

Probably the most Efficient and Safest Technology for Production of Ammonium Nitrate Solution "AMNIT PROCESS"

Mr. Gerard Malard
CEAMAG
Trappes, France

Summary

The AMNIT process for production of concentrated ammonium nitrate solutions combines high thermal efficiency, low maintenance cost, optimal environmental compatibility and operating safety.

The reaction of ammonia with nitric acid occurs, without production of any process vapour, in a pressurized recycle flow loop. The recycle solution, in which a slight amount of free ammonia is maintained, supplies heat to the various exchangers of the loop, for the final AN concentration to 97.5% which is suitable for the major part of granulation processes. The free ammonia in the production off-take is neutralized before pressure reduction and subsequent concentration steps.

A specific feature of the AMNIT process is the self-regulating auto-thermal pre-concentration step. No external heat supply is required. The high thermal efficiency is combined with ease of operation and low maintenance. Efficient pH controls achieve a liquid effluent with the most stringent conditions of pollution control.

All the significant features and benefits of the original CARNIT process, which started up in 1990 have been maintained: absence of corrosion, low maintenance cost and high on stream times of 99+%, for a capacity of 2750 tpd in a single process line. The production rate can be varied between 30% and 100% of design capacity.

This paper has been presented during the Asian Nitrogen & Syngas Conference 2013 in Singapore.

2013 | Asian Nitrogen + Syngas

Probably the most efficient and safest Technology for Production of Ammonium Nitrate Solution “AMNIT PROCESS”

GERARD MALARD

CEAMAG

Trappes, France

The AMNIT process for production of concentrated ammonium nitrate solutions combines high thermal efficiency, low maintenance cost, optimal environmental compatibility and operating safety.

The reaction of ammonia with nitric acid occurs, without production of any process vapour, in a pressurized recycle flow loop. The recycle solution, in which a slight amount of free ammonia is maintained, supplies heat to the various exchangers of the loop, for the final AN concentration to 97.5% which is suitable for the major part of granulation processes. The free ammonia in the production off-take is neutralized before pressure reduction and subsequent concentration steps.

A specific feature of the AMNIT process is the self-regulating auto-thermal pre-concentration step. No external heat supply is required. The high thermal efficiency is combined with ease of operation and low maintenance. Efficient pH controls achieve a liquid effluent with the most stringent conditions of pollution control.

All the significant features and benefits of the original CARNIT process, which started up in 1990 have been maintained: absence of corrosion, low maintenance cost and high on stream times of 99+%, for a capacity of 2750 tpd in a single process line. The production rate can be varied between 30% and 100% of design capacity.

INTRODUCTION

The process technology for production of Ammonium Nitrate has shown a continuous trend towards a gradual increase of thermal efficiency combined with the production of more concentrated solutions, together with sustained attempts to improve the safety of operation and minimize the environmental impact

Some process diagrams combine the neutralization reaction and the evaporation in a single vessel, with internal recirculation. Sometimes both operations may take place in separate vessels which are associated in a simple external loop with forced or natural recirculation

In order to minimize the entrainment by the process vapour of any free ammonia, which might be present in the solution at the evaporation stage, such processes are operated in an acidic condition. Acidic conditions combine the risk of corrosion and the safety risks which are associated with high temperature acidic conditions must be set low enough to ensure stability.

Successful control of pH in a narrow range combines the problems of accurate material balance control of the reactants with the difficulties related to pH measurement.

The pH signal is not linear. In the steep region B-A of the S shaped titration curve, fig 5, a large change of pH corresponds to such a small change of reactant concentration, that the controller gain.

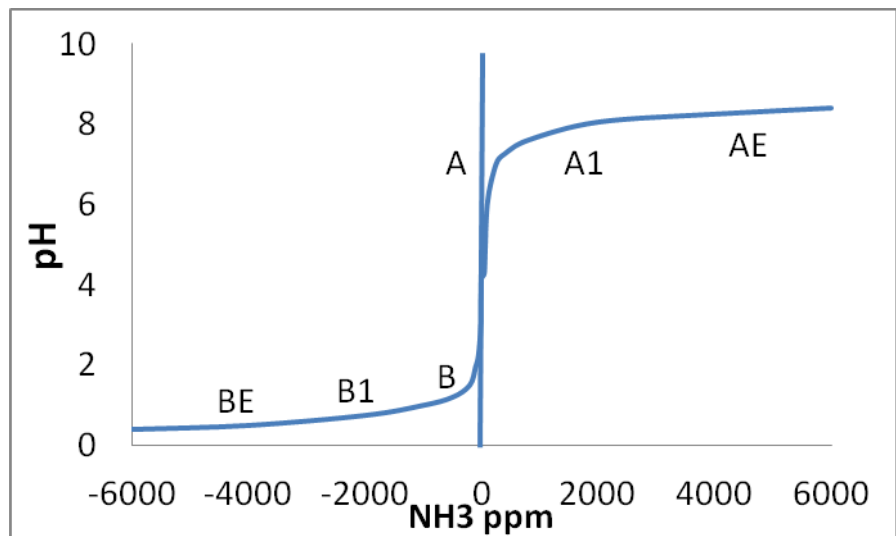


Fig.1 Titration curve of AN solution

In the flat range of the curve B1-BE, a small change of pH corresponds to a large change of reactant concentration, and a controller with low gain becomes inefficient.

It is known that for the case of stable acidic operation, the pH should in practice be maintained in the narrow range of $1.5 < \text{pH} < 2$. Due to the particular shape of the pH curve, fluctuations around a baseline of $\text{pH} = 2$, extend easily beyond the pH inflection point, with resulting high ammonia losses. At low pH values, the response time of pH electrodes slows significantly, and time constants in excess of 50 seconds are known to appear at pH values below $\text{pH} = 1.5$. With a baseline of $\text{pH} = 1.5$, poor pH electrode performance may induce an increased AN decomposition risk.

In order to overcome the unreliability of the pH electrode at $\text{pH} < 1.5$, some processes have relied on frequent analysis of the solution. Continuous monitoring of the N_2O content of the process vapour has also been used to detect the onset of a potentially dangerous situation.

The AMNIT process for production of concentrated ammonium nitrate solution has originally been developed at the Tertre KEMIRA plant in Belgium, as the CARNIT process, in order to combine a minimal impact on the environment with a high thermal efficiency together with mild operating conditions and maximum possible safety of operation. The original Carnit process flow-sheet incorporates the production of low-pressure export steam, whereas the more recent AMNIT version does no longer require the production of LP export steam.

PROCESS DESCRIPTION

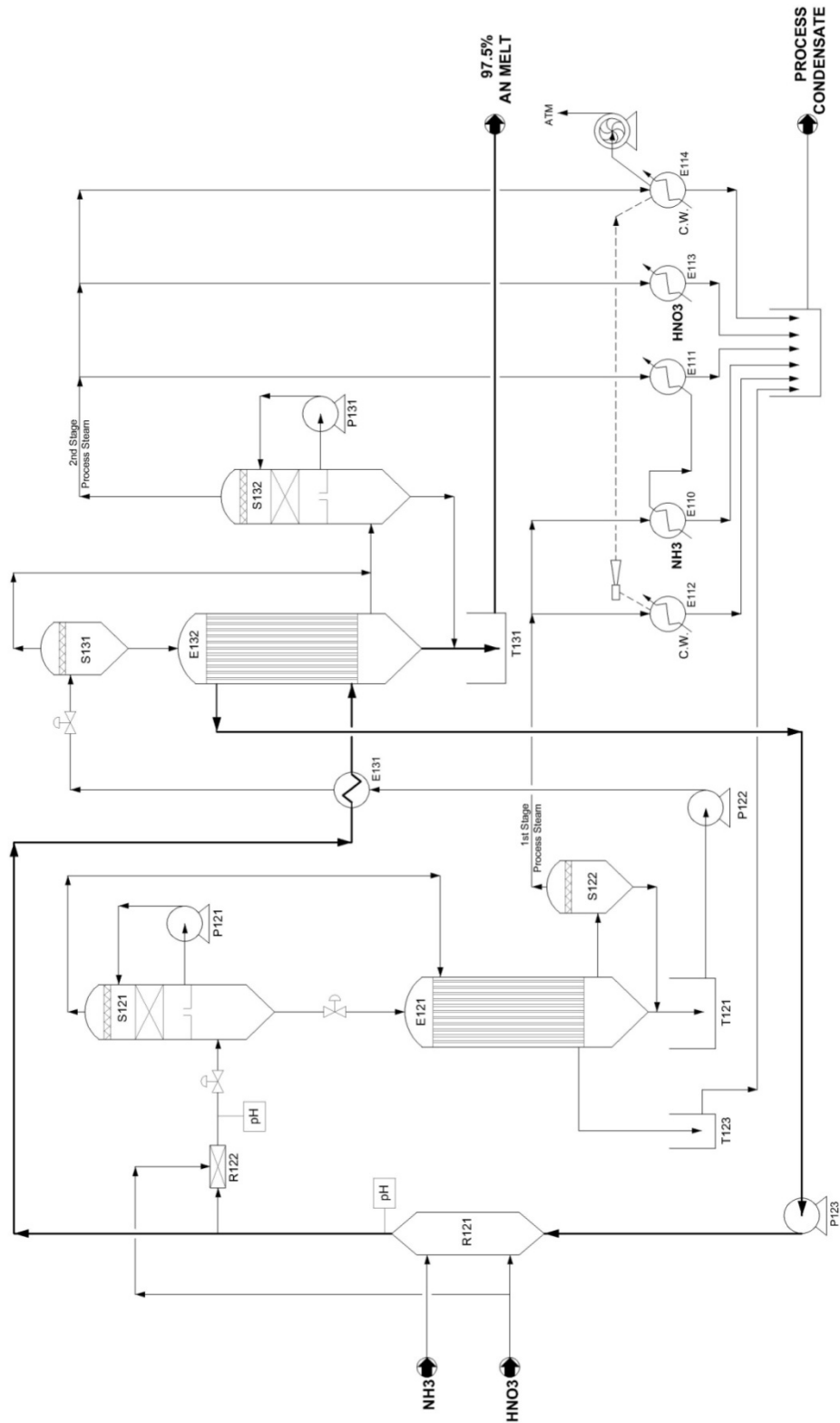


Fig. 2 AMNIT FLOW SHEET

The AMNIT process uses standard feed-stocks, i.e. liquid or gaseous ammonia and aqueous nitric acid with concentration as low as 55%. The neutralization and the concentration of the resultant AN product solution occur in two well separated operation stages.

Neutralization loop

The neutralization of reactants occurs in the liquid loop which includes the main reactor R121 and the final AN concentration system. The loop is composed of:

- The Neutralizer R121,
- The Final Pre-evaporator E131,
- The Final Evaporator E132,
- The Neutralization Loop Circulator P123.

The heat evolved by reaction in Neutralizer R121 is transferred as sensible heat by the solution and is removed in the AN concentration system.

The reactor operates under a slight excess of ammonia at about 800 kPa. When using 58% Nitric Acid, concentration of the AN solution is about 63.5%. The entire loop is in liquid phase. Conditions of reaction are such that there is no process vapour immediately after the outlet of the Neutralizer.

The 63.5% AN solution produced is sent to the trimming Post-Reactor R122 where the pH is decreased for elimination of the excess of ammonia before being sent to the Primary Concentration.

Primary concentration

At the exit of the Trim Post-Reactor R122, the AN solution concentrated to about 63.7% is flashed in Flash Separator S121.

The upper part of the separator acts as gas scrubber of the vapour phase in order to eliminate the ammonia excess. Washing solution flow rate is ensured by the Flash Circulation Pump P121 and neutralization of ammonia is achieved by nitric acid injected in the circulating stream under pH control.

At the top of the Flash Separator S121, vapours will be used to concentrate AN solution in the Primary Evaporator E121.

The AN solution from S121 is expanded through the flash control valve. The AN solution then flows into the Primary Evaporator E121 where it is concentrated to about 73%. The process steam and AN solution are separated in the bottom of E121. Process steam is sent to the Primary Evaporator Separator S122 and is finally used in the Ammonia Evaporator E110. AN Solution collected from the bottom of the Primary Evaporator E121 is recovered in the Primary Concentration Seal Tank T121.

Final Concentration

AN solution from the Primary Concentration Seal Tank T121 is pumped to the Final Pre-Evaporator E131, by means of the Pump P122. The solution is pre-heated by the recirculation loop stream coming from the Neutralizer R121.

The AN solution leaving the Pre-Evaporator E131 is expanded in the Secondary Concentration Separator S131. Vapours from S131 are washed in the Final Concentration Separator S132 under pH control while AN solution flows to the Final Evaporator E132.

The process steam coming from the Final Concentration Separator S132 is used for superheating the Nitric Acid and Ammonia Gas before they enter in the Neutralizer R121

Ammonia feed

Liquid Ammonia from Battery Limit is sent to the Ammonia Evaporator E110. The evaporation of ammonia is achieved by the 1st stage process steam produced at the stage of AN Pre-Concentration. The ammonia gas leaving the evaporator is then superheated in the Ammonia Superheater E111 by the 2nd stage process steam before being feed the Neutralizer R121 under pH control.

Nitric Acid feed

Main stream of Nitric Acid is pre-heated in the Nitric Acid Heater E113 by 2nd stage process steam produced at the stage of AN Final Concentration. A very small part of the overall flowrate is sent to the Trimming Post Neutralization Reactor R122.

Process condensates

The Flow sheet in Fig.2 shows a typical recovery of process condensates, in a pool tank. Depending upon the uses of condensates (scrubber of granulation plant, return to nitric acid plant, draining) the process condensates can be split and each concentrations optimised in order to optimize the scrubbing systems.

In any case, the excess of process condensate which would be drained due to specific site situation shall meet the most stringent regulations of pollution control.

Table 1			
Typical operating Data			
	Concentration (%wt)	Temperature (°C)	Pressure (kPa abs)
Reactor Input			
HNO ₃ liq.	60	65	800
NH ₃ gas	100	65	800
Recycle Solution	65.6	155	
Reactor Output			
AN solution	65.6	180	650
Concentration section			
AN solution E121	82-83	81-83	20
Product			
AN solution E132	97.5	155	40

KEY PROCESS PARAMETERS CONTROL

The production rate is set by the NH₃ feed stream, with an ammonia/nitric acid ratio control which adjusts the nitric acid supply. In order to stabilize the ratio of reactants, the acid feed is monitored on the basis of a constant HNO₃ supply. To this effect, an on-line measurement of acid density is used to adjust the flow control settings.

A varying acid concentration induces varying water loads and heat releases in the system. These variations are taken care of by the self-adjusting mechanism of the primary and final concentration, and by the temperature control of the recycle loop which is based on the automatic adjustment of the heat recovery to the heat load.

The heat requirement of the circulation loop is closely related to the water evaporation duty of the exchangers E131 and E132.

The setting-point pressure of the primary concentration step is modulated in order to adjust the balance between water evaporation duty of the exchangers of the Final Concentration section, E131 and E132, and the heat load which is brought into the loop by the neutralization reaction.

A very accurate flow control of the acid feed is essential, as one of the features of the AMNIT process is a tight control of the pH of the circulation loop, where the free ammonia content is to be maintained in the range of 400 to 800 ppm. With available flow measurement instruments, it is not possible to achieve such an accurate metering of the reactants.

In order to maintain the pH value of the solution at all times within the chosen narrow control limits, the fine tuning of the acid feed input is attributed to a pH controller, which monitors the pH of the solution at the outlet of the reactor.

One of the points of paramount importance is the necessity to insure that the sample used for pH control of the loop, is adequately and reliably representative of the actual composition of the solution at the exit of the reactor. This requires that, regardless of the rate of production, the reaction is effectively terminated at the exit of the reactor and that a stable and homogenous flow pattern is achieved before reaching the sample point. Much effort has been devoted to achieve that the flow pattern of the reactor is adequately adjusted, so that a steady and representative flow pattern can be combined with a minimum instrument dead time (lag between acid injection point and pH sample point).

The AMNIT process operates with a constant recycle flow throughout the whole range of design operating capacities. The temperature spread between inlet and outlet of reactor will therefore change according to any variation in operating capacity or feed acid concentration.

A constant recycle flow reduces to a minimum any possible variation of the instrumentation lag times. The excellent performance of the pH control of the solutions in the concentration and vapour scrubbing sections, guarantees a stable quality of the effluents, which are monitored on the basis of their conductivity.

PROCESS CONTROL SYSTEM AND SAFETY

The instrumentation of the unit is designed so that safe operation will, at all times, be achieved. Whenever a parameter appears to move in a direction which can lead to a major deviation of the unit, a potential trip situation is indicated.

All the primary parameters which may lead to a trip situation are monitored. Any important parameter deviation or rate of change starts an alarm before the actual trip would occur. As the reason for the possible trip is known immediately, the operator can react rapidly and efficiently in order to maintain the unit on stream.

The integrated process control is organized so that set-point adjustments which may be required, such as in the case of a change in operating capacity are done automatically by the DCS system. In normal operation the only parameter which must be adjusted by the operator, is the ammonia flow set-point, which sets the production capacity.

The automatic adjustment to changes of the acid concentration or to changes of the rate of production provides the desired flexibility of operation.

The time required for a hot restart to reach full capacity varies between 15 and 25 minutes. The limiting factor is the performance of the effluent section, where the requirement of a steady effluent quality is paramount. The effluent quality is monitored by an on-line conductivity measurement.

For a cold restart, after complete draining of the unit, the preparation and reloading before start-up will require 2 hours, followed by a stepwise increase of production which will take approx. 2 hours.

The AMNIT system is designed so that safe plant operation will, at all times, be achieved without any supervision.

The most obvious risks in any AN unit relate to high temperature and high concentration solutions which may become acidic, and where overheating together with a significant decrease of density resulting from the presence of bubbles may lead to a run-away situation.

In the AMNIT system, such risk situations cannot exist, as the highest temperature that can be reached is that of the low concentration recycle solution, in which a controlled amount of free ammonia is maintained at all times, and which is maintained under a sufficiently high operating pressure so that no vaporization can occur.

In case of a sudden equipment failure in the hot circulation loop, which would lead to the emergence of a free jet of solution, depressurization of the loop would activate the shut-down procedure. The depressurized solution in the jet to atmospheric pressure will produce cold solution with a concentration of approx 73 wt%. There is no risk of producing dry, low-density and detonation prone AN.

In the high concentration section, the pH of the solution pumped to the final concentrator is maintained in the alkaline range of pH = 6.6 to pH = 7. The same pH range is maintained for the concentrated solution of 97.5 wt%.

In the concentration procedure, whenever a flashing of the AN solution occurs, a preferential vaporization of ammonia may tend to induce an acidic condition of the solution. A compensating ammonia injection, which is monitored by a pH control, is used to restore the alkalinity of the solution.

EFFLUENT CONTROL

There is no gaseous effluent, with the exception of the continuous purge from the vacuum system of the very small amount of non-condensable in the feed reactants, and of the occasional small air leaks into the reduced pressure zones. All process output streams, i.e. concentrated AN solution and condensed process water vapour are in liquid form.

The nitrogen content of the pooled process condensates has been reported in the existing plant at a constant monitored value not exceeding 15 ppm wt.

The only AN product loss, which occurs exclusively in the process condensate, is so low that the overall process yield exceeds 99.99 %wt.

ENERGY SAVING

By making the fullest possible use of latent heat in the off-take product stream, the maximum possible amount of heat is retained in the hot circulation loop, where it is available for high temperature duties. The high temperature heat supply is used exclusively for high temperature duties such as final concentration of the solution. The thermal efficiency of the process can be put to good use for production of concentrated 97.5 wt% AN solution even with relatively dilute Nitric acid (concentration down to $\pm 55\%$).

The use of the low pressure process vapours, for preheat of the reactants, contributes to the overall energy recovery, and reduces the amount of heat which must be removed through the cooler-condensers.

The energy saving effect of the first primary concentration step increases as the acid concentration decreases. Energy self-sufficiency can be maintained when producing 97.5 wt% AN solution even with dilute acid of 55 wt% concentration.

CONCLUSION

The specific operating parameters and design of the AMNIT process lead to numbers of advantages, in terms of OPEX, safety and pollution control. They are summarized here below.

- The neutralization reaction occurs at the lowest AN concentration, in comparison with all other processes.
- The pH inside the circulation loop being maintained basic, the corrosion is minimized and choice of material for equipment, in particular for the circulation pump P123 is not as critical as it can be for other processes,
- The process is thermally autonomous for producing 97.5% AN solution, even with low concentrations of nitric acid, such AN concentration being optimised for granulation processes,
- The process condensate quality can be optimised for any specific requirement, from almost pure condensate till diluted AN solution recycled to the scrubbers of granulation plants, allowing the CAPEX optimization for each project.
- The plant is highly flexible, representing a significant advantage when coupled with a granulation plant.

The author is grateful to the management of HECKE sprl for its willingness to supply and authorise the publication of the AMNIT process data