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ENVIRONMENTAL AND ENERGY OPTIMISATION WITH COLD PRODUCTION (CHILLED WATER) IN AN EXISTING AMMONIUM NITRATE PLANT[1]

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SUMMARY

An ammonium nitrate unit was modified to:

1. Obtain process steam with reduced content of pollutants to be recovered as input condensate to nitric acid absorption.

2. Increase reaction pressure to obtain higher thermal level process steam for heat recovery in this and other plants.

3. Increase liquor concentration and elimination of any live steam consumption in the evaporation stage.

4. Use the evaporation of ammonia for plant cooling water and to chill process condensates to nitric acid absorption.

The process steam is partially used as heat source in a Lithium Bromide Absorption cooling unit to provide the cooling necessary to a fluidised bed in a granulation plant. This innovative application in the fertiliser industry is particularly interesting where there is no possibility of consuming low pressure ammonia in the process and is more profitable than the conventional ammonia compression refrigeration system, especially if it is necessary to condense the process vapour with cooling water. The modified plant is in operation in the factory of Cartagena (South-east Spain) since June 1997. This is part of a project which deserved financial help from the EU programme LIFE.

RESUME

Une unité de nitrate d'ammonium a été modifiée pour :

1. *Obtenir de la vapeur de procédé avec une teneur réduite de polluants à récupérer pour alimenter l'absorption d'acide nitrique.*

2. *Augmenter la pression de réaction pour obtenir de la vapeur de procédé à un niveau thermique plus élevé pour récupérer de la chaleur dans cette unité et dans d'autres.*

3. *Augmenter la concentration de la liqueur et éliminer toute consommation de vapeur vive au stade d'évaporation.*

4. *Employer l'évaporation de l'ammoniac pour refroidir l'eau de l'unité ainsi que les condensats de procédé en vue de l'absorption d'acide nitrique.*

La vapeur de procédé sert en partie de source de chaleur d'une unité de refroidissement par absorption par le bromure de lithium pour fournir le refroidissement nécessaire pour un lit fluidisé d'une unité de granulation. L'application innovatrice dans l'industrie des engrais est particulièrement intéressante quand on n'a pas la possibilité de consommer de l'ammoniac basse pression dans le procédé et elle est plus rentable que le système classique de réfrigération de l'ammoniac par compression surtout s'il faut condenser la vapeur de procédé avec l'eau de refroidissement.

L'unité modifiée fonctionne à l'usine de Carthagène (Sud-est de l'Espagne) depuis juin 1997. C'est une partie d'un projet qui a mérité une aide financière dans le cas du programme LIFE de l'UE.

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[1] *Optimisation de l'environnement et de l'énergie avec production froide (eau froide) dans une unité de traitement d'ammonium existante*

Introduction: the problems to be solved

The fertiliser factory of Cartagena has two granulation units for the production of AN/CAN and NPK fertilisers with a capacity of up to 900 T/day each unit. The units are in operation since 1969. The production is based on AN liquor supplied by the neutralisation plant built at the same time and revamped in 1975 when a second nitric acid unit was built. The P_2O_5 is supplied as TSP or MAP. Other product of the plant is ASN based on AS supplied from the factory.

Since the concentration of the AN liquor from the neutralisation was not very high, a concentration unit was added in 1981 with steam consumption; however, at the present production levels the concentration obtained could not exceed 93%.

To get higher values it was necessary to stop the neutralisation unit and circulate AN liquor from the intermediate storage tank to the concentration section and from this back to the tank where the liquor was homogenised. This way of operation is not energy-wise and as the concentration of the liquor is an important parameter for the quality of the final product, a way had to be found for achieving the highest possible concentration in a straightforward manner and with reduced steam consumption.

The energy efficiency of the neutralisation unit was very poor as the process steam, due to its low pressure, was used only for the evaporation of ammonia and the preheating of ammonia and nitric acid.

Moreover the environmental performance was not good since the plant produced condensate and process steam with significant N contents.

Finally, although both granulation units are nearly twins, the capacity of one of them (unit) was substantially reduced during the hot season (about four months) because the fluid bed cooler of this unit did not have an air cooling system. The other unit (2), having an air cooling system based on ammonia compression refrigeration, was able to keep the same production level and the quality of the product throughout the year.

The five problems just mentioned (concentration, energy consumption, pollution, quality and production capacity) were jointly faced by the company with a project that was part of our permanent commitment to improve the environment, the quality of our products and our competitiveness.

The Options

The widest field for improving the energy use, the environmental performance and the liquor concentration is clearly in the AN liquor unit. The alternatives were:

- A completely new plant with a different process,
- A partial modification of the plant without a change in the process, and
- A partial modification of the plant with a process change

The first option (new plant) was the most interesting one from a purely technical point of view but was not considered the best option due to the high capital cost implied.

With the second option (modification with the same process) it was possible to meet the environmental goals but neither the desired concentration of the liquor nor the energy goals could be met.

So the possibility to study was to introduce process changes with some new equipment and instrumentation trying to make the best of the existing installation.

As for the improvement in the product quality and production capacity of the first granulation unit, the objective could be achieved by installing an air refrigeration system and there were again three options that have been used more or less extensively in the fertiliser industry:

- A system based on the evaporation of an ammonia flow to be consumed in some other point,
- A bulk flow heat exchanger using chilled water, and
- An ammonia compression refrigeration system similar to the one existing in the second unit.

The first alternative is clearly the best: using the coldness from the evaporation of the ammonia to be consumed in the process which otherwise would have to be evaporated with a consumption of energy. But the ammonia had to be consumed at a low pressure to get the required cold temperature and there were no consumption points in the factory at such low pressure. The only possibility was to have a neutraliser operating at low pressure being supplied with the ammonia evaporated to cool the air to the fluid bed cooler. This solution was not acceptable because it posed operating problems by linking the heart of the plant -the neutraliser- to the cooler in the granulation unit, something that was not desirable.

The plate heat exchanger was also rejected for the following reasons:

- High capital cost,
- Lack of references for AN, and
- Requires the use of chilled water which we did not have.

So we were left with the traditional compression refrigeration system (as the one in the second unit) which we did not like because of the high energy consumption.

We came to a stop but soon we came across the solution: absorption refrigeration with Lithium Bromide solution using low level energy sources. The idea came from the cogeneration units with energy recovery from the flue gases for the production of coldness. These absorption systems use the energy of hot gases, low pressure steam, hot water.... so why not process steam from an AN plant?

The integrated solution

With these basic ideas in mind our challenge was to design a process modification to meet the following requirements:

- Minimum investment,
- Production of process steam condensate with low N content so that it could be used in other plants, namely nitric acid and granulation scrubbers,
- The thermal level of the process steam must be high enough to use this steam in the absorption refrigeration unit and in some other points,
- The final liquor concentration must be around 96% but without steam consumption, and

The evaporation pressure of the ammonia must be the lowest possible to use the cooling effect for the cooling of water in a closed circuit to be used as cooling water.

These conditions could be achieved by modifying the process so that ammonia is evaporated at 5 bar abs. pressure and the process steam produced at 3 bar abs. At that pressure we can use the low temperature of ammonia evaporation for:

- Cooling water for refrigeration requirements of the AN plant, and
- Chilling process condensate to the nitric acid absorption towers.

The process was designed by the Technical Department and the new reaction loop revised by UHDE. Technical details are provided in the following chapters.

Description of the new AN liquor unit

For a better understanding of the modifications made to the plant it may be helpful to show the original design engineered by Fisons; the process is outlined in Figure 1.

Ammonia gas at 8 bar abs. is reacted with hot nitric acid in a venturi-type reactor (1) where the temperature reaches around 200ºC. The product from the reactor is discharged into a column packed with raschig rings (2) where the pressure falls to about 1.2 bar abs. Along the packing the product is concentrated giving off process steam at the same time the pressure drops. But in this process the final liquor is not in equilibrium with the steam produced since this steam is the result of the mixing of the consecutive flashes taking place through the column; despite the packing, there is not a perfect mixing of the liquor with the steam and as a result the steam is at a temperature higher than the liquor which means that there is an energy loss. Besides that, the reaction is not complete resulting in an alkaline vapour and an acidic liquor.

The liquor/steam mixture is discharged to a cyclone separator (3); from this the liquor is pumped to the storage tank and the steam which is not condensed by heating the raw materials is discharged to the atmosphere.

For the new process all existing equipment was reused except for the ammonia evaporator and the reactor. The process can be summarised as follows:

1. Ammonia is evaporated by water flowing in a closed circuit which provides cooling for the process condensates from the neutraliser and for the condenser in the concentration section.
2. Process condensate to the nitric acid absorption towers is chilled in the ammonia evaporator.
3. Ammonia gas and nitric acid are heated in the existing exchangers.
4. The reaction takes place in an Uhde type reactor with natural recirculation.
5. Process steam is scrubbed under pressure after separation from the liquor.
6. AN liquor is preconcentrated at 1.2 bar abs. by the reactor loop liquor in a heat exchanger.
7. Process steam from the preconcentration stage is separated from the preconcentrated liquor in the existing separator and then washed.
8. Final concentration from 93 to 96% takes place by flash cooling in the existing concentration unit without live steam consumption.

   Process steam from the reaction is used for:

- Heating demineralised water to the deaerator,
- Energy supply to the Lithium Bromide absorption cooler,
- Steam supply to the granulation units, and
- Consumption by the AN plant.

The process steam from the preconcentration stage is partly condensed by heating the raw materials. The balance of the steam is discharged to the atmosphere.

Description of the LiBr absorption cooling system

The technique of cooling by means of absorption processes is not a new one since it has been widely used by industry. The advantage of the process based on an aqueous solution of LiBr is that the product is harmless and its properties make it suitable to get temperatures of chilled water of 4ºC. Figure 2 shows the sketch of a typical unit. Although it can be found in scientific and technical literature, we will give a brief description of how this units work. The refrigeration cycle can be divided into 5 steps:

A. **Concentrator** (also called generator): A dilute solution of LiBr and water at 0.1 bar abs. is boiled by an external heat source (hot water, flue gas, steam) which in our case is the process steam from the AN reaction. The resulting concentrated LiBr solution goes to the absorber (D) and the water vapour is drawn into the condenser.
B. **Condenser**: The water evaporated from the LiBr solution in step A is condensed by cooling water flowing through the condenser tubes, and passes to the evaporator.
C. **Evaporator**: the water (this is called the refrigerant) is sprayed over a tube bundle where it is evaporated at a much lower pressure -about 0.01 bar abs.- by the “hot” chilled water which is thus cooled. The low pressure results from the absorption taking place in the absorber section.
D. **Absorber**: The refrigerant vapour is drawn into this section due to the vacuum effect caused by the absorption of the refrigerant in the concentrated LiBr solution (absorbent) coming from the generator A and being sprayed over another tube bundle in the absorber. As the LiBr has a high affinity for water, the water refrigerant vapour is absorbed by the concentrated solution which becomes more diluted. The degree of affinity of the absorbent for the refrigerant vapour is a function of the absorbent solution concentration and of temperature. The more concentrated and the cooler the solution, the greater the affinity for refrigerant vapour. Cooling water flowing through this bundle removes the heat of absorption. To complete the cycle the dilute solution has to be sent to the concentrator or generator A.
E. **Heat exchanger**: The dilute solution from the absorber is heated by cooling the concentrated solution coming from the concentrator reducing both the amount of heat to be supplied to the generator and the amount of heat to be removed from the absorber.

The chilled water from the refrigeration unit cools the air to the fluid bed in an aerothermic battery and returns to the refrigeration unit in a closed circuit.

The cooling system for our project was supplied by Trane which at the time was the only one supplying the tube bundles in stainless steel as required for the evaporator. Equipment data are as follows:

Heat source	Process steam
Process steam pressure	180 kPa
Process steam flow	2.76643 kg/kW.h
Concentrator n° passes	1
Cooling power	2019.05 kW
Power consumption:	
System pumps	11.19 kW
Chilled water pump	88 kW
Condensate pump	14 kW
Cooling water pump	57 kW

	Evaporator	**Absorber**	**Condenser**
Fluid	Chilled water	Cooling water	Cooling water
Inlet Temperature, ºC	8	32	*
Outlet Temperature, ºC	4.5	*	42.5
Flow, l/s	137.32	124.15	124.15
Pressure drop, kPa	104.55	-	34.69
Tube material	95/05 Cu Ni	316 SS	316 SS

* Tube bundles in series

Comparison with ammonia compression refrigeration

A measure of the performance of a refrigeration system is given by its ***coefficient of performance*** which for a compression cycle is defined as:

COP = (heat transfer rate to the evaporator) / (power input)

For an absorption system it is normally defined as

COP = (heat transfer rate to the evaporator) / (heat input)

For absorption cycles the value of COP is between 0.55-0.75 whereas for the compression cycles much higher values are achieved, between 2.5 and 9.5 depending on the type of refrigerant and the operating conditions.

It would appear from this that the choice of the absorption system is not a wise one but we must consider the energy we are going to use not only in what regards cost but also in what regards alternative use. In our case the energy used is that of a process steam which if not used in this refrigeration unit would have to be lost to the atmosphere either discharging the steam directly or what is worst having to condense it with cooling water.

As in the second granulation unit we have an ammonia compression cycle, we can make a comparison between the two systems by extrapolating the values of this unit to a refrigeration power equal to that of the absorption cycle installed in unit one.

	Compression existing	Compression extrapolated	Absorption LiBr
Refrigeration power, kcal/h	1350000	1730000	1730000
Compression power, kW	318	407	-
Oil pump, kW	55	70	-
System pumps, kW	-	-	11
Cooling tower fan, kW	12	15	40
Cooling water pump, kW	30	38	57
Chilled water pump, kW	-	-	88
Condensate pump, kW	-	-	14
Total, kW	415	530	210

The table shows that the total energy consumption (obviously excluding the process steam) for the LiBr system is about 40% of that of the ammonia compression cycle. Investment is very similar for the two systems so the choice was the absorption unit which in addition has the advantage of having low maintenance and does not pose safety and control problems. It only requires a closed space.

It may be argued that with this system, the operation of the refrigeration unit is dependent on the neutralisation so when this is stopped the other has to be stopped too. This inconvenience is easily overcome since the refrigeration unit can be operated with live steam from the plant headers when there is not process steam available.

The LiBr absorption system has been used mainly for air conditioning of large buildings and other industrial applications but as far as we know this is the first application in the fertiliser industry. This system helps to reduce the atmospheric pollution and at the same time uses a low level thermal energy. These points and the innovative application were key arguments to qualify this project for the **LIFE** program of the European Union that gave its financial support. (Life reference: Life96ENV/E/275 - Integral use of low thermal value contaminated process condensates with production of cold).

Conclusions

This presentation tried to show how energy, quality and environmental problems can be successfully overcome by means of joint integrated solutions regarding several processes and plant sections. In the Fertiberia AN/NPK plant of Cartagena the solutions described in the paper resulted in:

- Energy optimisation:
  - ⇒ Reduced steam consumption:
    - the existing AN liquor process was replaced by a new more efficient process.
    - Process steam is produced at a suitable pressure so that it can be used in process and heating applications.
  - ⇒ Reduction of existing or projected electricity consumption.

- Nitrogen recovery and reduced pollution:
  - ⇒ More efficient AN process.
  - ⇒ Process steam scrubbing.
  - ⇒ Process steam use in granulation.
  - ⇒ Process condensate recovery in nitric acid plants, scrubbers in granulation plants.
- Improved quality:
  - ⇒ More concentrated AN liquor.
  - ⇒ Better cooling of final product.
- Capacity increase:
  - ⇒ Better cooling of final product.

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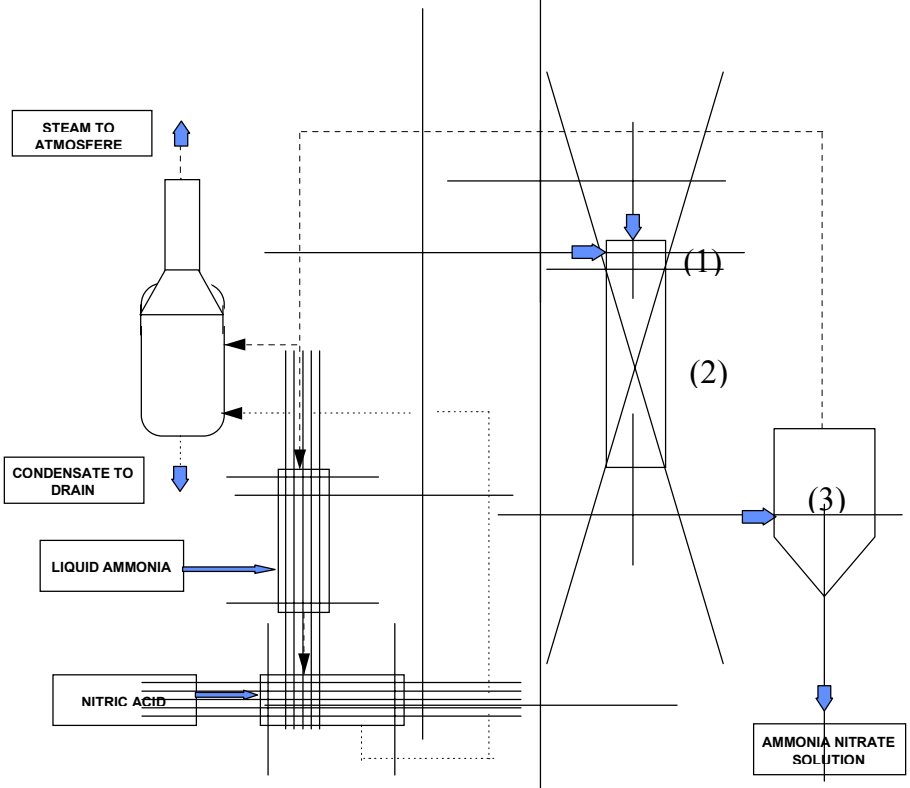

FIG. 1 Old Ammonia Nitrate plant. Fisons design.

Li Br Refrigeration System