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Krupp Uhde Nitric Acid Technology

Enhanced Plant Design
for the Production of Azeotropic Nitric Acid

by

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Enhanced Plant Design

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1.   Abstract

Azeotropic acid of about 68 % by weight can replace concentrated nitric acid in some applications like nitrations. Due to the increasing market demand, Krupp Uhde has designed an enhanced process design for the reliable production of azeotropic acid.

Important process features for the production of azeotropic acid are presented. Besides supplying a sufficient absorption pressure, the overall water balance for an azeotropic acid plant is of major importance. Based on the water balance, a theoretical limit curve is derived showing if any external cooling for the intake air is required. By these measurements Krupp Uhde can predict the limits, for example, the intake air humidity and the required NO_x partial pressure at absorption inlet, within which the specified azeotropic acid quality can be achieved. Technical solutions including a tailor-made secondary air drier configuration are introduced.

Except normal operation, also other plant conditions like partial load operation are highlighted. The effect of a change of key parameters like absorption pressure or cooling water temperature on the absorption performance is visualised by simulation plots.
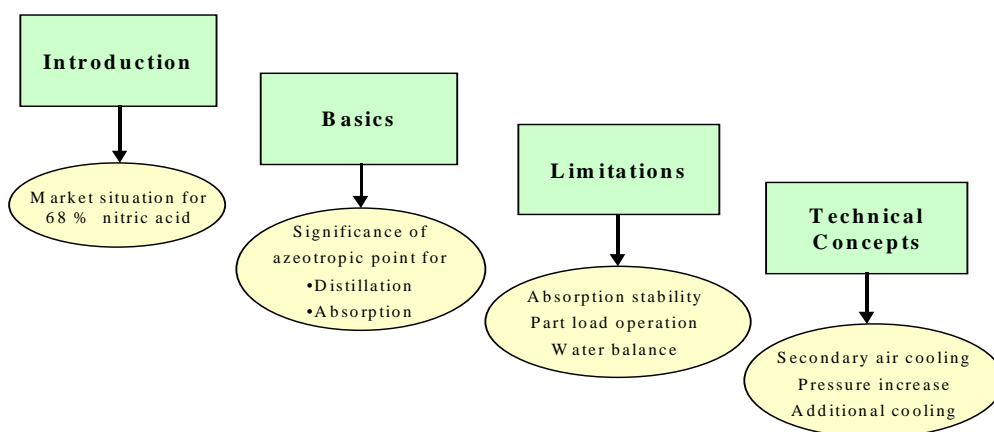
Fig. 1: Azeotropic Acid Plant Features

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2. Market Situation for Azeotropic Acid

As shown in Fig. 2, about 80 % of the nitric acid production is used for fertilisers. The main product is ammonium nitrate (AN) and its various derivatives as calcium nitrate (CN), calcium ammonium nitrate (CAN), ammonium sulphate nitrate (ASN) and liquid N fertilisers (UAN). The other main branch is nitrophosphate (NP) compounds.

Non-fertilisers are dominated by explosive grade ammonium nitrate (LAN). Nitric acid is also required for chemicals, represented in this graph by caprolactam, adipic acid as an intermediate product for nylon and toluene diisocyanate as an intermediate product for polyurethane.

In the recent past, the world market has exhibited noticeable demand for so-called azeotropic acid with an elevated concentration of about 68 % by weight. Obviously some nitrations which only took place in the presence of high concentrated nitric acid in the past can be performed under less severe conditions nowadays. That means concentrated nitric acid can be partly or completely replaced by azeotropic acid.

Consequently, Krupp Uhde has developed an enhanced process design for the reliable production of azeotropic acid.
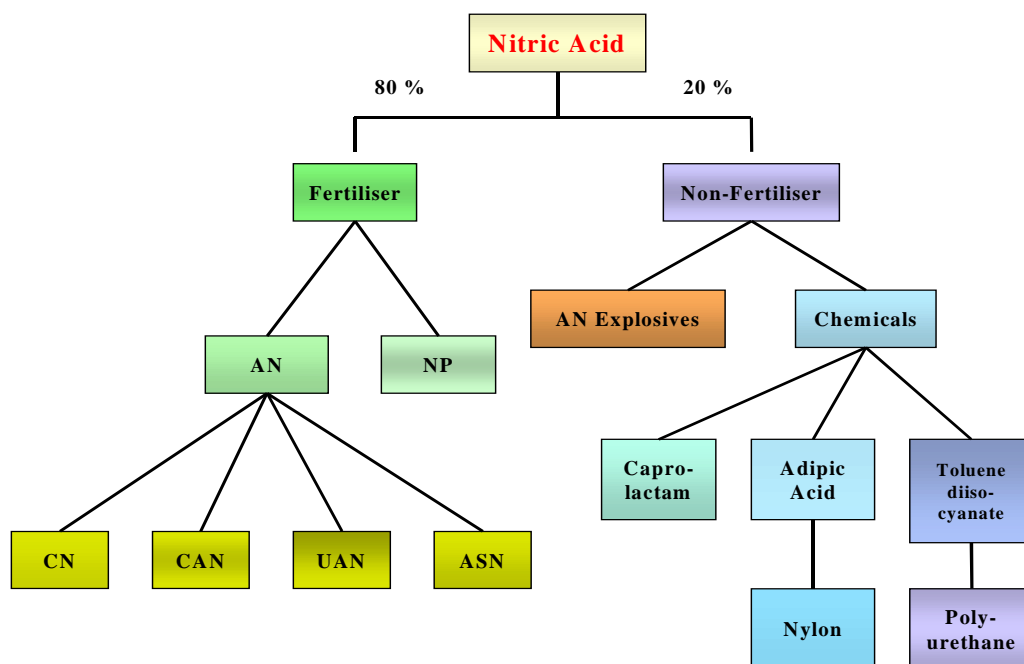
Fig. 2: Nitric acid Applications

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3. Production of Azeotropic Nitric Acid

3.1 Basics

3.1.1 Significance of the Azeotropic Point for Distillation

Fig. 3 depicts the vapour-liquid equilibrium for the nitric acid / water system. For atmospheric pressure the well known azeotropic point occurs at a liquid concentration of 68.4 %. That means by distillation the separation of vapour (y) and liquid with different concentration (x) can only be performed below this azeotropic point, since the vapour concentration y is equal to the liquid concentration x. The azeotropic point is thus a natural barrier for distillation.

The azeotropic point can be shifted slightly by a pressure change. For lower total pressure it is shifted to a lower liquid concentration.
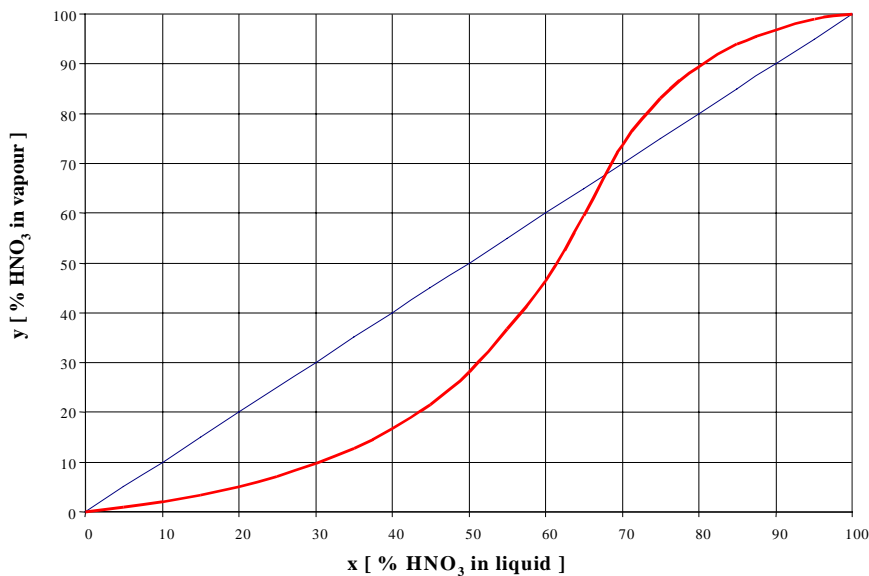

Fig. 3: Vapour Liquid Equilibrium Nitric Acid-Water

Another possibility to shift the azeotropic point is the basis for concentrating diluted nitric acid. Fig. 4 shows the effect of addition of sulphuric acid to a nitric acid / water solution.

By increasing the H_2SO_4 concentration stepwise from 0 % via 20 % and 40 %, the azeotropic point is shifted to lower liquid concentrations, and finally at a concentration of 67 % H_2SO_4 the azeotropic point has vanished.

Then it is possible to distillate concentrated nitric acid. The nitric acid is the lighter phase and extracted as vapour, while the sulphuric acid will be further diluted in the liquid phase.
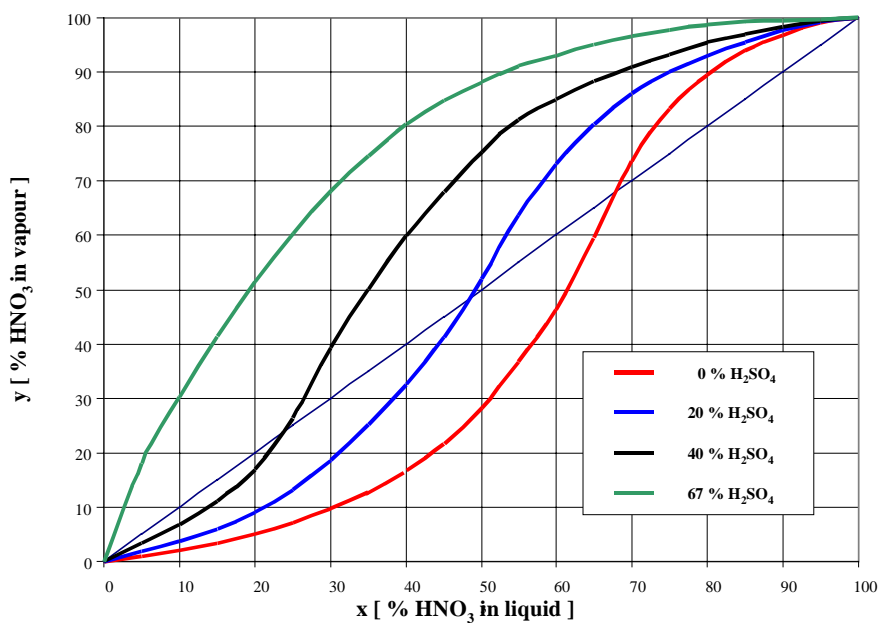

Fig. 4: Vapour Liquid Equilibrium Nitric Acid-Water (Parameter: H_2SO_4-Content)

3.1.2 Absorption Reaction Model

Is the azeotropic point also a limitation for absorption?

A simplified model for the complex reactions based on the film theory is shown in Fig. 5. NO_2 is in equilibrium with N_2O_4 in the gas bulk as well as in the gas film. Only N_2O_4 is transported through the gas film to the gas-liquid boundary and is hydrolysed, while NO_2 - hydrolysis can be neglected.

The HNO_2 formed intermediately is decomposed to nitric acid, water and nitrogen monoxide. The NO gas formed in the liquid phase limits the absorption because it has to be transported back to the gas phase. There it is oxidised to NO_2 which is in equilibrium with N_2O_4 to close the circuit. The overall reaction in the liquid phase can be summed up as follows:

$3 NO_2 + H_2O = 2 HNO_3 + NO$

$$2 NO + O_2 \longrightarrow 2 NO_2$$

Gas phase $2 NO_2 \rightleftharpoons N_2O_4$

Gas film $2 NO_2 \rightleftharpoons N_2O_4$

Liquid film $N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$

Liquid phase

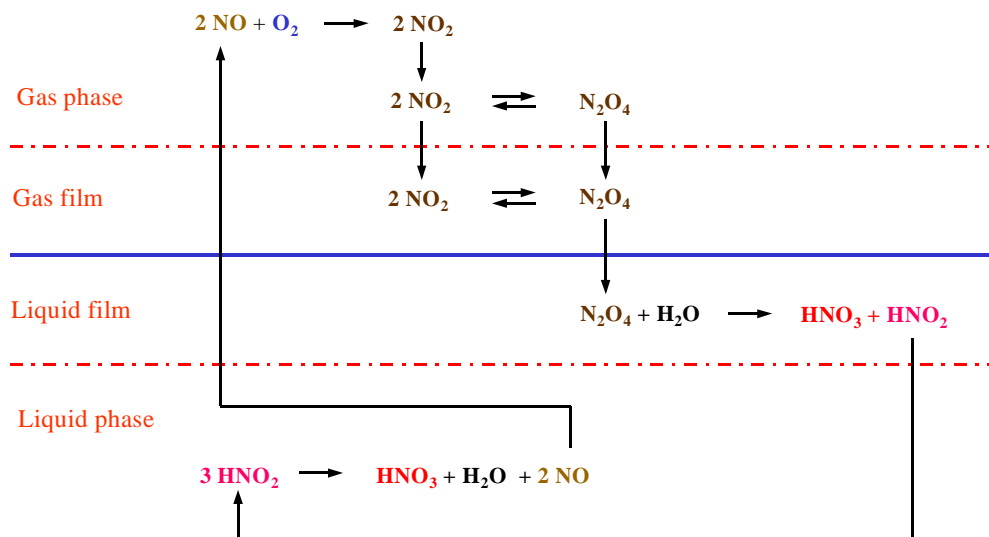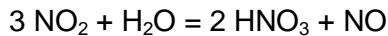$3 HNO_2 \longrightarrow HNO_3 + H_2O + 2 NO$

Fig. 5:   Simplified Absorption Reaction Model

It can be concluded that the physical laws ruling the absorption are completely different from the distillation as discussed before. Therefore the 'classic' significance of the azeotropic point to limit the nitric acid strength is only valid for distillation.

For absorption the partial pressure of NO and NO_2 at the absorption tower inlet is crucial. According Krupp Uhde's experience a certain total NO_x partial pressure in the range of 1 bar is required to produce an azeotropic acid in an absorption tower.

The technical concepts as well as physical limitations for azeotropic acid production are discussed later.

3.2 Limitations

3.2.1 Special Absorption Profile Measured During Commissioning

The concentration profile shown in Fig. 6 was measured during the start-up of a mono high-pressure nitric acid plant. Plant design is 300 MTPD with acid strength of 65 % by weight and the absorption pressure was 9.4 bar abs.

During start-up by mistake only about 50 % of the design process water flow was supplied to the top of the absorption tower. As a result, nitric acid of much higher strength was formed at the bottom of the tower.
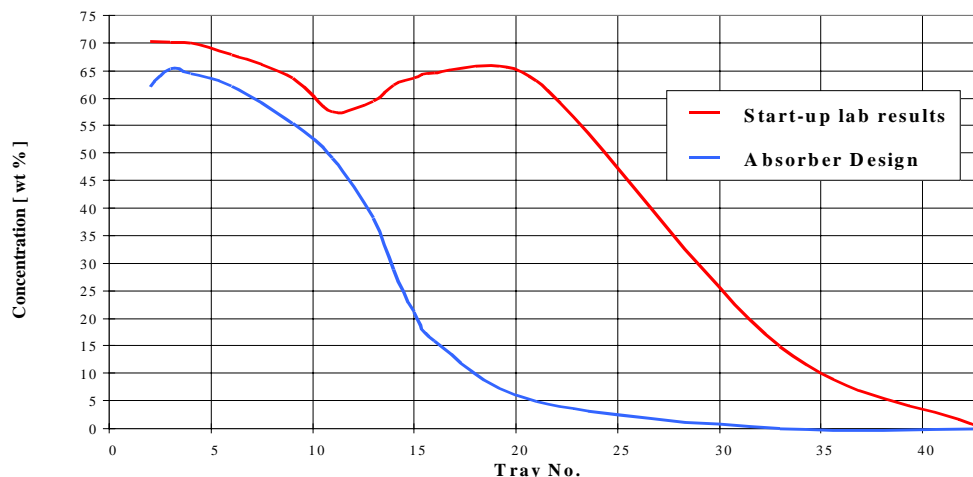

Fig. 6: Measured Absorption Profile

The higher concentrations result in a notch in the concentration profile at tray 12, which is the entry point of the crude condensate delivered by the cooler condenser.

This notch occurs because the concentrations on the previous sieve trays were raised considerably. Consequently, the crude condensate concentration at tray 12 is far too low and disturbs the profile. Therefore the acid concentration at the subsequent absorption trays 12 to 17 rise again, or in other words these trays show desorption. After passing a maximum at tray 17 with a concentration of approx. 66 %, the column had stabilised and absorption took place again. Overall, the entire acid profile was shifted to the right. The absorption tower profile was maintained for some hours, so a quasi stationary state was reached.

On the first trays, the laboratory even determined concentrations above 70 %. Even though taking into account an inaccuracy of the density measurement of about 0.5 to 1 %, the corrected concentration calculates to approximately 69.5 %. So during start-up of this plant a superazeotropic nitric acid was produced in a production absorption tower, but on the other side also the NO_x-value in the tailgas measured to 370 ppm was increased above the permissible limit.

3.2.2   Simulated Acid Profile for a Dual Pressure Plant

At Krupp Uhde a sophisticated computer program is used for the reliable design of the absorption tower. Furthermore, this program is capable to predict the limits within which the absorption will work.

Fig. 7 visualises a simulation for the absorption behaviour of a column in a dual pressure plant, where nitric acid of two concentrations is produced. The major part of 60 % is taken from the absorber as 68 % nitric acid, the remaining side stream as 60 % nitric acid.
Now the acid strength is shifted up to 70 % in steps of 0.5 % by simulation. The higher the concentration, the worse the absorption tower works, resulting in a less steep concentration profile. This effect is increased after the crude condensate has been added, since its concentration no longer matches that of the tray acid. As a result the whole concentration profile is shifted to the right.

Fig. 8 is a detail of the previous one, focussing on the first absorption trays Nos. 3 to 7. As mentioned in connection with the measured profile presented earlier, another criterion of stability is if the respective tray absorbs or desorbs. Here the trays No. 1 and 2 are so called oxidation trays, which will only increase the NO_2 content of the incoming NO gas. The raw acid is extracted from tray 3 with the higher concentration, while the 60 % acid is taken from a tray with similar concentration.
Regarding the slope between tray 3 and 4, below 69 % the negative slope refers to absorption, while above 69 % the tray desorbs, characterised by a positive slope. The nearly horizontal slope at 69 % represents the limit of stable absorption, i. e. at the particular tray number no additional acid formation takes place nor acid decomposition.

Summing up these simulation results, this absorption tower works stably until a concentration of 69 % by weight. This result is in accordance with measurements taken during practical operation of this plant.

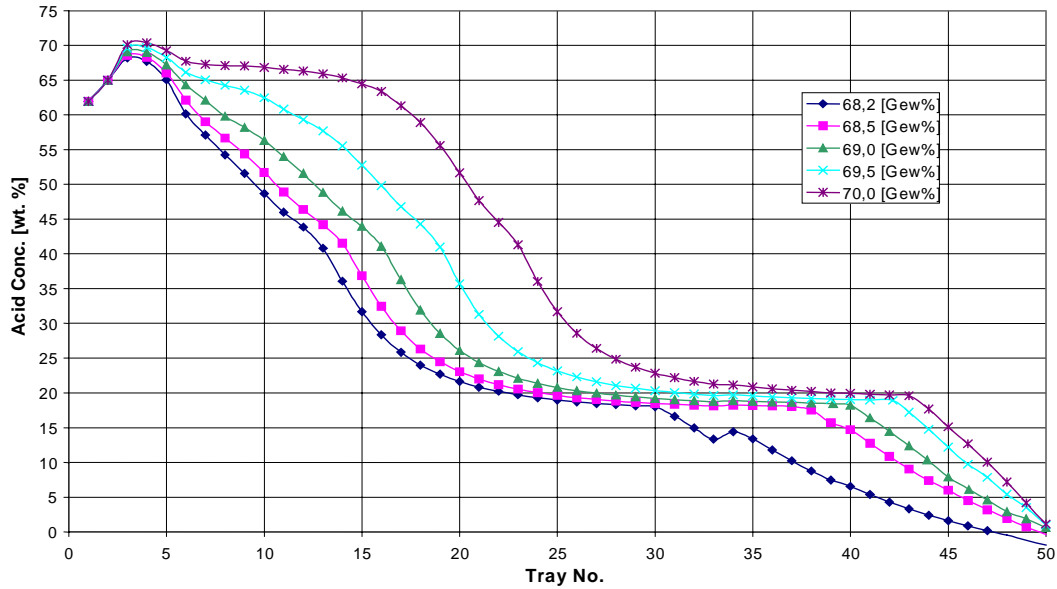The absorption stability also depends on the pressure and cooling water temperature as discussed later.
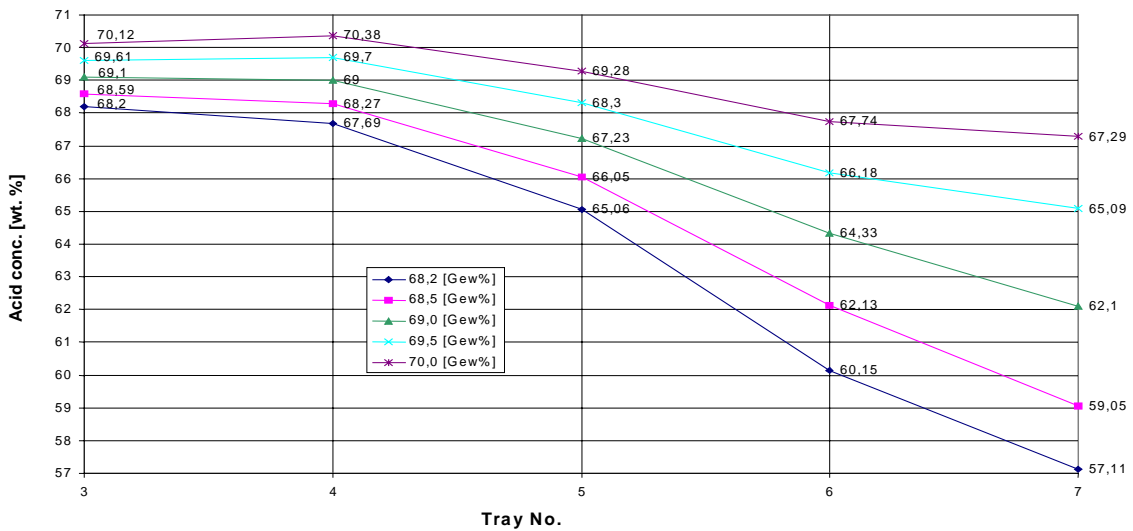
Fig. 7: Simulated Acid Profiles for Dual Pressure Plant

Fig. 8: Detail Simulated Acid Profiles for Dual Pressure Plant

3.2.3 Partial Load Operation

Depending on the client's production requirements, some nitric acid plants are operated for a longer time at partial plant load. Then the available absorption pressure is naturally lower, depending on the characteristic machine performance curve. Therefore especially if the production of a 68 % azeotropic acid has to be maintained, partial load operation is an additional critical absorption tower design case.

Fig. 9 shows the acid profile of an absorption tower as derived by simulation. Due to the decreased absorption pressure of about 9 bar abs. at partial load, compared to about 12 bar abs. at full load, the concentration on any given tray is increased with respect to the full load case.

The NO_x-content in the tailgas also increases with respect to the deteriorated absorption performance, in this case from 190 to 310 ppm by volume (Fig. 10).

Nowadays, most of the new nitric acid plants are equipped with a selective catalytic tailgas treatment unit (SCR) to meet environmental standards. So the NO_x-content at absorber outlet, the so called NO_x-cut, is evaluated under economical aspects. The investment costs for the absorption tower must be compared to the costs of the SCR unit, consisting of required catalyst volume and additional NH_3-consumption and pressure drop.

For this plant the NO_x-cut after the absorption was chosen to be 300 ppm by volume. The number of sieve trays was adjusted accordingly to ensure the production of 68 % azeotropic acid at partial load operation.
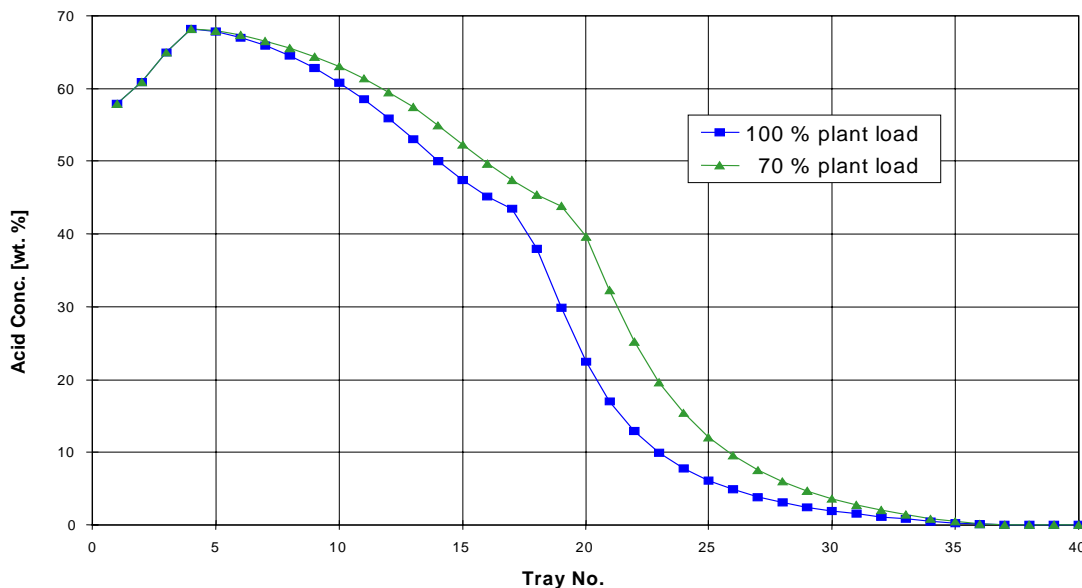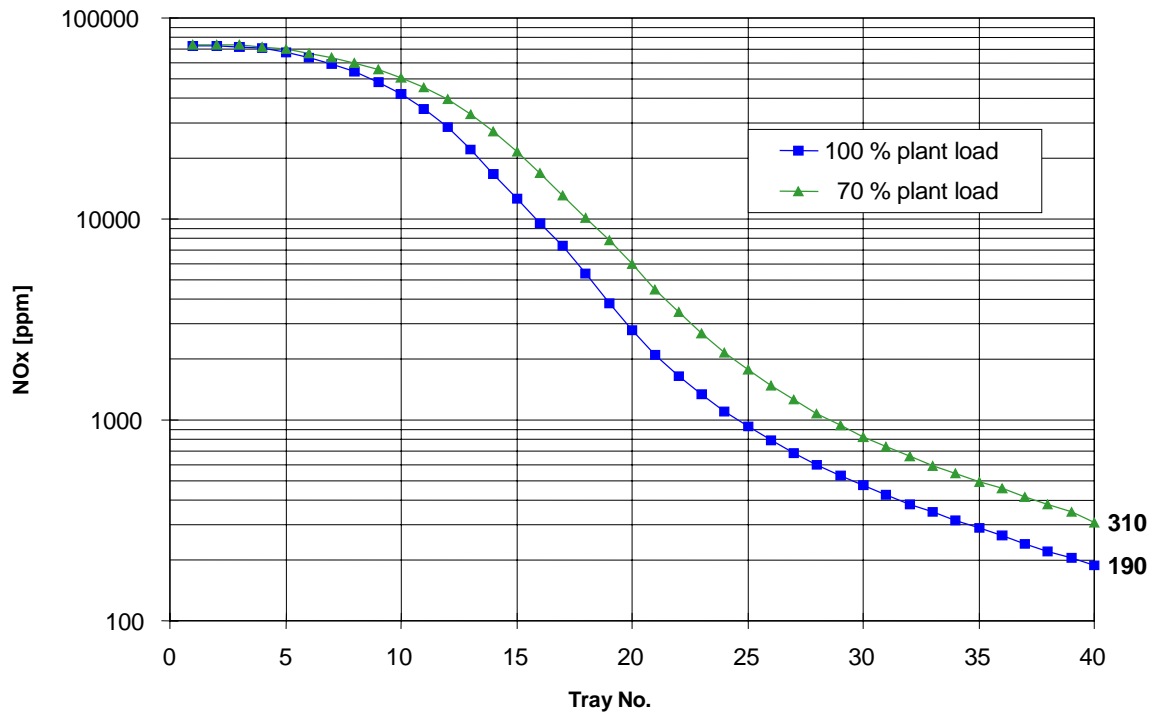

Fig. 9: Concentration Profiles

Fig. 10: NO$_x$-Content in Tailgas

3.3 Technical Concepts

3.3.1 Krupp Uhde's Dual Pressure Azeotropic Plant

Fig. 11 highlights the specific features of a dual pressure azeotropic acid plant.

To satisfy the overall water balance, it is mandatory to get rid of the water carried with the incoming air. The measures depend on the air humidity and temperature and therefore on the plant location / climatic conditions. Krupp Uhde is prepared to offer tailor-made solutions.

In case of a high ambient air temperature and humidity the installation of an additional air condenser is to be recommended. In order to reduce the water partial pressure as far as possible, this apparatus would be cooled with chilled water. As usual in Krupp Uhde dual pressure plants, there is an extra chilled water circuit linked to the ammonia evaporation.

The machinery shown as an example is completely integrated in Krupp Uhde's compact bull gear concept. The first pressure level delivered by the air compressor is advantageous for the burner, while the final pressure delivered by the NO_x-compressor promotes the absorption so that azeotropic acid can be formed..
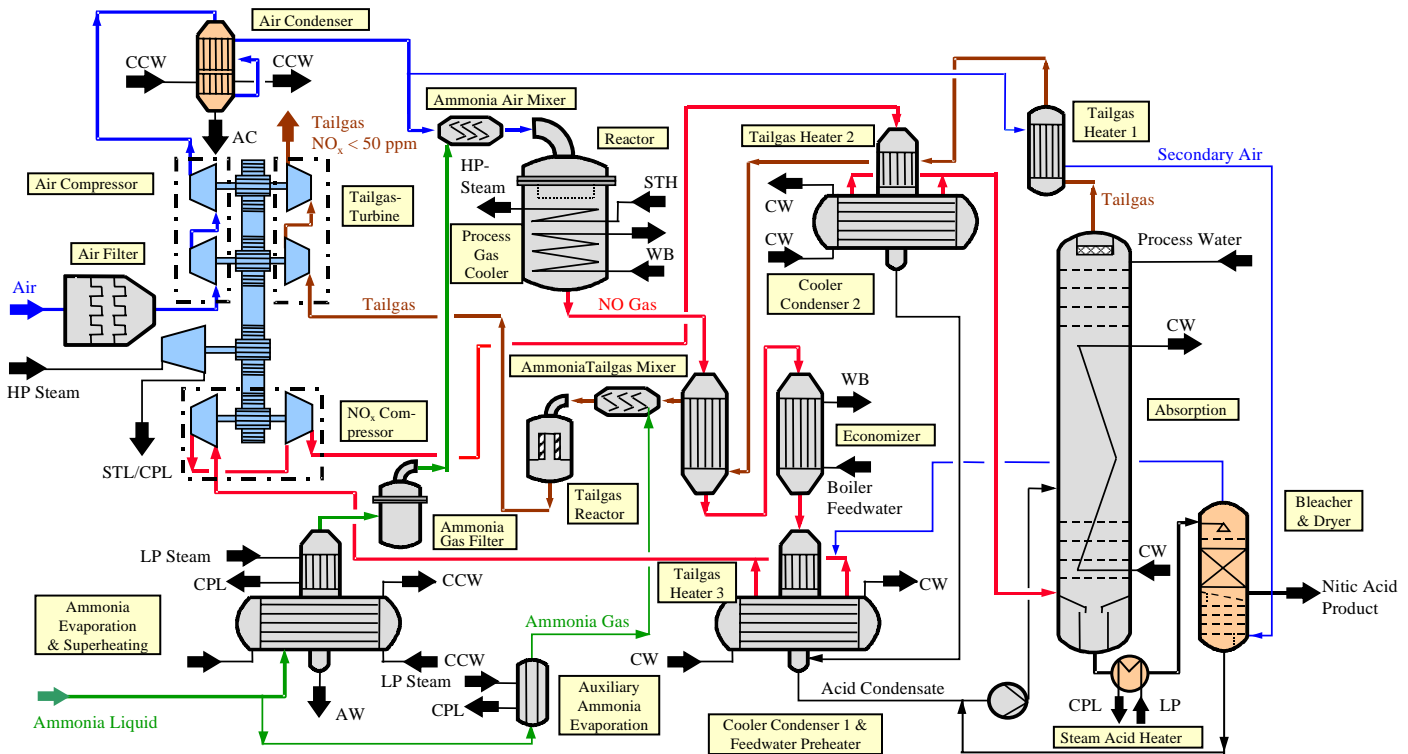

Fig. 11: Krupp Uhde Dual Pressure Plant Azeotropic Acid Product

3.3.2   Limitation of Acid Concentration

- **Outline of the Water Balance**

The water balance of the nitric acid process consists of reaction water, dilution water and water carried with the process streams (Fig. 12).

In the burner section water is formed by the main reaction to NO (1) and the undesired side reactions to N_2 (2) and N_2O (3). In the absorber section water is consumed according to the overall reaction (4) and for dilution to the azeotropic concentration of about 68 % by weight.

Also a major part of the water may be sucked in with the process air. The air humidity depends on the location of the plant as well as season and time of day. The remaining part of the water balance is satisfied by process water supplied to the top of the absorption tower.

- **Derivation of the Theoretical Limit Concentration**

Figure 12 highlights the specific reactions which take place in the ammonia burner section and the absorption. Considering the desired reaction (1), 1.5 moles of water are formed per mole of ammonia. For each mole of formed NO 0.5 moles of water are consumed in the absorption section. Overall there is a surplus of 1 mole of H_2O per 1 mole of ammonia fed to the plant, for a 100 % burner efficiency.

Taking into account a more realistic burner efficiency of 95 %, that means 5 % of the ammonia are converted to N_2 or N_2O according reaction (2) and (3) with no extra water, a maximum HNO_3-concentration of 76.6 % can be produced.
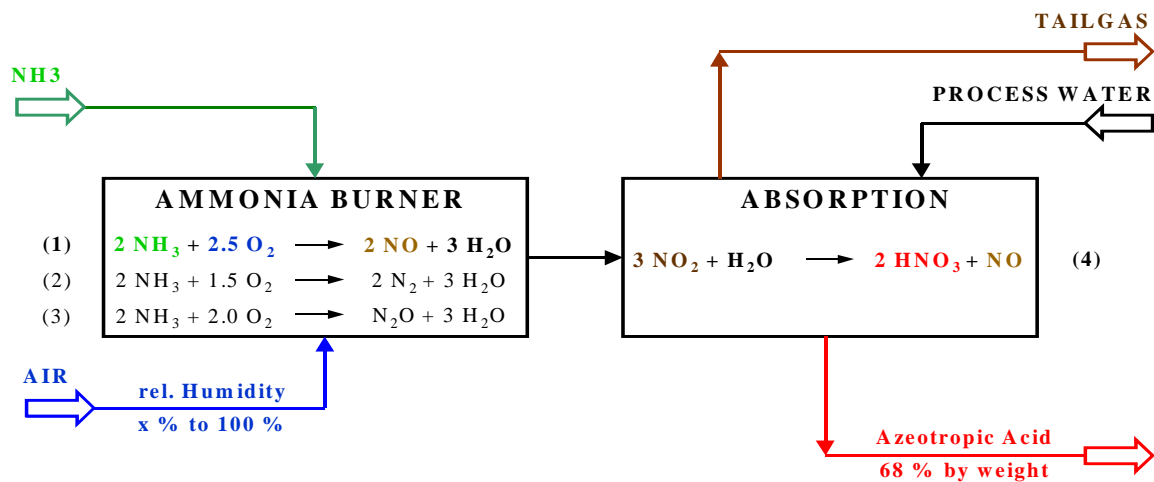
TAILGAS

NH3   PROCESS WATER

	AMMONIA BURNER		ABSORPTION	
(1)	$2\,NH_3 + 2.5\,O_2 \longrightarrow 2\,NO + 3\,H_2O$		$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$	(4)
(2)	$2\,NH_3 + 1.5\,O_2 \longrightarrow 2\,N_2 + 3\,H_2O$			
(3)	$2\,NH_3 + 2.0\,O_2 \longrightarrow N_2O + 3\,H_2O$			

AIR   rel. Humidity
x % to 100 %

Azeotropic Acid
68 % by weight

Fig. 12: Water balance for an Azeotropic acid plant

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- **Calculation of the Limit Water Load in Intake Air**

The absorption tower requires a minimum process water feed to ensure safe and stable operation of the plant. In practical operation it is mandatory to keep the NO_x content in the tailgas within the allowed limits. The minimum required process water fed to the top of the absorption tower can be assumed to approx. 30 kg per ton of 100 % HNO_3. Considering this value in connection with the limit concentration of 76.6 %, the final possible concentration comes out to be 74.9 %.
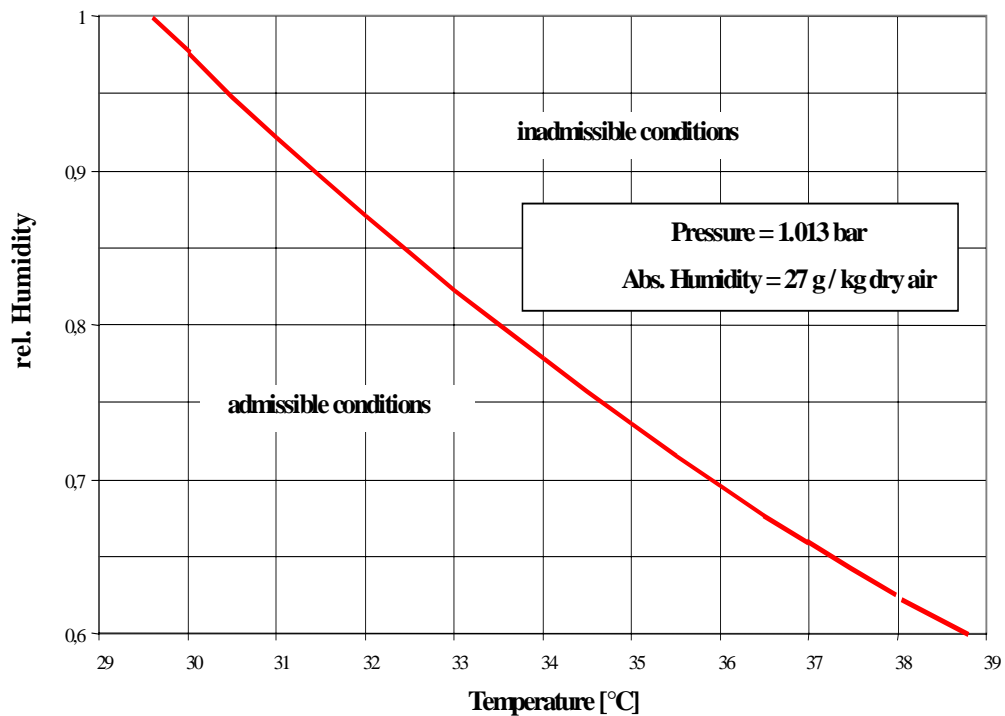

Fig. 13: Theoretical Limit Curve for intake Air Humidity

Related to the desired azeotropic acid concentration of 68 %, the remaining difference in the water balance amounts to 135 kg per ton of acid. This water is the maximum water content allowed to be carried with the intake air.

Taking into account an oxygen content in the tailgas of 2.5 % by volume, the intake air amounts to 4950 kg per ton of acid. Thus an overall absolute water content of about 27 g per kg dry air can be expected. Based on this figure and an ambient pressure of 1.013 bar, Fig. 13 shows the relation between relative air humidity and temperature.

Admissible combinations of ambient air temperature and humidity for the production of azeotropic acid lie below the limit curve.

Should the air condition lie outside the admissible area, the installation of an additional cooling facility is required.

An example of an extra chilled water cooler was given in Fig. 11.

3.3.3   Secondary Air Drying

Secondary air, which is about 20 % of the total air flow, is used for stripping of NO_x gases dissolved in the raw acid leaving the absorber. The secondary air carries the quantity of water corresponding to the climatic conditions or the conditions in the air condenser if installed. This water content would dilute the product acid leaving the sump of the bleaching tower. In order to maintain the specified acid strength, a secondary air dryer integrated in the sump of the bleaching column is installed.

The principle is to dry the incoming secondary air by means of the product acid, which is fed to the top of the bleaching column (Fig. 14). In contrast to the usual configuration there is a special drying section at the bottom where the secondary air comes in. The already bleached total product acid flow leaves the sump of the upper part. A small amount of the total product acid feeds the drying section below. The incoming secondary air is dried in counter-current flow to this acid. The drying effect is physically based on the fact that the partial pressure of water over the acid in the drying section is considerably smaller than in the compressed secondary air.

The acid leaving the bleacher is diluted by the water contained in the secondary air. Therefore this acid is added to the crude condensate and delivered to the appropriate absorber tray. In this way the circuit of this extra condensate stream is closed.
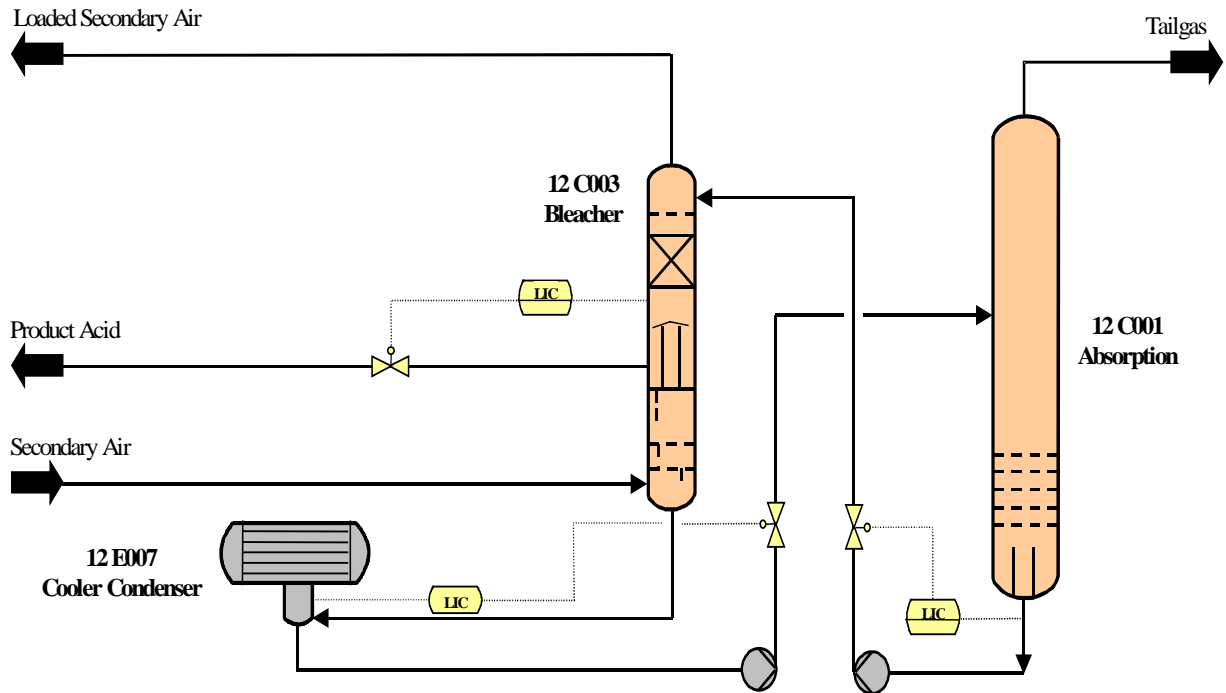
Fig. 14: Secondary Air Drying Configuration

3.3.4   Effect of Pressure Increase on Acid Concentration

An enhancement of the process pressure before absorption has two benefits. On the one hand, the absorption is promoted by the total pressure approximately by the power of 2.2. On the other hand, the partial pressure of the NO_x gas is increased, which is necessary to produce the desired acid strength.

Fig. 15 depicts the effect of a pressure increase. Starting point is the desired acid strength chosen to 67.5 %, corresponding to the medium curve. The acid concentration is lower on tray 4 than on tray 5, indicating desorption instead of absorption.

The bottom curve is derived by a pressure increase of 0.4 bar. The negative gradient indicates absorption, meaning the desired acid strength of 67.5 % can be produced by means of this pressure increase.

What maximum acid strength can be produced at this increased pressure? By simulation the acid concentration has been raised until the slope is horizontal, referring to the uppermost curve. At this concentration of 67.7 % the horizontal slope indicates the limiting value since neither absorption nor desorption occurs.
Summing up, in this example a pressure of 0.4 bar increases the acid concentration by 0.2 %.
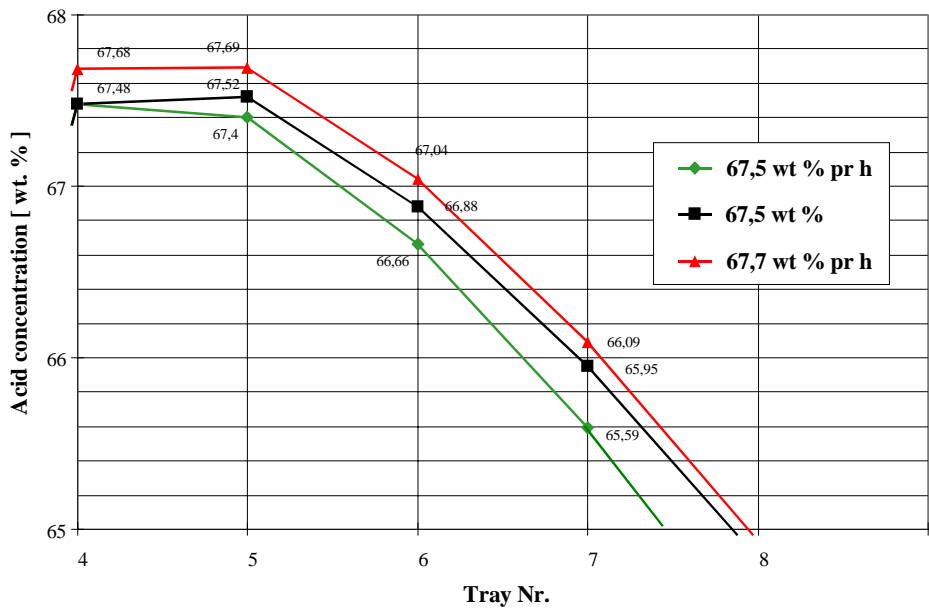
Fig. 15: Effect of Pressure Increase on Limit Acid Concentration

Of course the plant, especially the machine set, must be capable of providing an additional pressure if required. The design pressures of the relevant equipment have to be raised accordingly.

3.3.5 Cooling and chilled water supply

Due to the fact that the reactions governing the absorption are highly exothermic, the appropriate cooling of the absorption tower is important. With the aid of Krupp Uhde' s sophisticated computer program and experience, the number and distribution of the cooling layers are determined exactly in accordance with the heat loads on every sieve tray.

The cooling water temperature available on site is fixed for a given plant and depends only on the season.

Therefore if the desired acid strength with regard to the NO_x-limitation in the tailgas cannot be achieved by cooling water only, chilled water can be used to feed the cooling coils especially in the lower section of the absorption tower in order to increase oxidation and acid formation. A proven solution in Krupp Uhde plants is to use the ammonia evaporation heat to produce chilled water in an extra circuit. In order to avoid overloading of the ammonia evaporator, this measure is limited to maximum of approx. 80 % of the total evaporation heat.

Theoretically it is also possible to provide an external chilled water circuit if necessary. However, this solution is expensive and therefore should only be considered if all other measures discussed before are not sufficient.

4. Summary

Unlike for distillation, the azeotropic point itself has no significance for the production of azeotropic acid. However, the elevated concentration of 68 % by weight implies process constraints which have to be considered especially for the absorption section. Obviously the NO_x content in the tailgas has to be limited due to environmental requirements, especially during partial load at decreased pressure.

The simulation runs performed were based on measured data if available. By means of a sophisticated computer program the absorption was brought to the limit, under variation of the respective process parameters like absorption pressure or cooling water temperature. Thereby operation limits could be predicted reliably, at the elevated concentration and pressure ranges which characterise an azeotropic acid plant.

For the entire azeotropic acid plant, a detailed consideration of the water balance is mandatory. As a result, an explicit figure for the absolute humidity of the intake air was derived. Consequently, a limit curve for the relation between relative air humidity and temperature could be established. With the help of this tool a quick check can be made as to whether external cooling is required. If so, Krupp Uhde is prepared to offer tailor-made solutions. As an example, a secondary air drying configuration was discussed in more detail.