by the expansion turbine
    - The disadvantage is:
        - Temperature is either too high (downstream exchanger 1, over 500ºC) or too low (before the same exchanger, 140ºC) for the catalyst reaction to take place.
- In the low pressure part of the plant, downstream, the expansion turbine.
    - The advantage is:
        - Gas temperature suitable for a conventional abatement,
    - The disadvantages are:
        - Greater catalyst volume,
        - Larger size of equipment and piping,
        - Great influence of the SCR reactor pressure drop in the power delivered by the expansion turbine.

To overcome the energy imbalance derived from the removal of the propane combustion there were two possible solutions:

- To recover energy from the process gas at the outlet of the ammonia burner so that the tail gas could enter the expansion turbine under conditions similar to the original ones. But again more questions came up:
  - **What would be the profile of the heat exchanger train (mainly the temperature)?**
  - **How much steam would the unit be able to export, if any?**
  - **Where to place the additional heat exchanger that is required?**

- To reduce the flow area through the expansion turbine to avoid the reduction of pressure at the inlet, due to the reduction of temperature, also some new questions would have to be answered:
  - **By how much should the area be reduced?**
  - **What would be the energy balance of the plant?** Due to the lower gas temperature and lower efficiency, the energy delivered by the expansion turbine will fall and more power will have to be supplied by the steam turbine; how much steam would be exported, if any?
  - **What would be the production capacity at the point of operation in which the plant is under balance?**

It is obvious that a solution had to be found that would solve all the problems and that all the questions had to be answered before making a decision so that this would be the most optimal possible. No less obvious is that it was necessary to simulate the performance of the plant in a rigorous way to compare all the possibilities and evaluate its consequences in terms of investment and cost/profit.

The simulation model

The model of simulation that was developed for this project will be shown. The simulation includes:

- Ammonia burner (gauze efficiency, ammonia to gas ratio and production capacity),
- Heat exchange with parallel oxidation reactions, pressure loss and heat transfer coefficient,
- Cooling condenser,
- Absorption tower by a simplified method according to empirical formulae,
- Compressor,
- Steam turbine,
- Expansion turbine.

Data from several operating runs were matched against the model and in general good concordance was found. In a few cases where there were significant differences, bad measurements by instruments were detected which after calibration led to good results.

Simulating the more extreme alternatives led to the following:

Preliminary Results

The first alternative -recovering energy from the process gas- is more favourable than reducing the flow area in the turbine.

Although the production of steam drops, it is still enough for the needs of the plant and for some export. The temperature of the air going to the burner is lower which makes it possible to increase the ammonia to air ratio and the production. The reduced process gas temperature results in a reduced pressure drop through the heat exchange train, which also allows a capacity increase. The lower superheated steam temperature has a negative effect: less power delivered, but this could be compensated through bypassing the compressed air exchanger.

For the second alternative -reduced flow area- the simulation program gives the operating conditions required to keep the pressure with different flow areas (theoretical value). The power delivered by the expansion turbine is reduced so much that the steam production was not enough. Besides that, the production of the plant was smaller.

An important conclusion for both cases was that the steam boiler has a regulating effect in that downstream the boiler, the process gas temperature is always about 230ºC and the temperature profile from this point is the same or very similar.

In both cases there is an energy deficit as compared with the original situation. To overcome or at least compensate this, attempt to increase the efficiency of both the air compressor and the steam turbine by improving the cooling system was made. If instead of cooling the water in air coolers (closed circuit) it is cooled in a cooling tower, the temperature can be reduced by 12º; this improves the efficiency of the compressor and, by reducing the vacuum in the condenser, increases the power delivered by the steam turbine. The energy deficit in case one was compensated to a larger extent than in case two.

The cooling water temperature reduction had the additional advantage of improving the absorption, i.e. reducing the concentration of NO_x in the tail gas with two consequences:

- Increased nitric acid production for the same specific consumption of ammonia,
- Reduced consumption of ammonia in the SCR.

The location of the SCR unit

Looking at the alternatives already commented above might have led to the conclusion that only one was possible because of temperature restrictions: downstream the expansion turbine, with its negative effect on the power delivered by this machine due to the added pressure drop. Besides this, the heat of reaction of the SCR would not contribute to that power.

Since such a solution was not very acceptable, some brainstorming was required based upon two facts:

- After the boiler, the process gas temperature was always around 230ºC.
- Just after the boiler there was and empty space, which was left by the removal of the platinum filter.

Why not accommodate a heat exchanger there to heat the tail gas to a temperature level enough for the catalytic reaction to take place?

The simulation program allowed the checking that for the two main cases the tail gas temperature at the outlet of this new exchanger would always be over 180ºC for which several catalysts could be found in the market. So it was possible to place the SCR between this exchanger and gas-gas exchanger 1. Besides the advantages already mentioned of this solution, it also contributes to the power of the expansion turbine with the temperature increase of the SCR and, also importantly, the heat withdrawn from the process gas by the tail gas is not lost to the atmosphere, thus reducing the cooling required in the cooler condenser.

The final decision as to the location of the SCR was taken together with the selection of the catalyst, integrated with cost comparison:

- The direct cost of the catalyst and the reactor,
- The cost of the exchanger for the location/catalyst requiring it,
- The energy costs derived from the expansion turbine performance when the SCR is placed after this turbine: the power delivered would be smaller due to the higher outlet pressure, which means that more steam would have to be supplied to the steam turbine.

A payout analysis helped to decide both the position of the SCR and the catalyst manufacturer. The SCR was to be located before the gas-gas exchanger 1 and a new exchanger was to be installed in the space of the filter.

The new design of the exchanger below the burner

Since the solution of heating the tail gas with process gas to compensate the heat supplied by the combustion of propane was proved to be more energy-wise, the only loose end now is where to place this exchanger.

A possible solution could be a new exchanger installed below the burner and on top of exchanger 1. This required a complete modification of the reactor area to accommodate the new equipment and posed also design problems, all this resulting in a very high investment.

A new exchanger of the same type (1 pass shell side, two passes tube side) but with an increased surface did not permit to reach the desired temperature of the tail gas because with this design the temperature was limited by thermal cross.

Again the brainstorming had a happy end: to convert the exchanger into a different one equivalent to two exchangers. The shell side flow was split into two streams by a longitudinal baffle; the top stream flows counter current with the tail gas in the half upper part of the tube bundle while the bottom stream flows concurrent with the tail gas in the half lower part of the tube bundle. In this way the thermal cross is avoided and the desired temperature reached. An engineering company that also made the mechanical design checked the thermal design.

The profits of the project

The expected results of the project were:

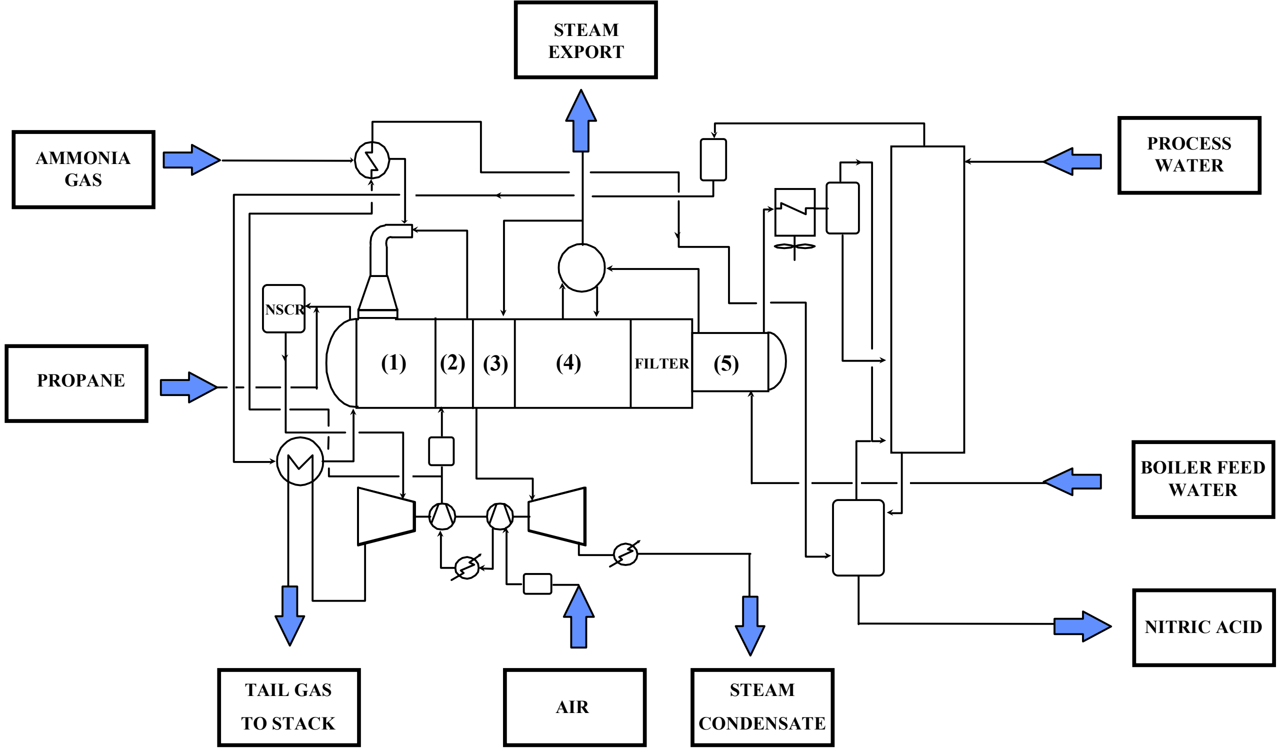
- Saving of propane in the NSCR unit, about 2500 T / year equivalent to 30 x 10^9 Kcal / year
- Saving in electricity: by stopping the air cooler fans and water circulation pump, against the electricity consumption of the cooling tower fans and pump, the balance is a saving of 375 kW.
- Saving of ammonia: although the new SCR unit is consuming ammonia, the project has to be credited with the ammonia saved by reducing the temperature through the absorption tower and consequently the NO_x content from 1500 to 900 ppm(v). Otherwise this NOx would had to be reduced by an ammonia consumption of about 235 T ammonia / year.
- A similar amount of ammonia is saved due to the improved absorption equivalent to the additional acid produced.
- The main drawback of the project is the increased consumption of raw water as makeup for the cooling tower: about 65 m^3/h.
- The reduced steam export, if any, would be more than compensated: preheating boiler feed water to the deaerator (by condensing process steam in the AN unit) and supplying process steam from the AN unit to several steam consumers.
- Less important were the cost of water treatment and some increase in maintenance costs.

A comparison between the expected results and those actually achieved will be provided.

Acknowledgements

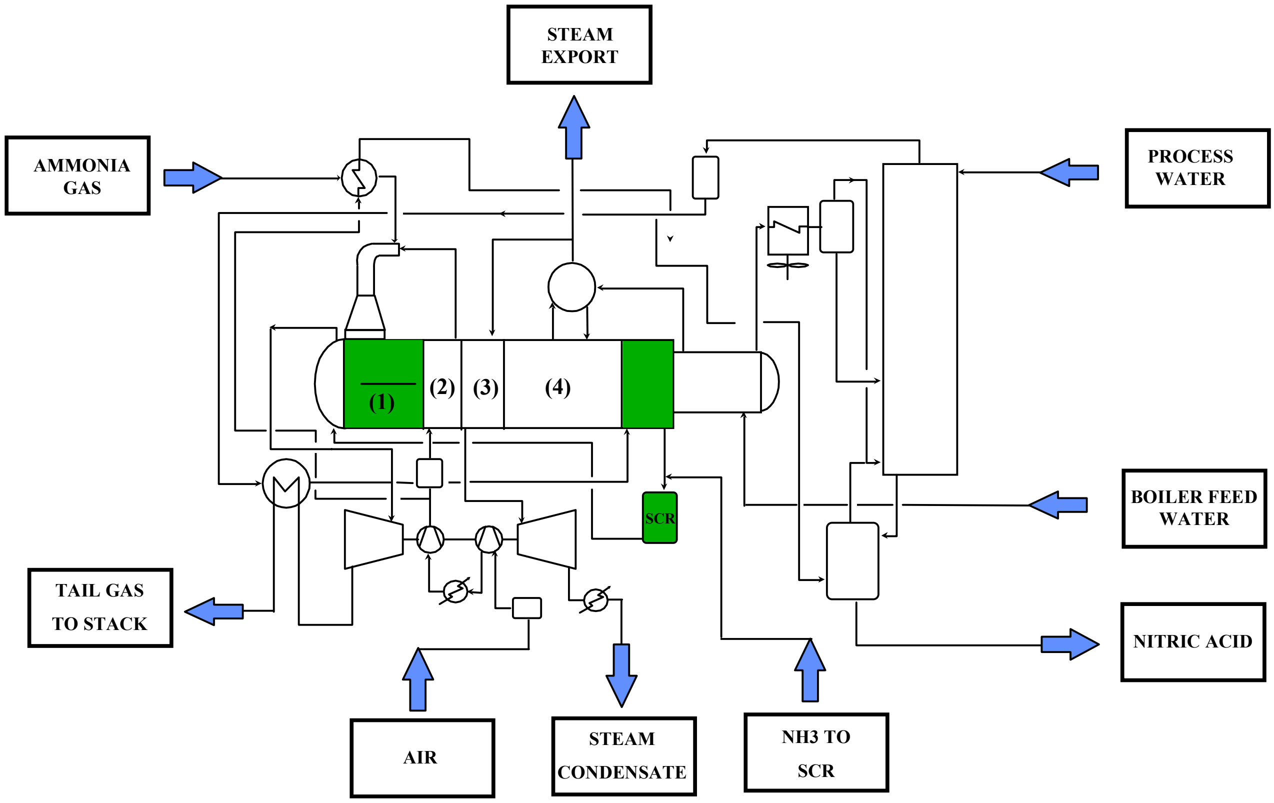
We want to thank all the people who contributed to the success of the project and in particular **G. Jimenez** for his analysis of the performance of machinery.

Figure 1



PROCESS DIAGRAM - NITRIC ACID UNIT 2
(BEFORE MODIFICACION)

Figure 2



PROCESS DIAGRAM - NITRIC ACID UNIT 2
(AFTER MODIFICACION)

Figure 3

	BEFORE	**AFTER**	
COMPRESSOR	456.0	447.6	**kwh/T**
EXPANDER	360.0	360.0	**kwh/T**
TURBINE	96.0	87.6	**kwh/T**
STEAM CONSUMPTION	516.0	438.0	
STEAM PRODUCTION.	1308.0	1117.4	
STEAM EXPORT	792.0	679.4	
PROPANE CONSUMPT.	15 (=343 kg	steam)	**kg/T**
NET EXPORT	0.449	0.679	**T/T**
AIR COOLERS +	43	-	**kwh/T**
COOLING TOWER +	-	21.74	**kwh/T**

COMPARATIVE RESULTS OF THE ENERGY BALANCE