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AZF AMMONIUM NITRATE SOLUTION BY PIPE REACTOR : A SAFE AND ENVIRONMENT FRIENDLY PROCESS

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ABSTRACT

Ammonium Nitrate Solution (ANS) is one of the main nitrogen source used for producing fertilizers as well as technical products.

When specific conditions are present (confinement, high temperature, low pH, contamination by chloride, oil, copper...) decomposition reactions can occur which can lead to explosion of confined equipment. In case of explosion, the larger the ANS quantity involved, the wider is the zone of effects of explosion.

Another issue of ANS production is the nitrogen pollution by the process condensate to be eliminated. Because of the water balance of the process, condensate containing some ammonium nitrate, free ammonia or nitric acid has to be recycled back to the process and sent to the sewer.

Confinement, temperature and pH controls have to be the key parameters for process design.

In the AZF pipe reactor, the reaction takes place in the pipe reactor itself, so the quantity of material in the reaction zone and at high temperature is the smallest among all the processes designed for ANS production. The temperature of reaction is controlled. As all the pieces of equipment of the process are operating at almost atmospheric pressure, confinement is avoided.

A special design of the ratio control with short response time gives a proper control of the pH which is measured and adjusted thanks to a two-step process.

Moreover, the AZF pipe reactor is also improving the safety of operation by its flexibility: shut down is immediate (no vessel to be emptied), start-up to full capacity with stabilized parameters takes less than 30 minutes. This makes it possible to minimize buffer tanks capacity downstream the ANS plant.

The environmental issue of the process condensate has been improved on industrial scale through a special technology that has been implemented in the AZF pipe reactor (and conventional) process successfully delivering water containing less than 50 ppm of ammonium nitrate, solving the pollution problem.

Production of ANS by the AZF pipe reactor technology gives a positive answer to safety and pollution reduction.

1. INTRODUCTION

In the 1940's development of ammonia and nitric acid processes enabled to abandon the manufacturing of ammonium nitrate based on sodium and calcium nitrate routes.

Up to now ammonium nitrate is produced by direct reaction between nitric acid and ammonia producing Ammonium Nitrate Solution (ANS).

The total world Ammonium Nitrate Solution (ANS) production could be assessed to 40-45 million tons.

The ANS is used to produce straight N fertilizer such as 33.5 % N – 34.8 % N ; CAN ; UAN and compound fertilizers such as NP and NPK. Another use of ANS is the production of technical grades for N₂O and explosive manufacture.

GRANDE PAROISSE developed in the 1980's the technology of Pipe Reactor for ANS production. This process has been continuously improved till this time. The main improvements have concerned flexibility of operation, environment and safety. These improvements are described in this paper.

2. GP ANS PIPE REACTOR PROCESS DESCRIPTION

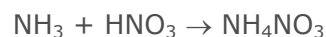
2.1.Capacity Range

The first Pipe Reactor was installed in a Grande Paroisse plant at Mazingarbe with a capacity of 250 MTPD. The largest one is located in DSM Geleen, The Netherlands. It was installed in 1993 and the present capacity is 2000 MTPD.

2.2. Process Description

2.2.1 Difficulties with conventional processes:

Ammonium nitrate is produced (in a vessel called a neutralizer) by the reaction of ammonia with nitric acid:



This exothermic reaction produces some heat which is used as much as possible within the process itself.

In all the processes, the first use of the heat is to vaporize part of the water fed along with the nitric acid as process steam directly in the neutralizer. Then, the operating

conditions of the neutralizer (P, T, ANS Concentration) are dependant on boiling properties of the ANS (Figure 1)

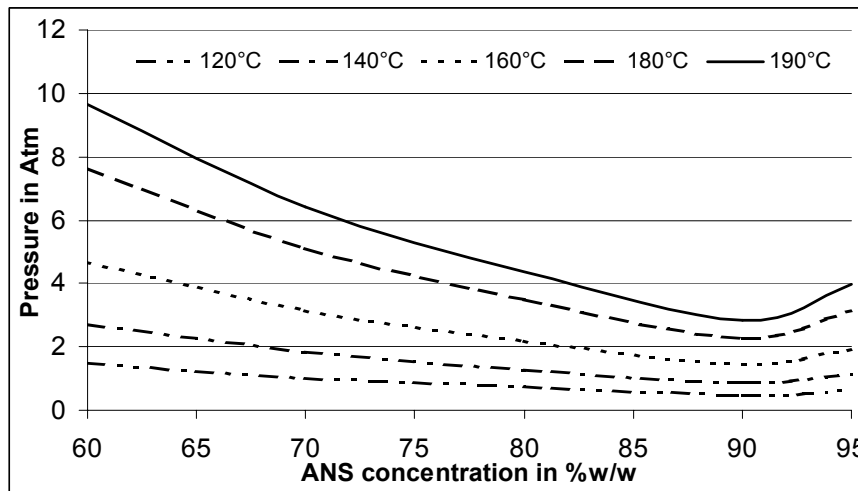


Figure 1

As an example, when operating a neutralizer at 4 Atm., if the ANS concentration is controlled at 76% W/W, the temperature is 180°C.

Thanks to the evolution of the nitric acid processes, the concentration of the acid has increased giving the opportunity of making more concentrated ANS as less water is fed to the neutralizer.

But because of safety consideration, temperature within the neutralizer shall be limited. So, in conventional processes, it is not possible to take full advantage of the increase in concentration of nitric acid. In those processes, part of the condensed process steam is recycled back to the neutralizer in order to control the temperature of the vessel ie 180-195°C. Doing so is equivalent to feed the neutralizer with nitric acid as weak as 55%.

As for all reacting vessels, the faster the production rate, the bigger the vessel to is required for the reaction. In those processes, it can be as large as 15m³ (ie 21 Tons of ANS) for a 1200 MTPD plant resulting in a large quantity of ANS in the reaction zone.

2.2.2. GP Pipe Reactor process:

The heart of the GP Pipe Reactor process is the pipe where the reaction takes place. Due to its special design giving an efficient mixing of the two raw materials, the residence time is minimized.

The GP Pipe Reactor process can be illustrated through the following block diagram (Figure 2)

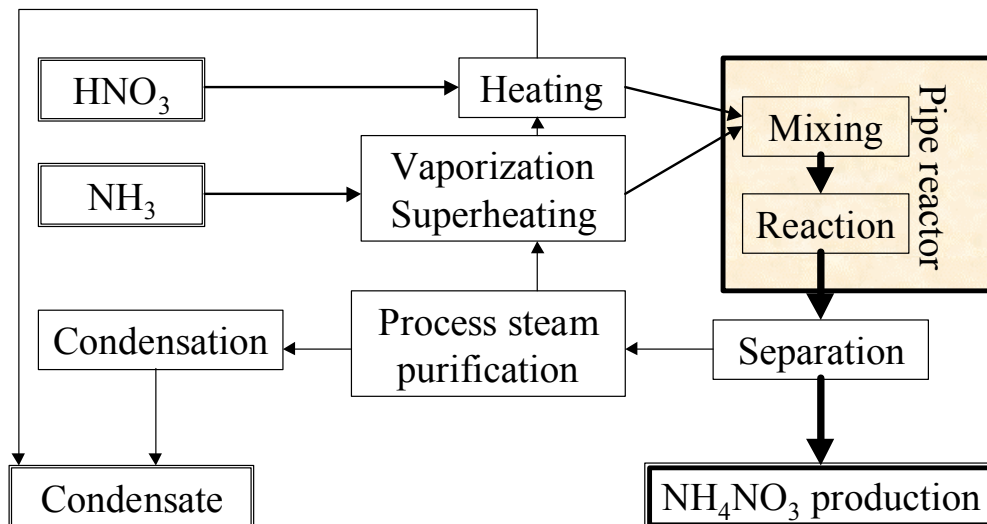


Figure 2

Ammonia vaporization/superheating: Ammonia is fed to the plant in the liquid form. Its flowrate is measured in liquid phase in order to increase the measurement accuracy. Then ammonia is vaporized and superheated up to 90°C in a special heat exchanger designed so that the ammonia holdup is minimized. Heat is provided by condensation of the process steam generated by the reaction. Superheated gaseous ammonia is fed into the Pipe Reactor.

Nitric acid heating: Nitric acid flowrate is measured and controlled through ratio control from the ammonia flow. Nitric acid is heated in a heat exchanger fed with process steam to increase energy input in order to get a more concentrated ANS.

Pipe Reactor Mixing/Reaction: As soon as nitric acid and ammonia are fed to the Pipe Reactor, they are intimately mixed. Then, the instantaneous reaction starts and goes on all along the Pipe Reactor. Because of the mixing and reaction within the Pipe Reactor, the pressure decreases along the reactor from the reactor head (4~7 abs. bar) to the separator tank (~1 abs. bar). The volume of the Pipe Reactor is lower than 0,2 m³ for a 2000 MTPD plant. (Figure 3)

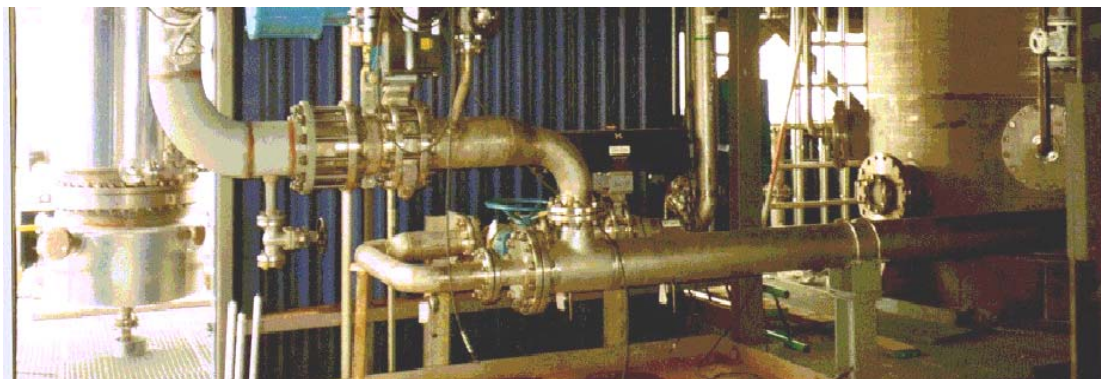


Figure 3

Separation: The Pipe Reactor outlet is located in a vessel called the separator tank. At Pipe Reactor outlet process steam flashes thus process steam and the ANS separates out. The ANS flows down in the bottom of the separator tank and the process steam flows up. The separator tank is designed so that the volume of ANS is as low as around 2 m³ for a 2000 MTPD plant.

NH₄NO₃ production: The ANS overflows by gravity from the separator tank into the buffer tank where a small flow of gaseous ammonia is fed to automatically adjust the pH of solution.

Process steam purification / condensation: Those two parts are described in Part 3

2.2.3. ANS concentration

Depending on the downstream requirement for ANS use and the available nitric acid concentration, the ANS concentration can be adjusted.

The ANS concentration is linked mainly to two parameters:

- Nitric acid concentration
- Temperature of the nitric acid fed to the Pipe Reactor.

The following diagram (Figure 4) gives the ANS concentration vs. the nitric acid concentration.

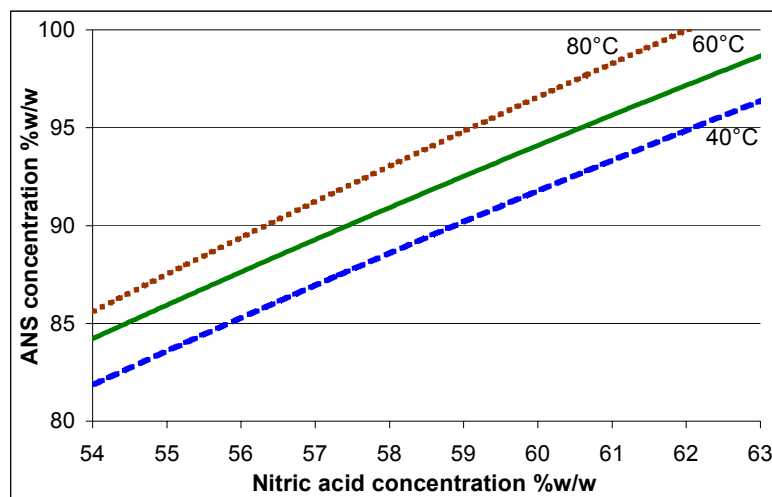


Figure 4

It can be noticed that when Pipe Reactor plant is fed with 63% nitric acid at a temperature of 60°C, it is possible to get straight some 97% ANS.

2.2.4. pH control philosophy

For safety and environmental reasons, the pH of all ANS has to be controlled.

In GP Pipe Reactor process, pH is controlled in two steps (Figure 5) :

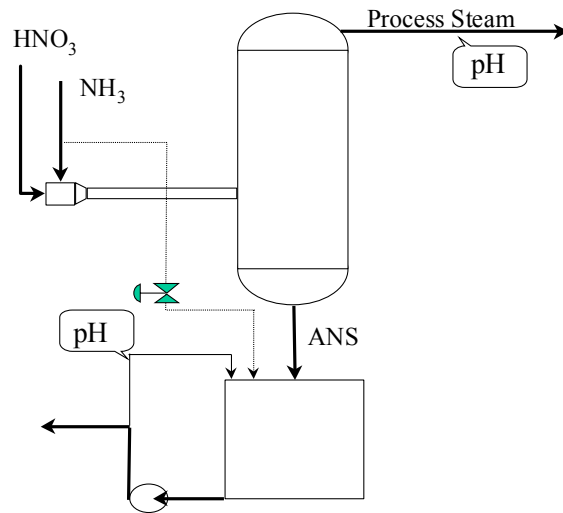


Figure 5

First, in the reaction zone, the pH is controlled by the ratio of the two raw materials fed to the reactor.

Measuring the pH of the process steam gives a faster response whatever the process if the steam sampling system is properly designed. The sampling system designed for the GP Pipe Reactor process has a time lag shorter than 15 seconds. This one of the key design feature for this process.

The sensibility of the pH measurement is also higher in the process steam than in the ANS. As process steam is made mainly of water, only a small amount of NH_3 or HNO_3 makes a big change in the pH value. A typical record of the instantaneous process steam pH measurement is given below (Figure 6)

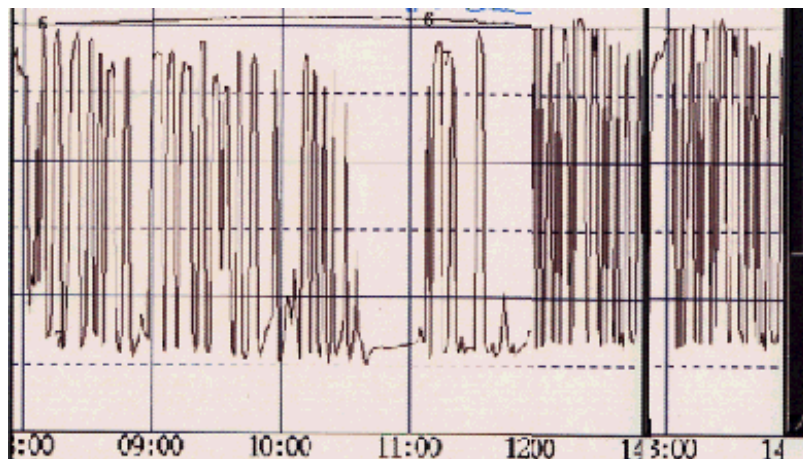


Figure 6

The controller uses two values of the pH: the instantaneous one and the average value over 20 minutes. Both of them correct the ratio Nitric acid to Ammonia.

The way this ratio is adjusted is also an important safety point. If the nitric acid flowrate was to be the master flow, then it would be possible to feed the Pipe Reactor with only nitric acid in case Ammonia was not available. To avoid that, the ammonia flowrate shall be the master flow so that nitric acid is fed only if ammonia is present.

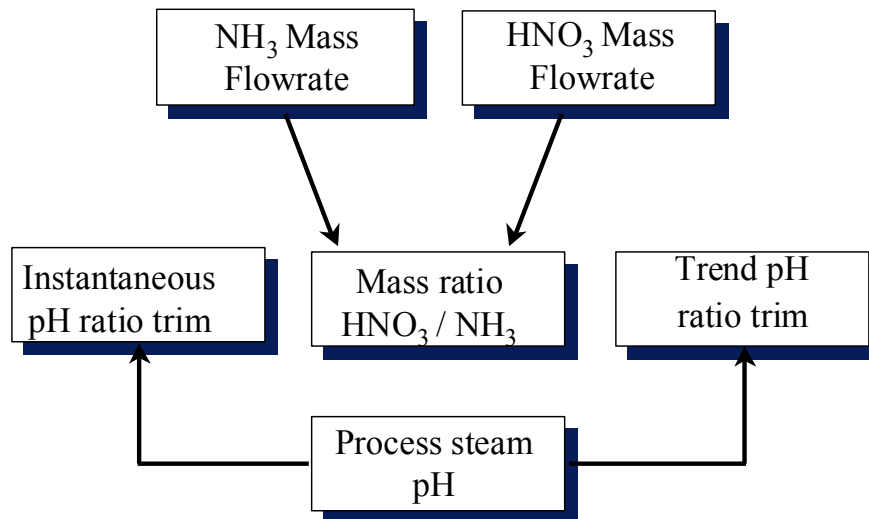


Figure 7

The pH of the ANS has to be adjusted to a fixed value depending on the downstream process. So this pH is controlled in the buffer tank where a slight amount of gaseous Ammonia can be continuously injected into the ANS. The ammonia flowrate to adjust pH from 3 to 5 represents less than 0.1 % of the total ammonia consumption.

2.2.5. Flexibility

As the volume of the reaction zone is small, startup and shutdown of the plant are very quick.

It can be seen on the following record that startup from 0 to maximum production rate takes around 30 min. and that the shutdown is immediate. (Figure 8).

This figure has been recorded on an industrial plant with a nominal plate around 600 MTPD.

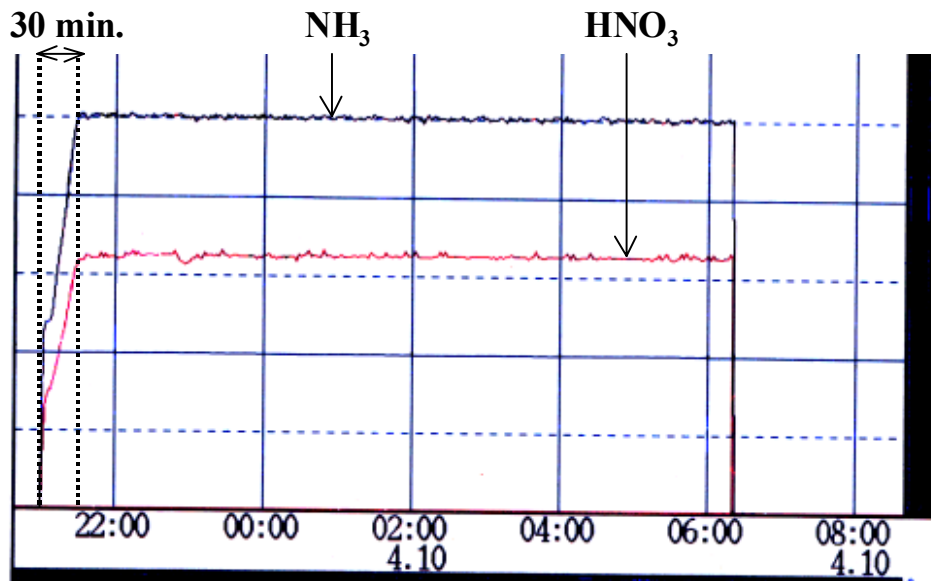


Figure 8

Because of this flexibility, one of our licensees has been able to operate with only one buffer tank of very small capacity. Its residence time was less 10 minutes at full production range, even though the ANS plant was feeding ANS to two granulation plants

3. CLEAN PROCESS

The two raw materials to produce ANS are ammonia and nitric acid. The latest one is fed as a solution in water. So whatever is the Process, some water is fed along with Nitric acid.

3.1. Water Balance Issue

Depending on the use of the ANS, its concentration is fixed. For technical grade AN , ANS concentration has to be around 96% and for AN fertilizers between 98% and 99.8%.

Today, depending on the process used to produce the nitric acid, its concentration can vary within the range of 56% to 63%.

As only a part of the water fed with the nitric acid is going out with the ANS, there is an important remaining quantity (excess water) to be rejected out of the ANS plant. But depending on the treatment process of the process steam, this water can be polluted by some amounts of ammonium nitrate and nitric acid / ammonia. So it has to be treated before being rejected as waste water or it has to be recycled in some other processes.

3.1.1. Without any recycling of process condensate

On the following chart (Figure 9) is shown the balance of water for a 600 MTPD ANS plant.

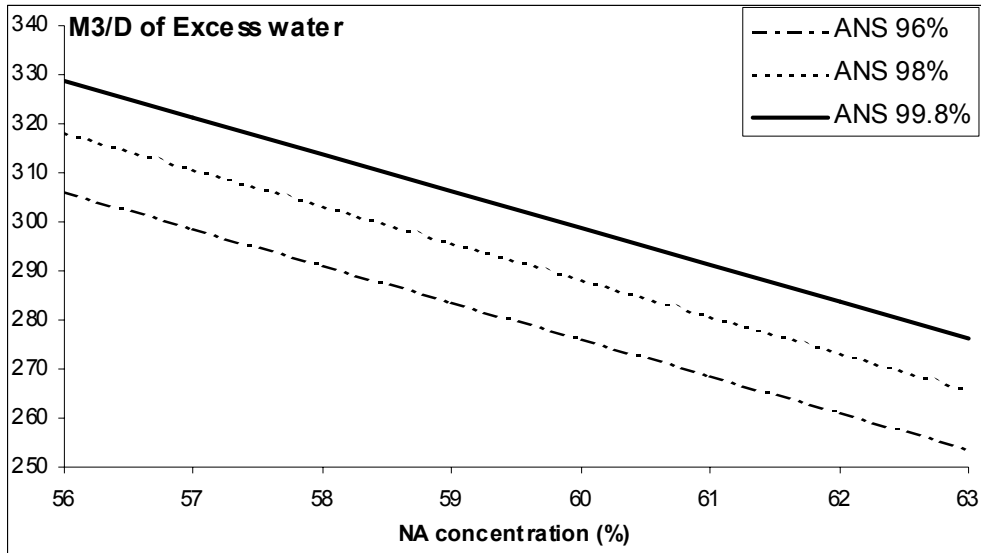


Figure 9

Some order of magnitude can be extracted from this chart:

- The excess of water is 0.5 m³/D per MTPD of ANS.
- A change in the concentration of the ANS results in a change of 5 m³/D of the excess water per % of ANS concentration.
- An increase of 1% of the Nitric acid concentration decreases the excess water by 6 m³/D.

3.1.2. When recycling part of the process condensate back to the nitric acid plant

Usually, there is always at least one nitric acid plant on the same site as the ANS plant. All the nitric acid plants are using some water for their absorption tower.

Depending on the required quality of the nitric acid, this water can be replaced by part of the excess water from the ANS plant. When some technical nitric acid is sold to some chemical industry, there might be some limitations on its ammonium nitrate content; in such a case, it may be not possible to use some excess water at the absorption tower.

For safety reasons, the quality of the excess water fed to the absorption tower of the nitric acid plant is also important. First of all, this condensate shall be maintained acidic. Otherwise, there is a risk that some ammonia could leave the absorption tower

along with the gases and form some ammonium nitrate in the downstream heat exchangers or expanders. Secondly, the ammonium nitrate concentration of this excess water shall be limited to avoid that some ammonium nitrate could be entrained along with the gases leaving the absorption tower, resulting in the same risk.

On the following chart is shown the balance of water for the same 600 MTPD ANS plant, assuming an ANS concentration of 96% (AN96). It can be seen than the quantity of water that can be recycled to the nitric acid plant (Recy cond) is decreasing as the concentration of this acid increases. The result is that the excess quantity of water (Excess cond) does not vary a lot according to the nitric acid concentration.

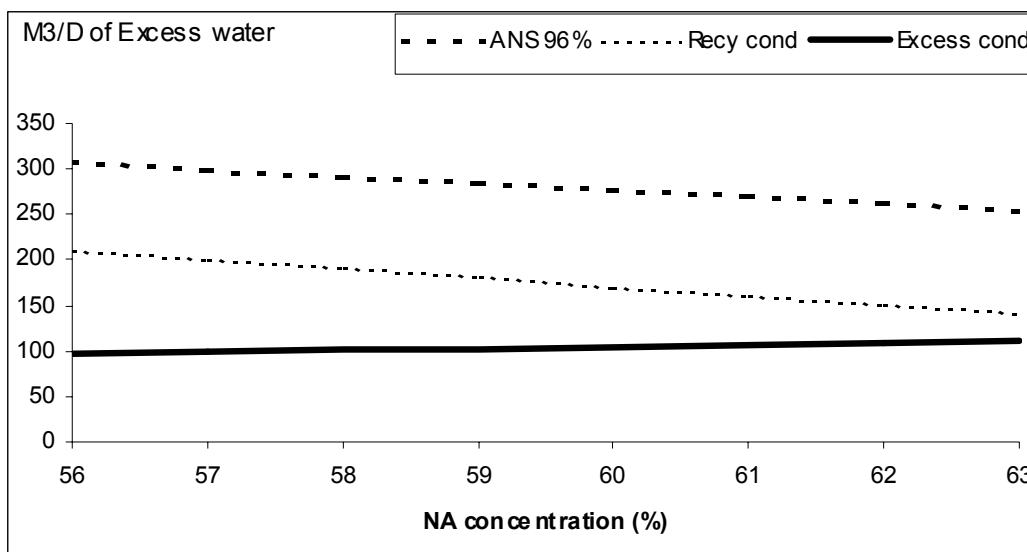


Figure 10

Some order of magnitude can be extracted from this chart:

- The excess of water is 0.16 m³/D per MTPD of ANS.
- An increase of 1% of the nitric acid concentration increases the excess water by only 2 m³/D.

3.2. Possible Treatments of the Process Steam

Depending on level of N that can be accepted in the process condensate, the process steam treatment can be adjusted. If no treatment is apply, the AN content of the process condensate is about 15 g/l.

Three steps can be implemented. From each one, it is possible to improve the system by addition of the further one above the previous one.

3.2.1. Filter candles

The first treatment that can be installed is a filtration of the process steam with the separator. This filtration is made through some filter candles (Figure 11). Different type of filter candles can be used.

As we do operate some ANS plants fitted with filter candles and we license too, we have been able to collect a lot of data about the filter candles. The selected ones are made of PTFE and the velocity of the process steam through the candles is about 1 m/s.

Due to our experience, we can anticipate and discuss with the supplier the quality of the fiber to be installed as the fiber quality is the determining factor for controlling pressure drop and efficiency.



Figure 11

Some trials have been made to test low velocity type of fiber candles (0.1 m/s). This type, which is the most efficient for treatment of the air exhausting a prilling tower, does not surpass the selected ones.

According to a 15-year experience without any problem, GP has agreed some suppliers for this application. This cheap treatment has been shown on industrial scale to be able to divide by two the AN content of the process condensate down to about 7 g/l.

3.2.2. Scrubbing column

In case only filter candles installation is not enough to get an acceptable quality of the process condensate, a scrubbing system can be installed.

Then, the process steam flow, from the separator, is directed to a venturi scrubber fed with a slightly acidic scrubbing solution to neutralize any ammonia. The scrubbing is completed in a cyclonic column where the same scrubbing liquor is sprayed on to the process steam passing afterwards through filter candles to remove the remaining AN droplets (Figure 12).

The filter candles in the cyclonic column are the same than the ones described above. When scrubbing system is installed, there are no more filter candles in the separator but only a simple grid to collect the largest AN droplets which could flow out of this vessel.

The scrubbing solution concentration is a 30 - 50 % ANS. Concentration is controlled by extracting some quantities which can be recycled into the buffer tank or into the Pipe Reactor. The scrubbing solution is kept acidic by a small flow of nitric acid controlling its pH. The level of solution in the bottom of the cyclonic column is controlled by some make-up water made of process condensate.

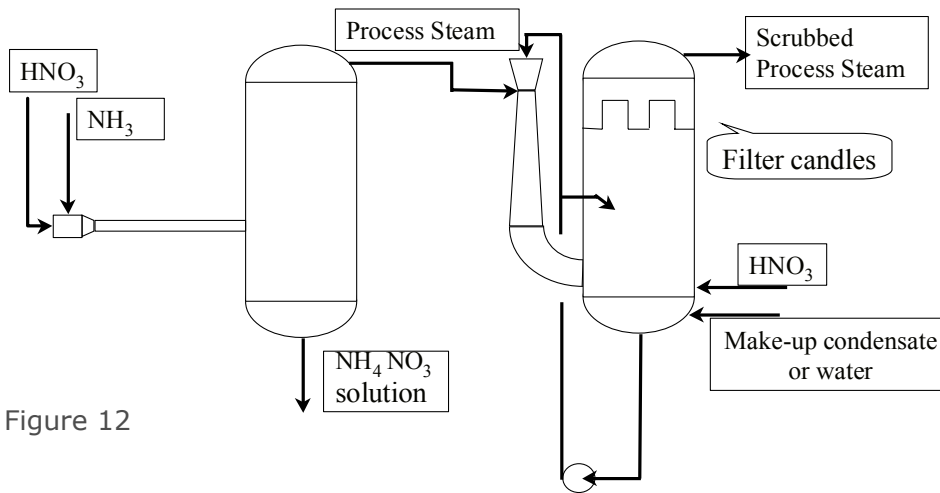


Figure 12

With this treatment the AN content of the process condensate can be reduced down to about 1.6 g/l.

3.2.3. Entropie® System

Then, if the AN content of the process steam is still too high to comply with the factory requirements, another treatment can be implemented: the Entropie® evaporator. With this system, zero pollution is possible

The basic idea is to use the energy of the contaminated process steam to produce pure steam and subsequently pure water.

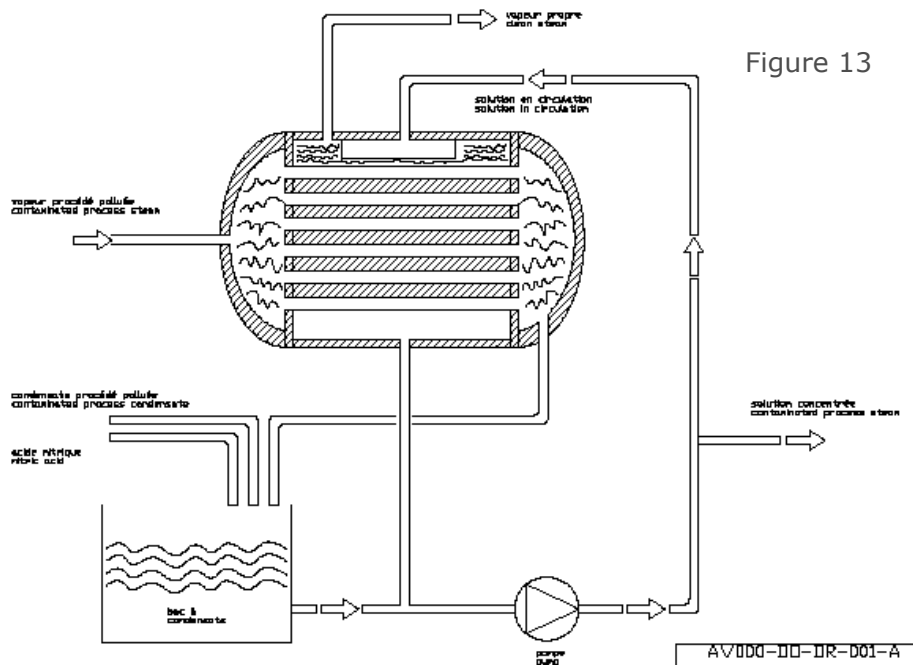


Figure 13

Part of the process steam is fed in the pipes of a shell and tube heat exchanger where it condenses and then the condensate flows down into the contaminated condensate tank. The other condensate are sent to the same tank where all the condensate are mixed.

From the outlet of the tank, the condensate are pumped, acidified and fed in the shell of the exchanger. Spraying trays installed above the tube bundle uniformly distribute the solution, which trickles around the tubes as a mixture of thin film and droplets. The part which has not been vaporized falls down back in the contaminated condensate tank.

The part which has been vaporized, called clean steam, is the condensed in another exchanger, to be some clean condensate.

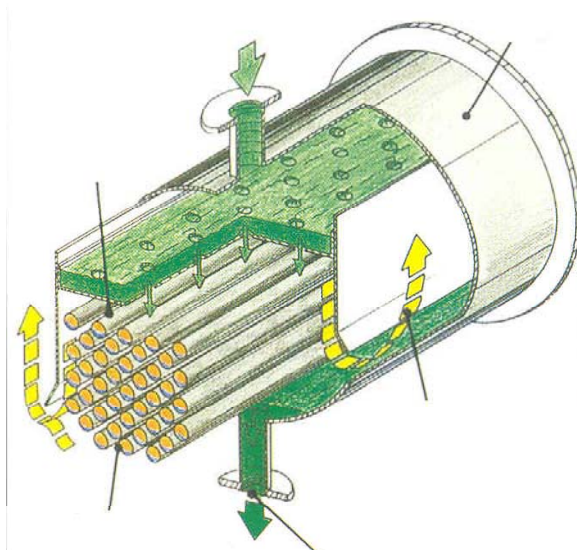


Figure 14

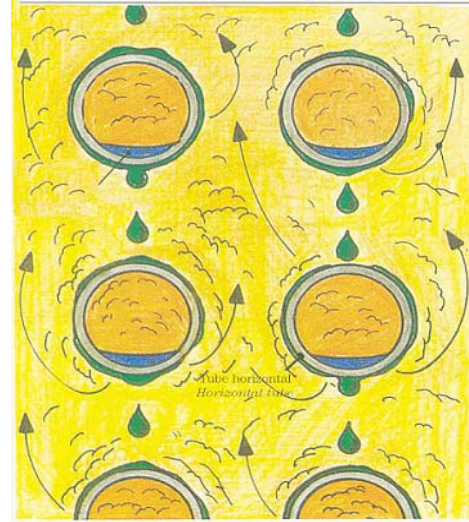


Figure 15

Doing so, there are two outlets to this system:

The excess of condensate in the tank is called contaminate condensate and can be recycled in the different already said places: scrubbing of the ANS plant, absorption tower of the Nitric acid, other plants.

The clean condensate is almost pure water: its AN content is less than 50 mg/l.

So, with this system, the quantity of polluted water is reduced and then the recycling of the excess water is eased.

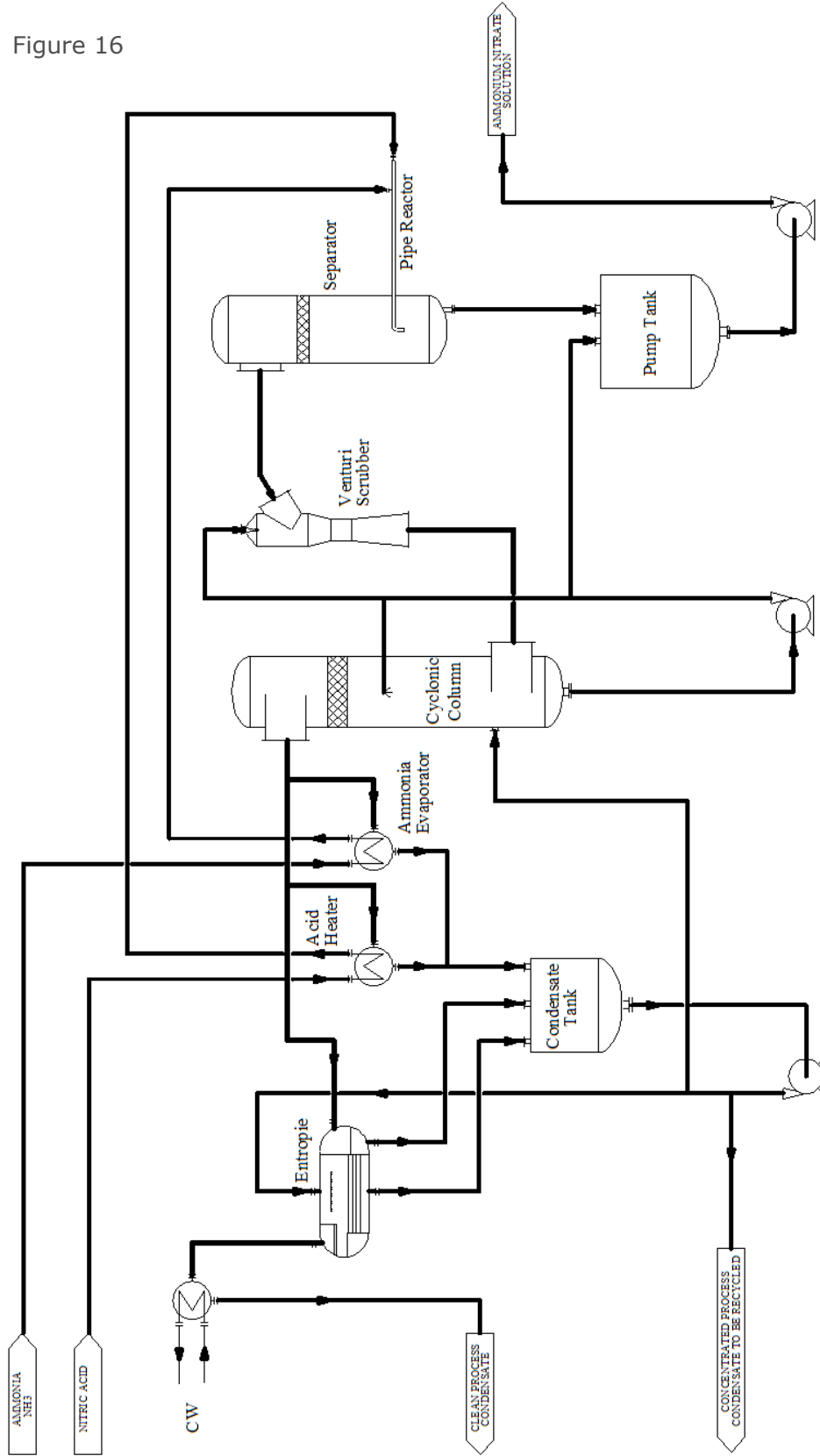
When compared with other processes used to solve the problem of the large flows of hot condensate contaminated with low quantities of pollutants (i.e. osmotic effect, ion exchange...) the use of an Entropy[®] evaporator is the cheapest process regarding investment and operation costs.

The operating costs are rather low as they include only the power for the circulation pump and 100 kg per hour medium pressure steam for the vacuum ejector. The only source of energy for condensate evaporation is the process steam itself.

3.3. Complete Process flow diagram

Even as presented above, GP Pipe Reactor process can be adjusted to almost every requirements coming from a factory, the PFD (Figure 16) presented below can be qualified as the best available schema for a GP Pipe Reactor plant.

Figure 16



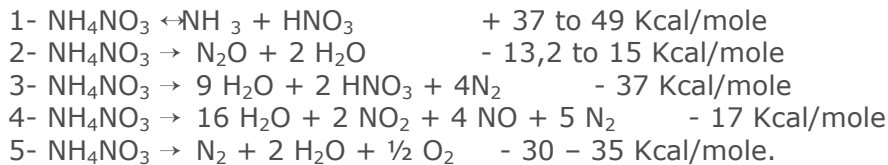
AMMONIUM NITRATE SOLUTION
A. Z. F. PIPE REACTOR PROCESS

4. SAFE PROCESS.

4.1. DECOMPOSITION REACTIONS OF ANS

The decomposition overall mechanism is complex, involving reactions both in liquid and gaseous phases.

The decomposition of ANS is usually described by the following 5 reactions, one being endothermic, the others being exothermic.



In the temperature range 190°C – 280°C, decomposition reactions 1 and 2 are prevailing.

Reactions 3 to 5 require higher temperatures : > 280 – 300°C.

The reaction rates increase with temperature of decomposition. Decomposition rate is very low at temperature lower than 190°C.

Organic matters, metals (as copper), contaminants, chloride accelerate the decomposition rates of ANS. Acidity increases the effect of decomposition (heat generation).

An increase of pressure reduces the kinetics of reaction 1, and so its endothermic effect.

Reaction 5 is also the reaction involved in a detonation process, if any.

4.2. Explosion

In a confined system, if Reaction 1 is not possible, only exothermic reactions are present and the decomposition conditions could lead to explosion. This explosion could be a detonation (velocity above 1 km/s). The chemical reaction involved in the detonation process is the N°5.

The temperature of ANS at which an explosion could be initiated is considered in vicinity of 380°C.

Higher is the pressure of the confined system, lower is the energy required by the system to make the detonation conditions possible. Therefore, uncontrolled decomposition reactions in a confined system could lead to a detonation process.

Detonation of ANS leads to very high pressures (> 10 000 bars) and very high temperatures (> 1500°C).

A detonation propagation requires a minimum diameter of ANS vessel or pipe (critical diameter).

The detonation generates a blast which will affect the surrounding area. The affected zone will depend upon the ANS quantity involved in the detonation process: the larger is the ANS quantity involved in the detonator, the more important are the effects.

The pressure wave is decreasing with distance from the detonation point. The pressure wave is composed of two parts: overpressure and underpressure.

Depending on the layout of the installation a crater can be created.

4.3. Run-away Reaction and Explosion in ANS Vessels and Pumps.

According to published documents till 1970:

We consider 6 explosions located in neutralizer reactors of ANS plants. Two among six have led to fatalities and important damages (USA 1994; CHINA 1998)...

5 explosions located in mixing tanks, filters and evaporators are reported with main cause of decomposition being a contamination by organic matters; one among the 5 led to a detonation.

Items where decomposition takes place the most often are pipes and pumps. The overpressure can lead to explosion which cannot be considered as a detonation according to the reported effects.

Nevertheless operation has to pay attention to pumps when ANS line is blocked and during pipe cleaning.

4.4. Assessment of the Effects of ANS Explosion.

In order to assess the blast effect of the detonation of ANS in confined conditions, we consider the following formula:

$$D = K (M)^{1/3}$$

D is the distance in meter at which effects are studied.

K depends on the blast wave overpressure

(ie K = 22 for 50 mbar; 10 for 140 mbar)

M is the TNT equivalent mass in kg.

1 kg of Ammonium Nitrate is equivalent to 0.3 kg of TNT

only 10% of AN mass is involved in the detonation process (values are consistent with values from a reported accident).

Blast overpressure leads to following damages according to reference data :

10 to 50 mbar	window break.
150 mbar	wall and roof damages
250 mbar	tank damages
300 mbar	house collapse
400 mbar	pipng break

This calculation demonstrates the benefits of reduction of ANS quantity in confined conditions.

4.5. Why ANS Pipe Reactor is a Safe Process.

- Control of process parameters prevents decomposition initiation.

Ratio between ammonia and nitric acid is firstly adjusted by mass flowmeter and a final tuning is operated through pH measurement.

Operating pressure of separator is continuously monitored. Any increase trips the plant.

Temperature is continuously measured. Temperature is limited by the energy balance of the reaction itself. There is no external energy input.

Safety high temperature and pressure devices trip the plant and raw material feeds.

- Confinement is avoided.

Above the pressure control system a bursting disk, sized for process steam and decomposition gases, is installed to prevent any pressure increase.

- If for any reason, a decomposition occurs, temperature or pressure increases in the Separator / Pipe Reactor. If the safety limits for temperature and pressure are reached, it causes an instantaneous plant trip. Moreover, the separator is then drenched with a large amount of water.

- Quantity of ANS material is limited.

The hold-up of a 2000 MTPD plant is limited to 3-5 tons of ANS in the separator and less than 300 kg of ANS in the Pipe Reactor itself.

- Moreover as the flexibility of the plant is wide and as the start-up and shut down are very easy, the quantity of ANS to be buffered can be reduced by increasing the instantaneous production rate of the ANS plant.

- Tripping Philosophy :

As hold-up of the plant is low, any plant trip / shutdown is almost immediate. Pipe Reactor empties instantaneously, and it is almost the same for the separator. So

because of the tripping philosophy where trip is first, time is fully available afterwards to perform all the necessary checks and study to identify and solve the problem.

- Nevertheless a periodic control of raw material (ammonia and nitric acid) is required as well as a procedure and analysis of chloride content of nitric acid.

5. CONCLUSION

Today, ten Pipe Reactor plants have been designed with a capacity range from 250 MTPD up to 2000 MTPD of ANS.

This process is simple, flexible and reliable, its investment cost is always the lowest one for an ANS plant.

Thanks to its design and safety control philosophy safety of process has been improved.

Thanks to the new process development for reduction of nitrogen content of condensate it is environment friendly.

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