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THE CARNIT AMMONIUM NITRATE PROCESS
AN EMPHASIS ON ENERGY EFFICIENCY AND ENVIRONMENTAL COMPATIBILITY

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RESUME

Le procédé Kemira Carnit de production de solution concentrée de nitrate d'ammonium combine un rendement thermique élevé, un faible coût d'entretien et une compatibilité optimum avec l'environnement.

La réaction entre l'ammoniac et l'acide nitrique se produit dans une boucle de recyclage pressurisée où l'on ne produit aucune vapeur de procédé.

La chaleur de réaction est répartie entre plusieurs échangeurs de la boucle de recyclage par circulation de la solution ammoniacale. L'ammoniac libre dans les effluents de production est neutralisée avant réduction de la pression.

Un contrôle efficace du pH permet d'obtenir un effluent contenant moins de 50 ppm d'azote exprimé en nitrate d'ammonium.

Un trait spécifique du procédé Carnit est l'économie d'énergie et le stade de préconcentration autothermique et auto-régulateur. Aucun apport de chaleur extérieure n'est nécessaire et une vapeur propre à 6 bar est disponible pour l'exportation, même quand l'acide nitrique 60 wt % est utilisé pour la production d'une solution à 98.+ wt %.

Le procédé peut être optimisé soit en produisant une quantité maximum de vapeur à exporter, soit en réduisant les investissements quand aucune vapeur n'est nécessaire pour l'exportation. Le taux d'utilisation peut varier de 30 % à 100 % de la capacité théorique.

Une unité Carnit de 2100 t/j (100 % AN) a démarré à Tertre en Belgique en décembre 1990. Jusqu'au premier arrêt d'entretien programmé en juillet 1992, la production d'une solution à 97,5 % en poids a été continue avec un taux d'utilisation de 98,7 %.

Le procédé Carnit de production de nitrate d'ammonium est disponible pour octroi de licence auprès de Kemira Engineering en Finlande ou Kemira S.A. en Belgique.

Mots clés : Nitrate d'ammonium, effluent, contrôle du pH, production de vapeur.

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1. INTRODUCTION

The process technology for the synthesis of ammonium nitrate, AN, by reaction of ammonia and nitric acid, has shown a continuous trend towards a gradual increase of thermal efficiency together with the production of more concentrated solutions. The typical process diagram combines the acid/ammonia reaction with an evaporative heat removal. Such designs have to be operated in an acidic condition,as any free ammonia would be entrained by the process vapour.

A major drawback of the existing processes is the production of liquid effluents which contain more ammonium nitrate than can be tolerated by the existing or expected environmental regulations.

In the Kemira CARNIT process (1) for production of concentrated AN solutions, a high thermal efficiency is combined with a minimal or even negligible impact on the environment. There are no gaseous effluents, and the process condensate effluent has such a low nitrogen content that it can be made to match the drinking water quality requirements.

The CARNIT process uses the standard feedstocks, i.e. liquid or gaseous ammonia and aqueous nitric acid. The neutralisation and concentration of the resultant AN product solution occur in two well-separated operation stages.

The neutralisation occurs in a recycle reaction loop, with operating pressure always higher than the vapour pressure of the solution. There is no production of process vapour in the reaction loop, and no change of concentration of the reaction product. The heat of reaction is stored as sensible heat, in form of an increase of the temperature of the recycle solution. The temperature control of the loop is achieved by heat exchange in the final solution concentration exchanger and the export steam kettle.

The concentration of the solution occurs stepwise. The first step in the flowsheet is a combined flash and primary concentration stage of the hot solution off-take from the reaction loop. The following concentration steps derive their heat supply by heat exchange from the hot solution circulation of the recycle reaction loop.

A solution concentration of at least 97.5 wt% is obtained at the outlet of the final concentrator, and clean 6 bar export steam is produced, without any external heat supply, even with 60 wt% nitric acid.

2.   CARNIT FLOWSHEET

Figure 1 shows the basic CARNIT flow sheet, such as applies to the Tertre unit. Preheated gaseous ammonia and aqueous nitric acid are fed to the main tubular reactor R1, where they are injected in a circulating flow of ammonium nitrate (AN) solution. The concentration of the resulting AN solution is directly related to the concentration of the nitric acid feed.

The heat liberated by the exothermic neutralisation reaction induces a temperature increase of the solution , which is related to the recycle ratio. The maximum temperature at the exit of the reaction zone is set in the range of 180-190°C. The hot recirculating AN solution flows through steam kettle K and final falling film exchanger F2 where the solution of 97.5 wt% is produced.

In order to minimize corrosion problems, the recycle loop is operated with a slightly ammoniacal solution. The ratio of reactant feeds is adjusted so as to maintain a controlled amount of free ammonia in the circulating solution. The free ammonia in the production off-take is neutralised in the trimming reactor R2 by a small nitric acid injection. Net production off-take is removed through the pressure reducing valve A.

The first concentration step occurs upon pressure reduction through valve A and flash vaporisation in separator S1, which is fitted with a high-efficiency scrubber where the vapours are cleaned. The flashed solution undergoes a second pressure reduction through valve B, before further concentration is achieved in falling film exchanger F1 where condensation of the flashed vapour from S1 supplies the evaporation heat.

The solution from the primary concentrator F1 is pumped from the primary concentration seal tank to the final falling-film exchanger F2, which is heated by the circulating solution of the reaction loop. In F2 the solution is concentrated to 97.5 wt%.
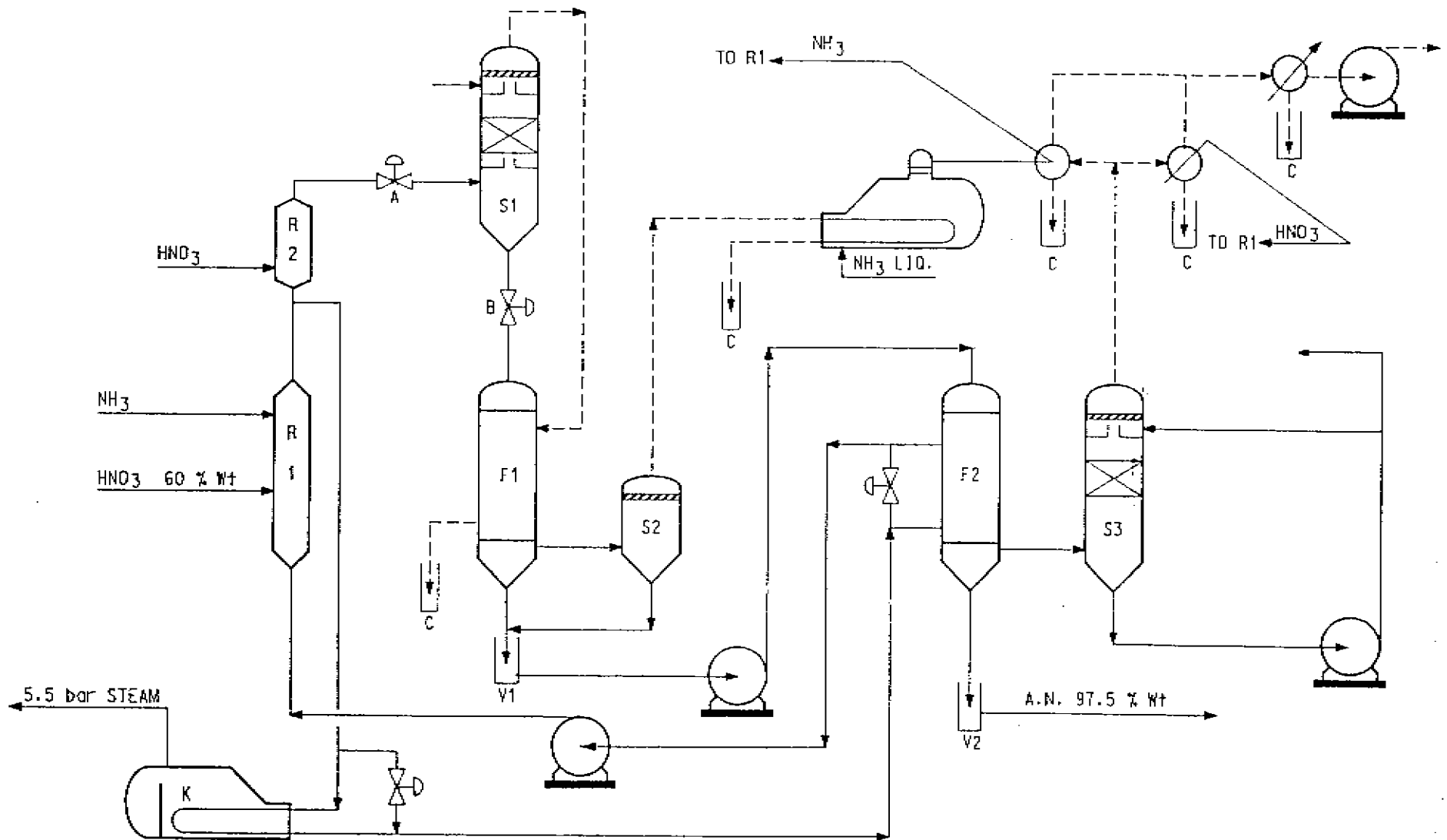
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FIG.1 - BASIC CARNIT FLOWSHEET FOR AMMONIUM NITRATE

The vapours which are released in F2, at a pressure of approx 0.4 bar, pass through the high-efficiency scrubber S3, after which they are used for superheating of the gaseous ammonia feed and preheating the nitric acid feed to approx 67°C. The low pressure vapours which are released from the primary concentrator F1, at a pressure of approx 0.2 bar, supply the heat required for vaporisation of the liquid ammonia feed. Any vapour in excess is condensed in the steam surplus condensers. Typical operating conditions are given in **Table 1**.

2.1. Neutralisation section

The exothermic heat of reaction of aqueous nitric acid and gaseous ammonia varies slightly with the concentration of nitric acid.

In the acid concentration range of 50 wt% to 65 wt%, the enthalpy release varies, for a reference temperature of 65°C for both reactants and products, from 1.28 GJ to 1.39 GJ/t AN **(curve 1 of Figure 2)**.

Part of the heat release is used to heat the reaction product to the reactor exit temperature of 185°C. The remainder is stored in the recirculating solution and distributed to the various heat exchangers of the loop. **Curve 2 of Figure 2** "heat supply in reaction loop" shows that it increases as concentration of nitric acid increases.

Table 1: Typical operating data

	Concentration wt %	Temperature °C	Pressure bar
Reactor Input - HNO_3 liq - NH_3 gas - Recycle solution	60 100 65.6	65 65 155	8 8 6.5
Reactor Output - AN solution	65.6	185	6.5
Concentration section - AN solution F1	83-84	80-82	0.175
Product - AN solution F2	97.5	155	0.4

The steam production in kettle K **(curve 3 of Figure 2)** increases as the heat duty of F2 decreases.

The temperature range of the loop is defined by the inlet and outlet temperatures of reactor R1. This temperature range, which reflects the heat release rate i.e. production capacity and acid concentration, will depend on the recycle ratio.

The concentration of the reaction product, and of the recirculating solution, depends on the concentration of the nitric acid feed.

The operating pressure of the loop must be adjusted in relation to the concentration of the solution, i.e. the nitric acid concentration. With more dilute acid, the loop solution is also more dilute, and its vapour pressure will increase. **Figure 3** shows the required operating pressure for acid concentrations in the range of 50 to 65 wt% and reactor exit temperature of 185°C.
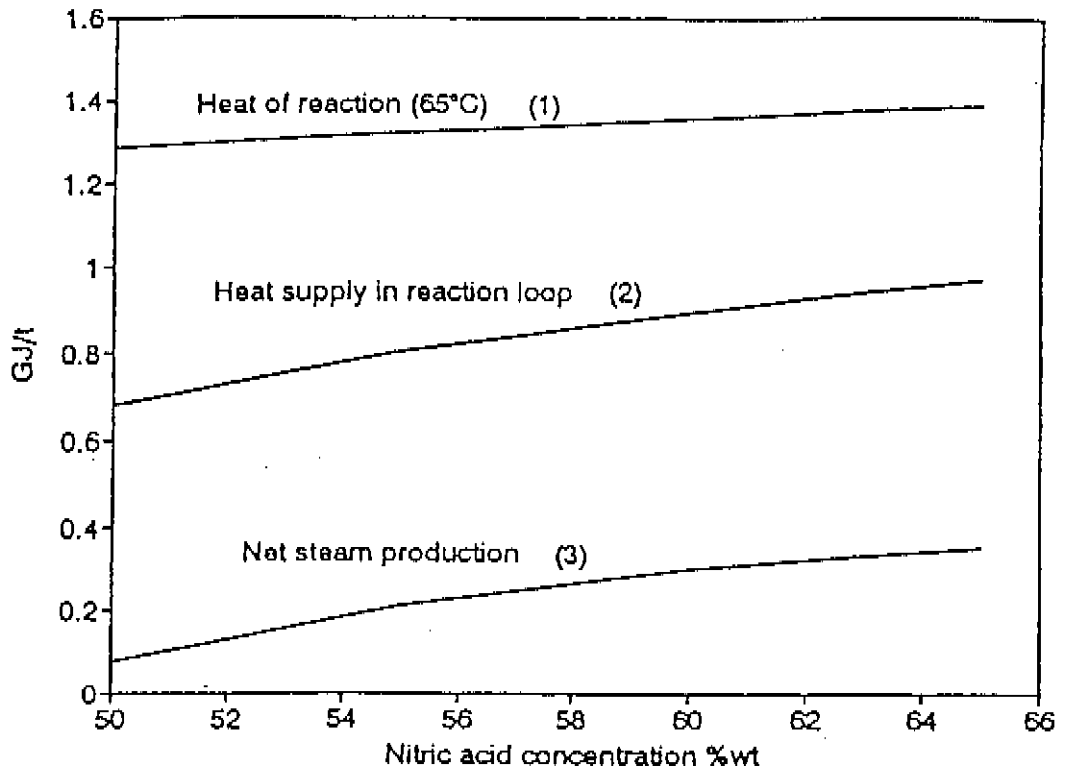
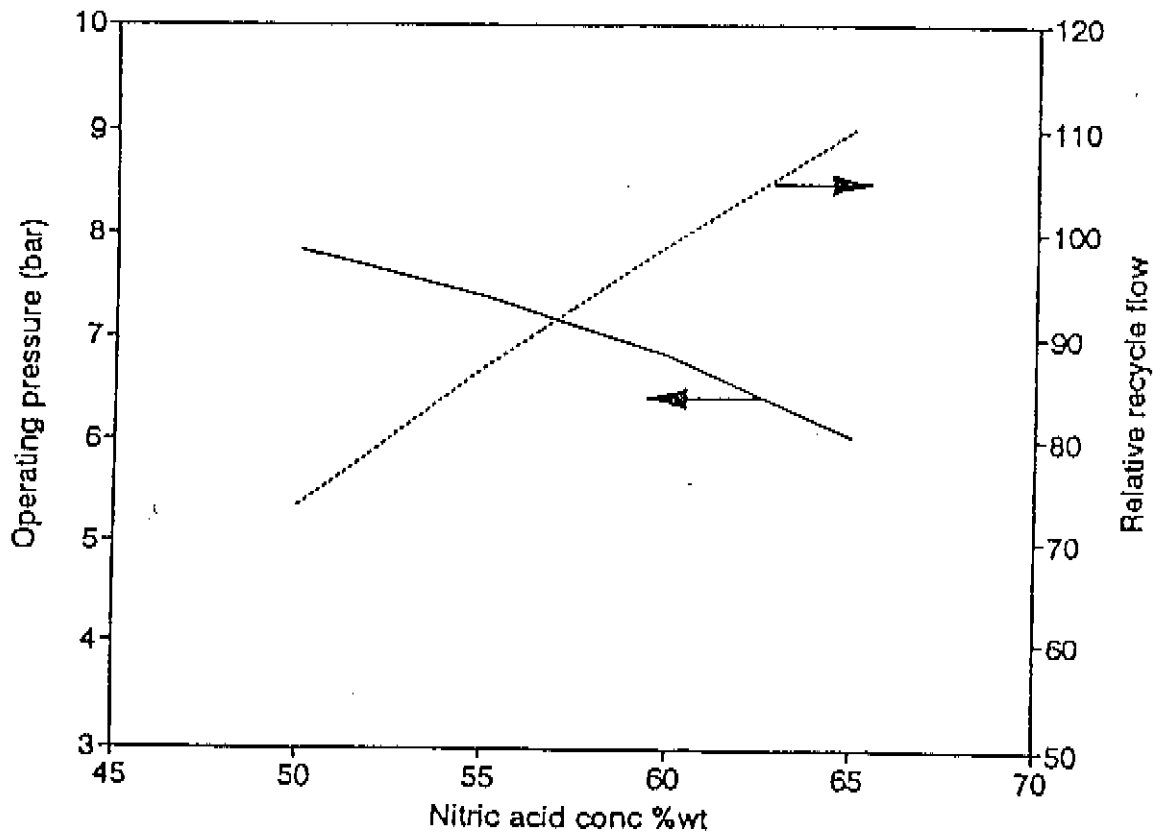Fig,2 NEUTRALISATION LOOP ENTHALPY DATA

Fig,3 NEUTRALISATION LOOP CONTROL DATA

2.2. Concentration section

The first step of the concentration procedure is a specific feature of the CARNIT process. It occurs when the solution off-take is flashed in the separation vessel S1, and concentrated in falling film exchanger F1 with the heat supplied by the flashed vapours from S1.

This combination of the adiabatic flash with a falling film evaporator F1, acts as a double-effect forward feed system. In such a double-effect system, the pressure setting on the solution side of F1 is the only operating variable.

Figure 4 shows a typical temperature vs concentration profile of the AN solution flow. Three different concentration steps are combined in the preconcentration section.

a. The solution composition and temperature at exit of the reaction loop are indicated at point A. Adiabatic flash vaporisation through pressure reducing valve A, into the separation drum S1, produces a concentration and cooling effect along the path from A to B.

b. A second flashing of the solution through valve B, into the falling film exchanger F1, reduces the temperature of the solution along the path from B to C below the condensation temperature of the flashed vapours which have been liberated at B. The position of the point C is only dependent on the pressure which is maintained in F1. Point C would move to C', by a further reduction of pressure in F1.

c. The concentration of the solution continues in falling film exchanger F1, along the isobaric path C-D, for which the heat supply is provided by condensation of the flash vapours from separator F1.

Such a system is entirely self-regulating.

The temperature of the solution is determined by the pressure which has been chosen for point C. If the operating pressure is decreased to point C', the temperature of the solution and of the tube wall decrease. The lower tube wall temperature induces a decrease of pressure in S1, with point B moving to B', and this increases the quantity of flashed vapour. The isobaric concentration path C-D moves to C'-D'. By decreasing the operating pressure, i.e. the pressure at point C, the final solution composition is brought gradually closer to the crystallisation curve, with the corresponding risk of freezing the solution.

A reasonable safety margin, which is mainly related to the uncertainty and inaccuracy of industrial instrumental data, must be taken into account when selecting the operating pressure of point C.

Up to this stage of the flow-sheet, no use has been made, for solution concentration purposes, of the reaction heat that is stored in the recycle solution of the reaction loop.

The solution from F1, point D, which has reached a concentration of the order of 83 wt%, is collected in intermediate storage V1. From there it is pumped to falling film exchanger F2, which is heated by the hot solution of the recycle loop. On Figure 4 the path D-E corresponds to the temperature rise of the solution up to its boiling temperature at the operating pressure of F2. Path E-F shows the isobaric evaporation process that leads to the desired concentration of 97.5 wt%. As in the case of point D, the distance between point F and the crystallisation curve indicates the safety margin relative to the salting-out risk.

These safety margins, are important for the reliability of plant operation. They also have an effect on the thermal efficiency limit of the process.
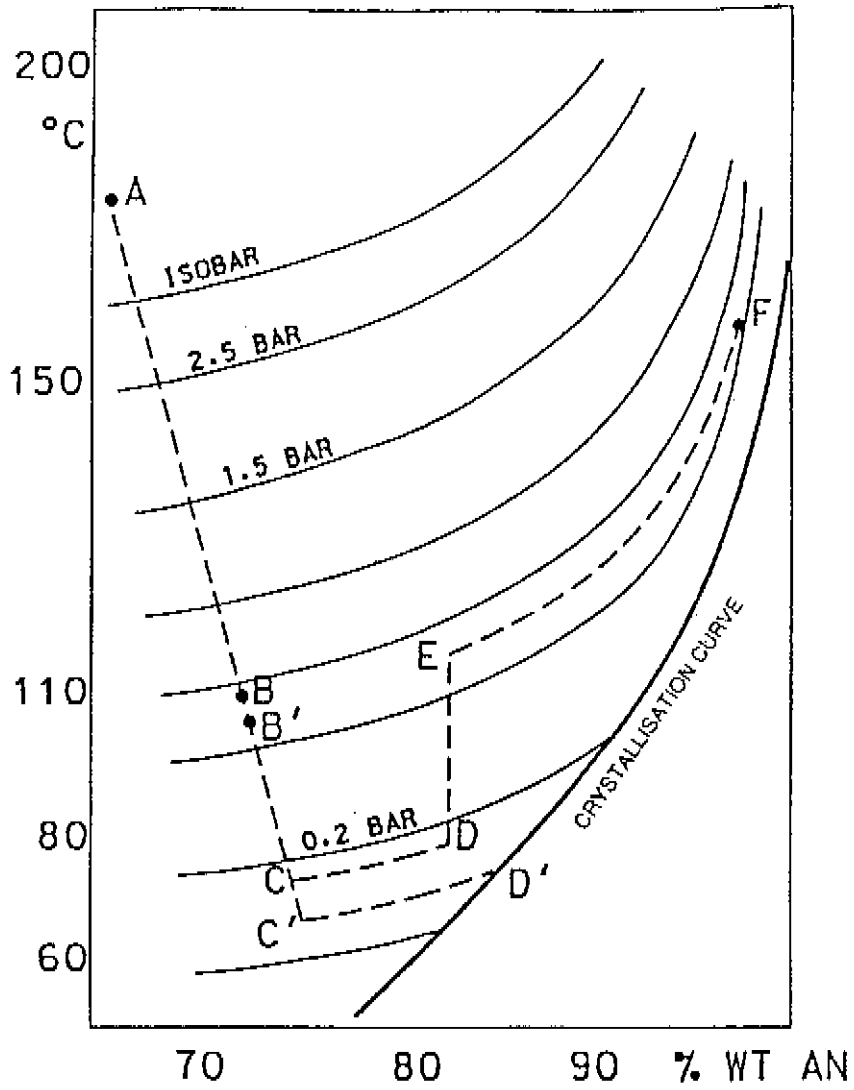
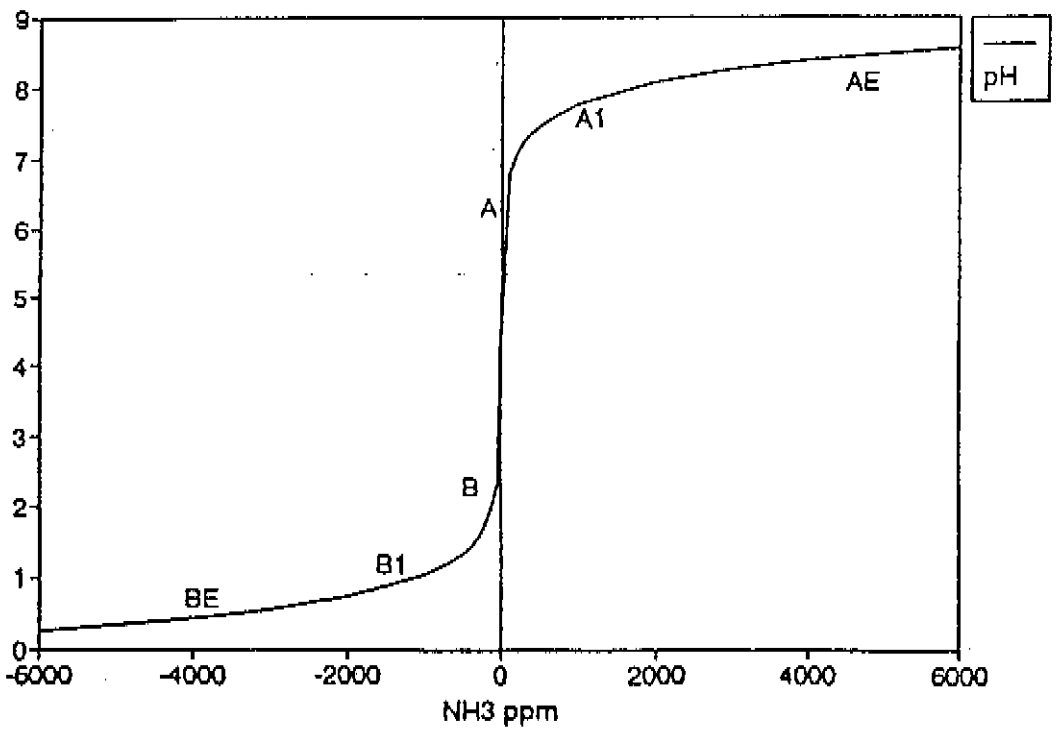Fig.4 TEMPERATURE CONCENTRATION PROFILE OF CARNIT PROCESS

Fig.5 TITRATION CURVE OF AN SOLUTION

3. PROCESS CONTROL

The production rate is set by the NH_3 feed stream, with an ammonia/nitric acid ratio control which adjusts the nitric acid supply.

The fine tuning of the acid feed is attributed to a pH controller, which monitors the pH of the solution at the outlet of the reactor.

The enthalpy release and water supply into the system vary, whenever the concentration of acid or the production capacity change.

The steam kettle allows to balance the loads of heat brought into or extracted by the circulation loop. It recovers the heat produced in the reactor, which has not been used by the process itself.

A specific feature of the CARNIT process is the close control of pH in the circulation loop, where a free ammonia content is maintained in the range of 400 to 800 ppm wt. In the off-take, the free ammonia is neutralised with nitric acid, in a trim reactor R2, to an acidic pH.

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, **Figure 5**, a large change of pH corresponds to such a small change of reactant concentration, that the controller gain must be set low enough in order to ensure stability around the inflection point. In the flat range of the curve, B1-BE or A1-AE, a small change of pH corresponds to a large change of reactant concentration, and a controller with low gain becomes inefficient.

A further difficulty of a pH based control system results from the pH electrode characteristics. The loop pH control has therefore to cope with the difficulties resulting from the sensitivity, rangeability, non-linearity, and time delay of the pH measurement.

Most commonly, the pH regulation is based directly on the pH signal. But pH is a concept which has no additive properties, and which by itself can not lead to a pH conservation balance.

In the CARNIT process the measured pH is related to a corresponding solution composition. It then becomes essential to know the titration curve of the solution under both the chosen operating and measurement conditions, in order to relate a change of the measured pH to a corresponding change of the solution composition.

The study (2) of the dynamic response of pH control in a CARNIT recycle loop has shown the importance, not only of achieving the shortest possible delay between action on the acid valve and recording of the results of the regulating action, but also of using the correct pH/concentration relation for regulation.

Adequate loop stability and efficient pH control require of course accurate valve responses to the temperature signals which determine the bypass flows in the loop and trim acid supply to the reactor.

Precise valve positioning is therefore of paramount importance.

4. INSTRUMENTATION AND SAFETY

The instrumentation has been designed so that safe plant operation will at all times be achieved without any supervision. If a parameter appears to move in a direction which can lead to a major deviation of the unit, a potential production trip is indicated.

All the primary parameters which may lead to a trip situation are monitored, which means that tripping the unit does not have to be postponed until the danger situation has been reached. Any important parameter deviation starts an alarm before the actual trip occurs.

As the reason for the possible trip is known immediately, the operator can react rapidly and maintain the unit on stream.

The integrated process control can be organized so that setpoint adjustments which may be required, such as in case of a change of 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 setpoint, which sets the production capacity.

In any AN unit, the most obvious risk relates to the high temperature and high concentration solutions, where overheating may induce acidic conditions and lead to run-away conditions. The risk pattern increases markedly when the solution contains free nitric acid.

In the CARNIT system, the highest temperature that can be reached is that of the circulating solution, in which a controlled amount of ammonia is maintained at all times.

Heat release in the reactor is dependent on the neutralisation reaction, which occurs between balanced amounts of reactants.

The temperature rise is limited by the dilution effect of the recycle flow. When an instrument failure leads to an increased supply of only one of the reactants, there is no increase of heat release, but rather a cooling effect.

An abnormal temperature rise could only occur in case of a continued balanced feed and total or partial failure of the recirculation.

With a reduced recycle solution flow, the amount of solution which could be overheated is limited to the small amount which has flowed through the reactor before reaching the temperature probes which control the trip system. A trip shut-off will also be triggered by the recycle flow measurement.

In case of a sudden equipment failure in the hot circulation loop, which would lead to the emergency of a free jet of solution, depressurization of the loop would activate the shut-off procedure.

As regards the depressurized solution in the jet, it can be seen from Figure 4, that adiabatic flashing (along line A-C) to atmospheric pressure, will produce cold solution with concentration of approx 73 wt%. The risk of producing dry, low-density detonation prone AN is thus non-existent.

5. ENERGY ECONOMY

The principle of energy conservation in the CARNIT process is to avoid, as much as is economically justified, every unnecessary degradation of available heat of reaction.

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, such as final concentration of the solution and production of clean export steam.

The use of the low pressure vapours at 0.2 and 0.4 bar, for preheating of the reactants, contributes to the overall energy recovery and reduces the amount of heat which must be removed through the cooling condensers.

For nitric acid preheating, where the exhaust vapour from concentrator F2 is used at a pressure of 0.4 bar, the highest metal temperature of the preheating equipment is limited to 75°C. The risk of corrosion in preheating and downstream equipment is thus minimized, without need for recourse to special metallurgy.

With the CARNIT process scheme the energy economy effect increases as the acid concentration decreases. The production of 97.5 wt% solution thus remains possible without external heat supply, even with dilute nitric acid of 55 wt% concentration.

6. EFFLUENT CONTROL

There are no gaseous process effluents, with the exception of the continuous purge of the very small amount of non-condensibles in the feed reactants, and of the occasional small air leaks into the reduced pressure zones. All output streams, i.e. concentrated AN solution and process condensates are in liquid form.

Process vapour is produced either in falling film evaporators, where entrainment of liquid in the vapour phase is minimal, or by flashing upon pressure reduction. The liquid droplet content of the flashed vapour is drastically reduced by high-efficiency scrubbing.

At every stage of the CARNIT process where vapour is reused as heating medium, the controlling temperature for ammonium nitrate vapour contamination is the temperature of the scrubber solution. All these temperatures are below 100°C so that the ammonium nitrate content of the condensed process vapours remains very low.

The total nitrogen content of the process condensate output of the Tertre CARNIT unit does not exceed 14 ppm wt. Control of the condensate pH is achieved by adjusting the operating conditions of the high-efficiency scrubbers.

7. PROCESS ECONOMICS

For a process where the yield of the reactants is close to 100%, the overall process economy results from a combination of different factors, such as consumption of energy and utilities, maintenance and investment costs, and effluent management.

There are various options to adapt the CARNIT unit to specific conditions of the plant. By considering these possibilities at an early design stage, substantial savings on total investment are possible.

The energy efficiency of the process can be optimised in two different ways:

- It may be chosen to use standard acid concentration, in the range of 60 to 63 wt%, in order to produce a maximum amount of 6 bar export steam. This alternative may be called H-E CARNIT because of its high-efficiency.

- Alternatively, if no additional 6 bar steam is required on the site, the energy efficiency of the CARNIT may be put to use by selecting a low investment flowsheet without steam production.

When investing simultaneously in a nitric acid and an ammonium nitrate solution production units, a careful look should be given to the overall balance of steam and condensate at the site. Nitric acid units are usually net exporters of L.P. steam. In addition there is the possibility to recycle part of the AN process condensate to the nitric acid absorption column.

These possibilities are taken into account in the low investment CARNIT flowsheet. In this L-I CARNIT flowsheet the energy recovery has been adapted so that there is no steam production. In addition, part of the process condensate is recycled to the nitric acid unit. The scrubbing system is thus simplified, as only the net export of condensate is to be of high purity quality.

The steam raising section (K) and the high-efficiency primary scrubber (S1) are no longer required.

The energy recovery in the primary concentration step, and the heat input into the loop are adjusted in order to achieve the adequate thermal balance of the loop.

This results in an overall reduction of investment cost of at least 20%.

Typical material balance and utilities consumption data for production of a 97.5 wt% solution with 60 wt% nitric acid feed are shown in Table 3.

Table 3: Material balance and utilities, production of 97.5 wt% solution

Base AN 100%	Units	H-E CARNIT	L-I CARNIT
Process		Input	
HNO$_3$ 60 wt%	kg/t	1 312.57	1 313.57
NH$_3$ 100 wt%	kg/t	212.51	212.51
		Output	
AN solution 97.5 wt%	kg/t	1 025.6	1 025.6
Process condensate	kg/t	500	300
AN loss in condensate	kg/t	0.025	0.015
Utilities		Input	
BFW	kg/t	133	
Electric power	kWh/t	1.85	1.85
Cooling water (= 10°C)	m^3/t	11	11
		Output	
Steam production 6 bar	kg/t	128	

The overall nitrogen recovery balance is improved, as the nitrogen of the condensate which is recycled to the nitric acid absorber is in fact not discarded, as it returns to the CARNIT unit with the feed acid.

The recycle of condensate achieves a saving of approx 200 kg/t of demineralized water supply to the nitric acid absorption column as well as a reduction of the overall nitrogen loss of the AN unit.

A condensate balance is shown in Table 4.

The high purity of the CARNIT condensates makes it advantageous to use them for production of demineralized water at a very low operating cost.

For units where solution concentrations in excess of 97.5 wt% are required, the final concentrator becomes the first exchanger in the loop after exit of the reactor.solution.

Table 4: Condensate Material balance production of 97.5 wt% solution

Base AN 100%	Units	H-E CARNIT	L-I CARNIT
AN solution 97.5 wt%	kg/t	1 025.6	1 025.6
Condensate output	kg/t	500	300
AN loss in condensate	kg/t	0.025	0.015
Condensate recycle	kg/t		200
AN in recycle			0.05

With a recycle solution temperature of approx 185°C at the hot end of the final concentrator, the temperature conditions which are required for production of solution concentrations of 99.+ wt% are available.

8. OPERATING EXPERIENCE

Since initial start-up of the Tertre (Belgium) 2 100 t/d unit in December 1990, production of 97.5 wt% solution has been maintained with a 98.7% on stream time efficiency until the first planned maintenance shutdown in July 1992.

Notwhitstanding the high number of possible trip actions, the unit was stopped only 5 times in 18 months of operations. The main cause of these trips has been a mistaken operation on the unit, such as closing a wrong valve.

Hot restart is an easy operation, which allows to reach full capacity in approximately 10 minutes. Start-up from cold takes approximately 6 hours to reach capacity.

During the first maintenance shutdown, which lasted 5 days, inspection showed that the unit was essentially corrosion-free. In the CARNIT process the risk of corrosion is greatly reduced in the reaction loop which is kept ammoniacal, and by the use of low pressure vapours for preheating nitric acid. This results in a low maintenance cost.

The Tertre CARNIT plant receives nitric acid from different nitric acid units, with acid concentrations which vary between 57 and 61 wt%. Due to layering in the main acid storage tank, fairly rapid changes of feed acid concentration are a frequent occurrence.

At initial start-up, it has been chosen to maintain a constant circulation flow, which means that the temperature range between inlet and outlet of reactor varies when the acid concentration changes. It was found that loop operation was quite steady under these conditions, and this operating procedure has been maintained.

The concentration of the final 97.5 wt% AN solution remains steady within a range of +/-0.15 wt%.

The quality of the process condensates remains quite steady. The current control parameters are the conductivity and pH of the condensates. Average nitrogen contents are 6 ppm wt ammoniacal and 7 ppm nitric. Upon neutralisation to pH 7, the average equivalent AN content remains below 50 ppm. Depending on the further use of the condensates, it can be chosen to operate the unit so as to produce slightly alkaline or slightly acidic condensates. The Tertre CARNIT condensates are used as feed to the water demineralization unit, and are therefore currently produced with a slight acidity.

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