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nitric acid production - improvements by revamping

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INTRODUCTION

Due to the deteriorating profits in the fertilizer sector world-wide, producers have for some years been reluctant to invest in new plants.

On the other hand, there has been growing interest to investigate possible modifications of existing plants with a view to improving the energy balance, increasing the capacity within economically reasonable limits and meeting the ever more stringent environmental pollution control requirements.

Revamps have been performed for various types of fertilizer plant including the associated acid production facilities.

This paper illustrates the different revamping options for nitric acid plants using both Uhde and other proprietary processes.

PLANT CAPACITY INCREASE AND THE RESULTING BOTTLENECKS

A production plant cannot be and should not be designed exactly for the specified capacity. It is also good engineering practice to provide a certain design in order to maintain flexibility of plant operation if any design parameters should change. How much over-capacity is provided depends directly on the commercial terms and conditions and the type of plant. Nitric acid plants are usually over-rated by 3 to 5%. Engineering experience has shown that a so-called design generosity in respect of an intended capacity increase is a highly effective option. For better understanding, the relations are presented in

diagram 01 : investment cost versus plant capacity

The diagram is divided into two sections:

> normal design capacity (built-in)
>
> max. capacity subject to a revamp

In the design curve, plotted in blue, the part between P0 and P1 represents the over-capacity margin which can be regarded as built in. If capital-cost estimates are performed by the exponential method using plant capacity-ratio exponents based on existing cost factors for 100% capacity, the plot can be extended, for instance, to P2 corresponding to a capacity of 130%.

If a revamp is intended to increase the capacity, for instance to 130% of the original design capacity, a similar plant curve can be calculated by the exponential method, however, with different capacity-ratio exponents. Very roughly, the performance reserves for the main plant items can be summarized as follows:

compressor set	-	5 %
absorption	-	10 %
heat exchangers	-	15 %
steam system	-	20 %

diagram 01 : investment cost versus plant capacity
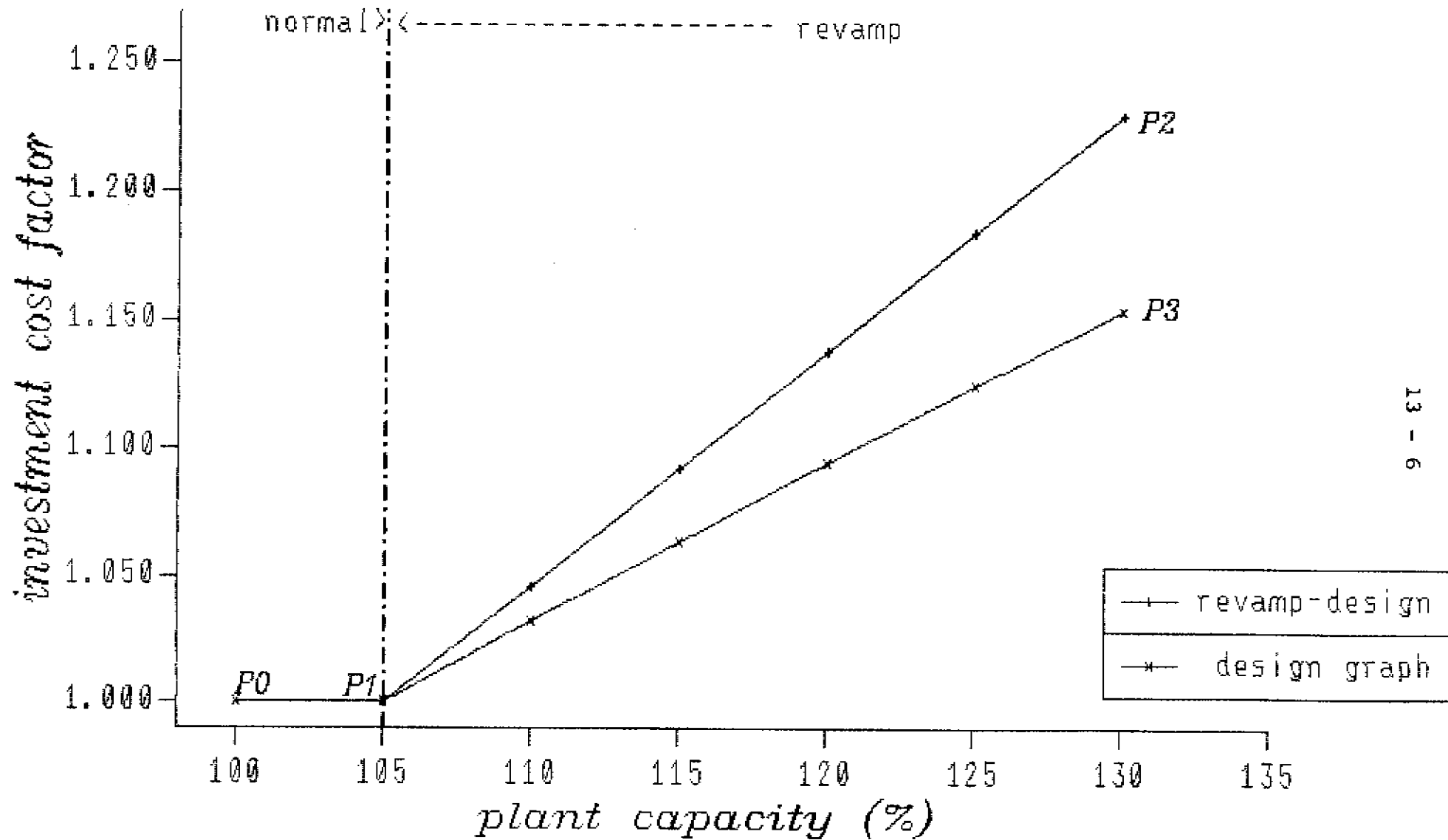
The sequence is also directly proportional to absolute equipment costs and represents the necessary steps for uprating the equipment to the new plant capacity. Modifications of the compressor set cause the highest expense, whereas modifications of the steam system can be achieved at relatively low cost. The given reserve of 20% for the steam system does not mean 20% more in steam production but is related only to the heat flux.

The revamp curve presented in diagram 01, plotted in red, is based on different capacity-ratio exponents, i.e. different from the plant exponent, depending on the equipment part in which it is to be integrated. In the above example, the first 10% increase in capacity is dominated by changes in and around the compressor set. The next 10% are governed by the absorption system and pipework. In many cases, a 20% increase is the limit for justifiable expense. In the given example, a revamp from 105% to 130% could be performed but is generally not guaranteed. From the plots in diagram 01 it can be concluded that the more reserves are provided initially the greater are the expected savings if the plant should be revamped later.

The additional oxygen required for a capacity increase can be made available by modification of the air compressor, installation of a secondary air compressor or by the addition of pure oxygen. The use of pure oxygen is normally very costly and in many cases a capacity increase with more air throughput is preferred. In any case, a higher air stream requires modifications to the tailgas turbine. The question as to which method of additional oxygen feed to the process is the best cannot be answered in general and should be subject to detailed investigations. A result of this short consideration is that the compressor set certainly represents the key to all revamp activities. For a planned future capacity increase, a future-oriented design with sufficient reserve capacity of the compressor set is a good investment in capital.

The overall pressure drop in a nitric acid plant can be calculated on the basis of a system having a number of resistances in series and then the items are summed up for the entire process-relevant parts. The pressure drop represents the key parameter for the internal energy change of the process gas streams and can be calculated according to the following equation:

$$\Delta\ p0\ =\ \Delta\ p1\ +\ \Delta\ p2\ *\ (p\ des/p\ x)\ *\ (Vn\ x/Vn\ des)\ E2$$

|		
Δ p0	=	total plant pressure drop, process
Δ p1	=	absorption pressure drop
Δ p2	=	pressure drop, other equipment
p des	=	design discharge pressure, air compressor
p x	=	discharge pressure, air compressor, new capacity
Vn x	=	air flow, new capacity
Vn des	=	design air flow, air compressor
n	=	cubic metres (at standard temp. and pressure) per hour

The formula is based on two parts; one half, i.e. the quadratic component, is derived from the gas stream velocity, the other half is determined by the factor from the absorption. The break-down of the total plant pressure drop by individual items of equipment at 100% capacity for a medium-pressure plant is the subject of

diagram 02 : main plant equipment and associated pressure drop

More than three quarters of the total losses occur in the absorption section and in the heat exchangers. Unfortunately, there is little chance of effective modification of these items of equipment.

The considerations regarding the pressure drop leads to the first main equipment item which should be discussed as a bottleneck, namely the tailgas turbine. The expander flow through the turbine is not only directly influenced by the pressure drop but also by the increasing process temperatures. These two limiting functions finally determine what capacity increase can be achieved. With reference to the revamp example for a capacity increase of 130%, the effective volume stream through the tailgas turbine is more than 40% greater than the original design and in most cases this means that a new rotor will be required.

diagram 02 : main plant equipment and associated pressure drop

3% waste heat boiler

4% mixer, filter

5% piping

6% control

26% heatexchange
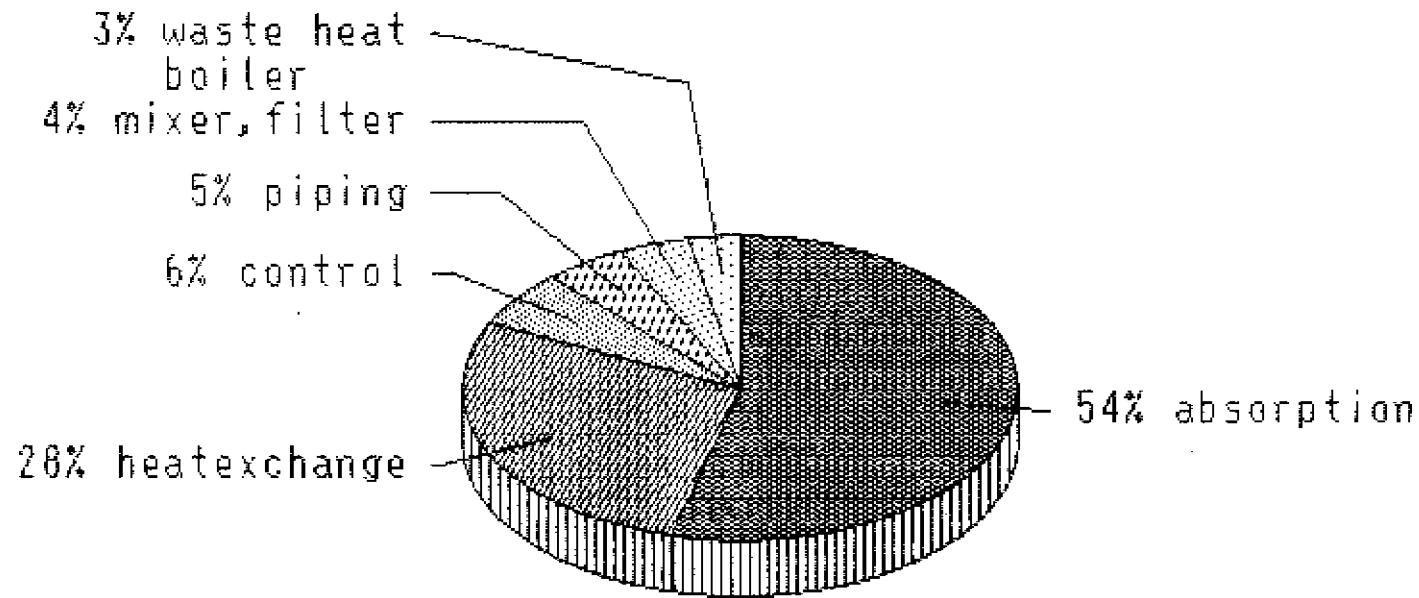
54% absorption

The next major bottleneck is the absorption section, not only with respect to process gas pressure drop but also to the nitrous gas contents in the tailgas leaving the tower. This aspect is in most cases more critical than the pressure drop which is divided into a wet part related to the liquid depth on the sieve trays and a dry part reflecting the losses through the column and the sieve tray holes. The ratio between the wet and the dry parts is roughly 3:1. To keep the nitrous gas concentration in the tailgas within acceptable limits, the system pressure must be increased, but the question as to whether this is feasible depends on the particular case. There is a more detailed paper in the following chapter referring to the subject of tailgas treatment.

For the steam generation system, consisting of waste heat boiler, steam drum, economizer and forced water circulation, it is a question of how to protect the superheater and pre-evaporating coils in the boiler against the expected higher heat flux. Other measures like increasing of La Mont nozzles, providing water separators at the steam drum outlet and modifications to the forced water circulation are of an accompanying nature for debottlenecking. The outlet temperature of the waste heat boiler influences directly the inlet temperature to the turbine via the downstream tailgas heater.

As shown in diagram 02, filters, mixers, piping, valves and fittings have no significant influence on the total plant pressure drop. A great advantage in modifying these equipment items is that they can be replaced very easily and that any additional pressure drop caused by newly installed equipment can be compensated.

In the following, a revamp procedure will be analyzed on the basis of an example to determine whether there is any advantage in doing it stepwise, including a calculation of benefits and interest gain as well as investment costs. The general situation can be described as follows:

The management must consider that, due to environmental requirements, nitrous gas emission with the tailgas must be reduced to max. 500 ppm within the next two years. The actual tailgas content varies between 1100 ppm and 1400 ppm. The decision was made to install a second absorption tower in combination with a capacity increase to 130%. The additional air is supplied by a secondary air compressor because there is insufficient steam for the steam-turbine-driven compressor set.

Summary of new or modified equipment:

- motor-driven secondary air compressor
- modifications to tailgas turbine including new rotor
- extended cooler condenser
- secondary air cooler
- extended ammonia evaporation
- modifications to the steam drum and water system of the La Mont boiler
- extended absorption, cooled by chilled water

It was intended to finish the reassembly of all equipment after a shut-down period of four weeks. The investment costs for this case are shown in diagram 01, plotted in red, revamp design. The graph was calculated by the exponential method with different exponents for the equipment involved.

A stepwise procedure for the given example can be split into three sections

I.   compressor air supply
tailgas turbine modification
expected plant capacity 110%

II.   installation of new heat exchangers
modification of waste heat boiler and water system
expected plant capacity 120%

III.   installation of an additional absorption tower
with chilled water cooling
expected plant capacity 130%

The above-mentioned red curve in diagram 01 is based on a total investment of $ 3.95 million including equipment, erection and civil works. A breakdown by sections yields:

I. $ 1.82 million

II. $ 0.75 million

III. $ 1.38 million

It is assumed that the shut-down period for the stepwise procedure is nearly the same as for the straight one. The investment period has been fixed at 24 months divided into three sections of 8 months each, the yearly total operating time being 8000 h. The interest rate is based on 8% per annum. Production costs are as follows:

- electric power $ 0.07/kWh
- steam $ 15.8 /mt   (40 bar, 340 °C)
- ammonia $ 115.8 /mt
- nitric acid $ 47.4 /mt

The profitability of the project was checked using the following formula:

$$K_n = K_o (1 + p/100) \exp n$$

where

K_n = accumulated capital + interest after n months

K_o = investment capital

p = % interest on monthly basis

n = investment period

It was assumed that the total investment of $ 3.95 million, corresponding to K_o in the above formula, could be invested on the money market for 24 months at an interest rate of 8% per annum. As a result of this, there would be an interest gain of $ 0.683 million. On the other hand, if the capital of $ 3.95 million is invested directly in the plant for uprating the capacity to 130%, the resulting gain due to increased production would be $ 0.864 million. The comparison of the outlined figures indicates that it is more economical to invest in the plant.

In the following table 01, the expected production gain, expressed in million $, is summarized. The right column contains the figure of 0.864 which means that, within the investment period of 24 months, the plant is operating at a capacity of 130% and $ 0.864 million is the production gain due to the increased capacity. In the left column, those figures are summarized which can be expected if the revamp is performed stepwise and the plant is operating in periods of 8 months each at the given capacities. The total of the

figures in the left column amounts to $ 0.605 million; therefore the question must be answered as to whether the remaining capital, which had not been invested within the 8 monthly periods, can equalize the difference by interest gains.

table 01 : summary of production data

capacity (%)	production gain (8-months basis)	production gain (24-months basis)
100	0	0
110	$ 0.143 million	
120	$ 0.174 million	
130	$ 0.288 million	$ 0.864 million

For the determination of what interest gain can be achieved, two models should be considered, table 02 for investment model 1 and table 03 for investment model 2. The difference between the two models consists of the different times when the revamp is started. Model 1 is based on investments in month 0, month 8 and month 16 and has two periods with interest gain and three periods with production gain. Model 2 is based on investments in month 8, month 16 and month 24 and has three periods with interest gain and two periods with production gain.

Under "A-capital" in tables 02 and 03 under the headline A-capital, the total investment and the remaining capital which is used for interest gain are listed by the periods in months outlined under "time". Under "I-capital", the investment is listed which corresponds to the revamp steps, see also the description on page 03.

A summary of the calculated results of the described procedures is shown in the following table 04. From the figures quoted, it can be seen that a stepwise revamp has advantages in costs according to the described investment model 2. The advantages depend on the actual interest rate and operating costs and vary from country to country.

table 02 : investment model 1

A-capital	time		I-capital	
3.95 mio	t0 (0 month)		1.82 mio	
			interest gain	0.116 mio
2.13 mio	t1 (8 months)		0.75 mio	
			interest gain	0.155 mio
1.38 mio	t2 (16 months)		1.38 mio	
	t3 (24 months)			

table 03 : investment model 2

A-capital	time		I-capital	
3.95 mio	t0 (0 month)		0.00 mio	
			interest gain	0.215 mio
3.95 mio	t1 (8 months)		1.82 mio	
			interest gain	0.239 mio
2.13 mio	t2 (16 months)		0.75 mio	
			interest gain	0.238 mio
1.38 mio	t3 (24 months)		1.38 mio	

Finally, it can be concluded that it is worth considering as to whether the revamp work for a capacity increase should be spread over a prolonged investment period. The described procedures can be worked out in more detail, if requested.

table 04 : summary of production and interest gain

capital investment survey	total gain (24-month basis)
capital on the money market	$ 0.683 million
capital invested, straight revamp	$ 0.867 million
capital invested, section revamp model 1	$ 0.876 million
capital invested, section revamp model 2	$ 1.010 million

TAILGAS TREATMENT

Due to environmental pollution control regulations it has become more and more important to reduce nitrous gas emissions even from nitric acid plants which have been designed some time ago. Particularly processes with selective reduction have convincing advantages, compared with non-selective processes using the residual oxygen for combustion purposes. Such a catalytic selective abatement system which allows the nitrous gas concentration to be lowered to below 200 ppm by volume nowadays desired in most countries, is well suited, under certain conditions, to be integrated into existing plants during a revamp.

The installation of an additional absorption volume improves process economics, but 200 ppm nitrous gas emission cannot be obtained in most cases with system pressures below 6 bar abs. Alkaline treatment methods are also suitable to obtain admissible tailgas concentrations, but with combined by-products.

The best method for a revamp is the combination of absorption extension and a following selective catalytic tailgas treatment. An example for this will be described later.

The abatement system described below is under license from Messrs. BASF, Federal Republic of Germany, and operates with the following main process parameters

catalyst	•	vanadium pentoxide
reactions	•	$6\ NO + 4\ NH_3 ==== 5\ N_2 + 6\ H_2O$
		reaction enthalpy $\Delta H = -1811\ kJ$
		$6\ NO_2 + 8\ NH_3 ==== 7\ N_2 + 12\ H_2O$
		reaction enthalpy $\Delta H = -2737\ kJ$
NO/NO_2 ratio	•	50% at reactor inlet is optimum
tailgas NOx	•	approx 3500 ppm max. at reactor inlet
		below 200 ppm at reactor outlet
		NOx reduction of 70 - 80 ppm
		results 1 in oK temperature increase of
		the tailgas

temperature	• 200 - 350 °C at reactor inlet
	> 90 °C at the tailgas turbine outlet
pressure	• 1.5 - 11 bar abs
pressure drop	• typically 0.09 bar for reactor
	and mixers

The ammonia consumption by the system is the key parameter for an economic estimate and depends on the inlet concentration of NOx with a given degree of oxidation expressed in %, which means the existing $NO_2/(NO + NO_2)$ ratio, process temperature and pressure. Under modern design conditions, namely

reactor inlet NOx concentration 650 ppm

reactor outlet NOx concentration 170 ppm

degree of oxidation at reactor inlet 50%

degree of oxidation at reactor outlet 20%

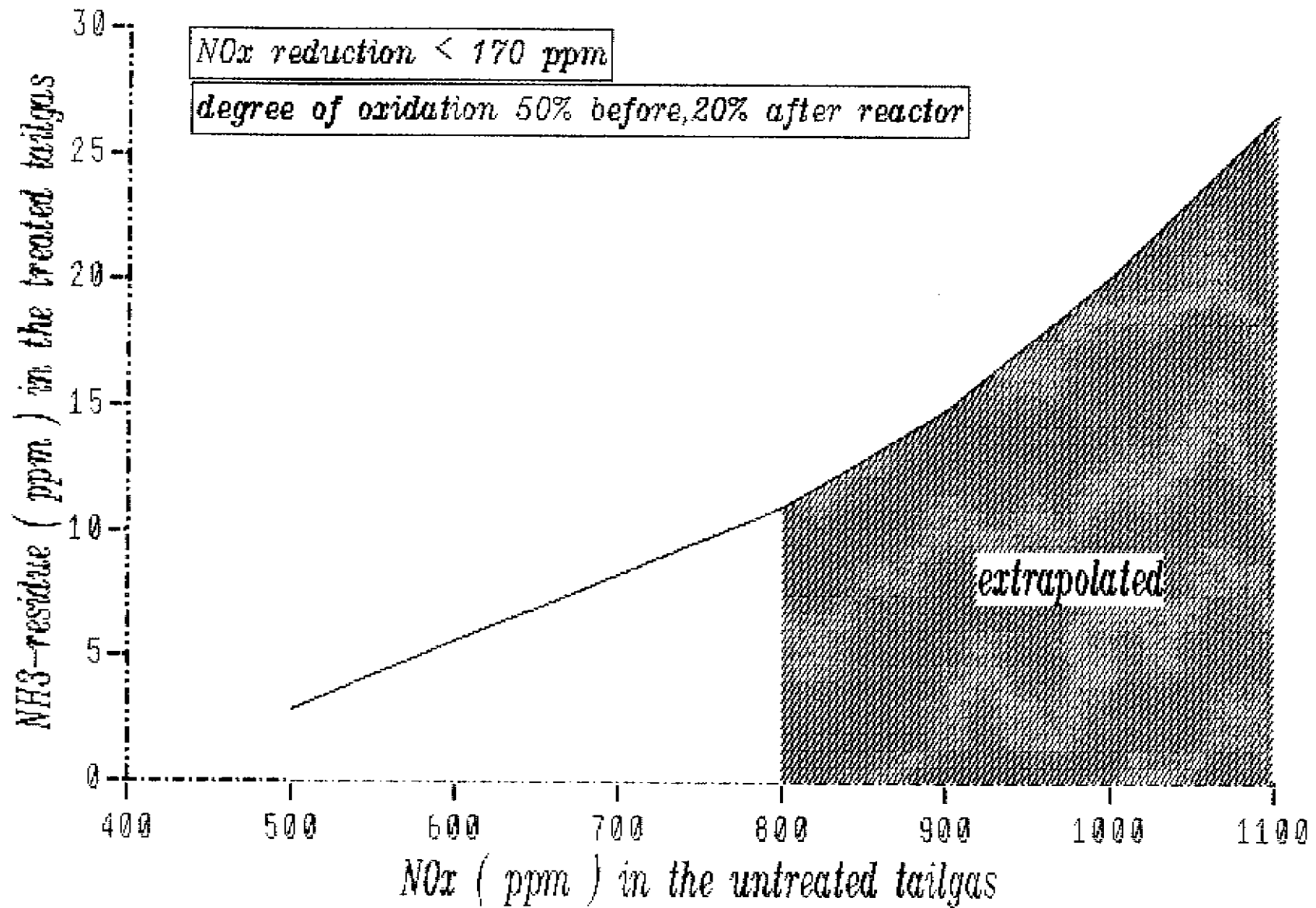inlet temperature 260 °C, system pressure 4.6 bar abs,

an ammonia supply of 0.36 kg NH_3/kg NOx is sufficient to operate the system. In many cases today there is also an emission limit for NH_3 which is below 15 ppm in the treated tailgas. The relationship of NOx in the untreated tailgas to the residual NH_3 in the treated tailgas is presented in

diagram 03 : NH_3-residue versus NOx

Diagram 03 shows the broad operation width of the whole system under the operating conditions mentioned and with a constant charged catalyst volume. For revamp purposes, each case must be designed individually. Nevertheless, it is possible to keep the residual NH_3 below the accepted limits of 15 ppm, even with considerable higher inlet NOx concentrations, but with a corresponding charged catalyst volume; see also the example quoted later.

The NOx reduction in the tailgas reactor is an exothermic process, in which the reaction enthalpy can be recovered by the tailgas turbine, as the net gain at the turbine

diagram 03 : NH3-residue versus NOx

NOx reduction < 170 ppm

degree of oxidation 50% before, 20% after reactor

extrapolated

NH3-residue (ppm) in the treated tailgas

NOx (ppm) in the untreated tailgas

shaft equals the gain by the temperature rise minus the loss resulting from the additional pressure drop in the abatement system.

It should be noted that the catalytic selective abatement system meets the opacity requirements for tailgas according to US EPA New Source Performance Standard (NSPS) for nitric acid plants. A plant equipped with a catalytic abatement system will produce an emission level of less than 10% opacity, which means 90% of light passes through the plume. The NSPS does require continuous stack recording for NOx.

The performance of an absorption system operating at 5.5 bar abs pressure is shown in

diagram 04 : absorption volume versus nitrous gas concentration

The plot is related to a modern medium-pressure plant of 500 mtpd and shows that, with nearly half the installed absorption volume, 95% of the nitrous gases are converted to acid, see reference line drawn at 2900 ppm. From 2900 to 630 ppm in this case, more than half of the total installed absorption volume is required, one third of the absorption pressure drop being related to this absorption part and approx. 14% of the total installed cooling area. There are very limited measures to reduce the absorption volume and often an advantage will be obtained at the expense of a lower process performance. For instance, an increase in tray weir heights for better absorption efficiency will entail a considerable energy loss at the tailgas turbine due to the greater pressure drop.

With reference to the liquid depth on the sieve trays in the towers designed by UHDE, a new Dynamic Absorption Calculation Method < DACM > has been developed, which allows, among other things, a more precise determination of the tray efficiency in relation to the liquid height on the trays. The example that will be shown later has been calculated with the aid of DACM and results in an improvement by 35 ppm compared with former methods using an optimization calculation for liquid depth on the trays.

Under revamp conditions it is even more difficult to obtain the desired process performance, because there is very little influence on the existing process parameters and

diagram 04 : absorption volume vs nitrous gas concentration
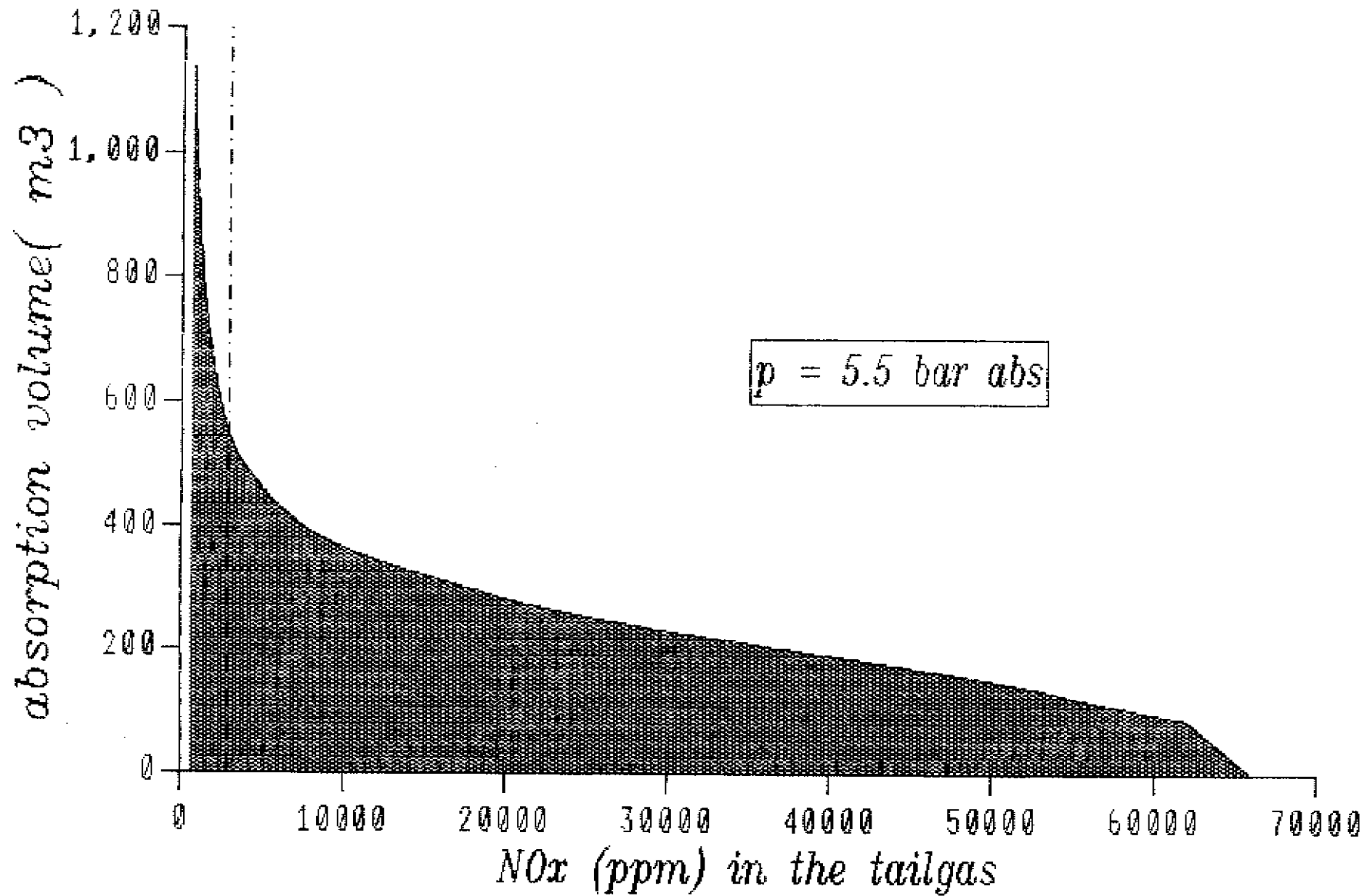
installed equipment, certainly with respect to justifiable economic expense. With reference to the details on the absorption volume pointed out, the following example should explain in which way an optimum can be determined between an extended absorption section and a selective abatement system. The result of this investigation yields the maximum nitrous gas concentration in the tailgas at which an extended absorption can be operated economically in combination with a selective abatement system.

The calculation considers the following process parameters:

- additional pressure drops caused by
  new equipment, absorption and abatement
  system
- additional acid production
- additional ammonia consumption
- energy, credit or debit
- investment costs for the absorption,
  the required absorption volume being cal-
  culated by weight only; for the abatement
  system only the required catalyst volume
  has been considered
- actual plant data, basis for revamp
  470 mtpd HNO_3 - 100%
  pressure at tailgas turbine inlet 3.65 bar abs
  NOx in the tailgas at outlet from absorption
  section 2500 ppm
  (beginning of extension)
  oxygen in the tailgas 3%

The calculation is performed in that, first, the selective abatement system is con-sidered alone to bring down the NOx concentration from 2500 to 200 ppm. Afterwards, in steps of 100 ppm, beginning at 2000 ppm, ending at 1000 ppm, the combination of absorption and catalytic abatement system is calculated. In each case the final NOx concentration is 200 ppm. The results are summarized to form a qualitative cost factor expressed as $/mt HNO_3 (100%), based on the process parameters mentioned above. The

graphic plot of the cost factor versus NOx concentration in the tailgas, showing the optimum is presented in

**diagram 05 : optimization, absorption/catalytic abatement**

The price basis for the cost factor corresponds to European standards, viz. DM 270 DM/t NH_3, DM 100/t HNO_3 and DM 0.12 DM/kWh electric energy. Due to the considered range of the specified NOx reduction, it was assumed that the engineering, civil works and erection would remain constant.

The plot in diagram 05 indicates that the reduction with an extended absorption is profitable to a NOx concentration of 1700 ppm. The shape of the plot is rather flat from 1900 to 1600 ppm so that small differences in prices may shift the optimum point. Nevertheless, it is worth discussing during the revamp a combination of extended absorption and catalytic selective abatement system due to the operating cost situation.

From the example it can be seen that the cost factor for a combination of tailgas treatment, consisting of absorption and catalytic abater, is lower than the single method of catalytic abatement alone.

The calculation method which is the basis of the plot in diagram 05 and is described in the above-mentioned example, is available as a fully computerized package. Taking into consideration all the important parameters, many examples of application can be handled.

diagram 05 : optimization, absorption/catalytic abatement
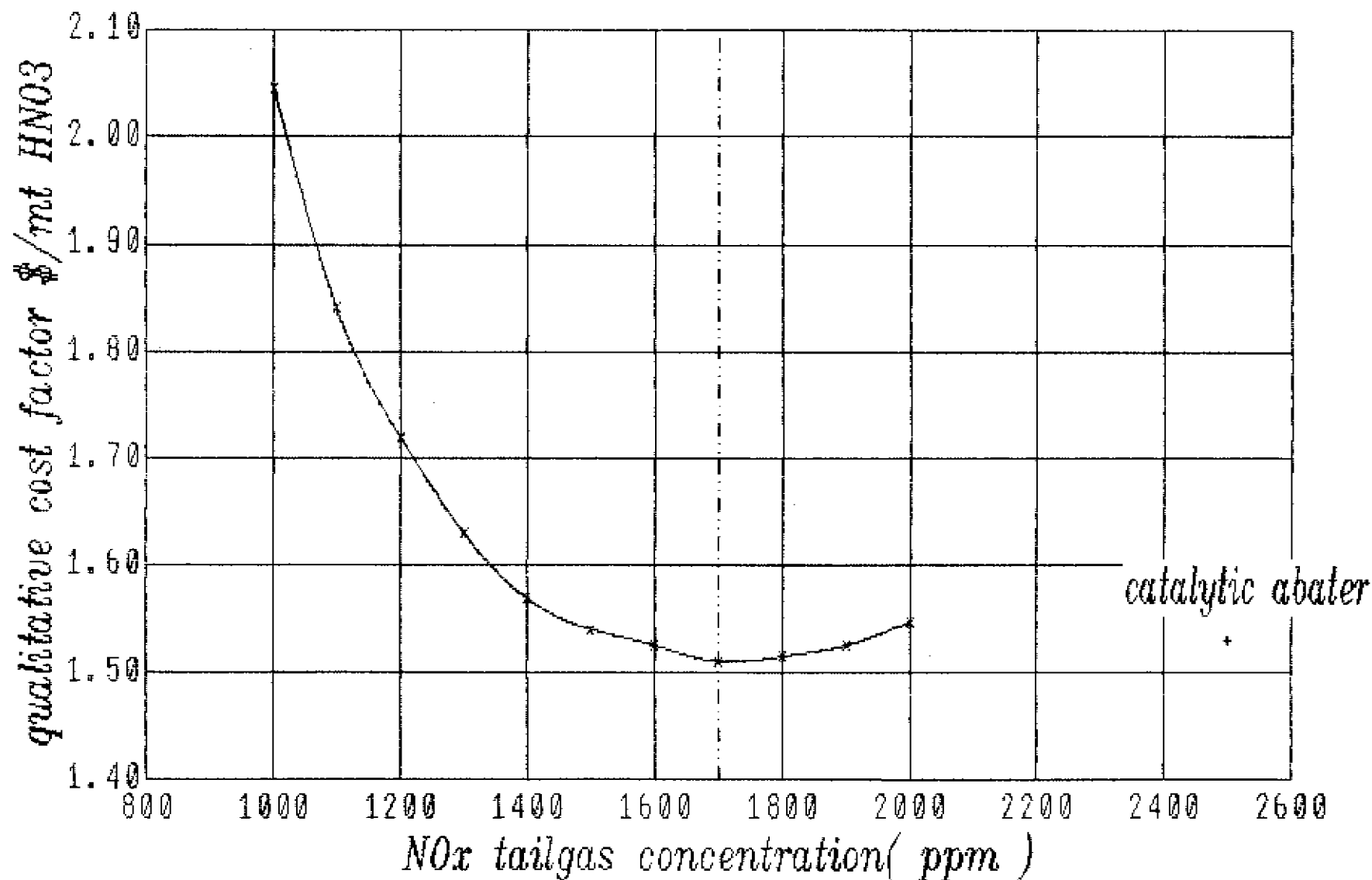
WASTE HEAT RECOVERY

The energy input required for the nitric acid process is composed of different portions, such as ammonia, air, process water, demineralized water, cooling water and electric energy for pump drivers. The percentage of these portions as part of the total is shown in table 05. Due to the chosen reference level of 25 °C and the basic enthalpy data for water of 104.77 kJ/kg, the active energy input can be reduced to ammonia and air as well as electric input for pumps.

As can be seen from table 05, the main part of the energy input is introduced to the process via the ammonia in the form of chemically fixed energy.

The given example is related to a 500 mtpd plant and represents the minimum energy input when a steam turbine drive is used for the compressor set.

table 05 : nitric acid process - energy input

	(kg/h)	(kW)		(%)
ammonia	5 889	36 220	a)	97.4
(25 °C, 15 bar)				
air	105 899	776	c)	2.1
(25 °C, 1 bar)				
process water	5 432	0	0	
(25 °C, 12 bar)				
demineralized water	0	0		0
(25 °C, 8 bar)				
cooling water	0	0		0
(25 °C, 6 bar)				
electric energy		198		0.5
total	117 220	37 194		100.0

basic data for calculation

reference temperature 25 °C, enthalpy 104.77 kJ/kg (water)

corrected specific enthalpy for water and steam

steam   (25 °C, 1.01 bar)   2 442.51 kJ/kg

gross calorific value for gaseous ammonia

             (25 °C, 1.013 bar)   22 254   kJ/kg

symbols   a)   gross calorific value

                 b)   sensible heat

                 c)   enthalpy of steam in the gas stream concerned

The input energy is split into the outlet streams as nitric acid, tailgas, waste water, cooling water and export steam. The percentage of the output energy as part of the total is shown in table 06. Reference is made for this example to a 500 mtpd plant. As can be seen from the figures given, most of the energy, i.e. more than 91%, is covered by the combined energy contents of the streams. The expression 'combined energy contents' is the sum of all heat flows to either cooling water or steam generation. The split percentage into the cooling water reads 48.6% whereas 42.9% is left for steam generation.

table 06 : nitric acid process - energy output

(%)		(kg/h)	(kW)	
1.5	**nitric acid**	33 605	545	b)
	(47 °C, 5 bar)			
5.6	**tailgas**	83 615	2 070	b + c)
	(106 °C, 1 bar)			
0.4	**waste water**		162	b)
	(60 °C, 1 bar)			
91.4	**combined energy contents**		34 021	b)
1.1	losses		396	
total 100.0		117 220	37 194	

basic data for calculation

Reference temperature 25 °C, enthalpy 104.77 kJ/kg (water)
Corrected specific enthalpy for water and steam

steam   (106 °C, 1.01 bar)   2 580.94 kJ/kg
water   (60 °C, 1.01 bar)   146.39 kJ/kg

symbols

     a)   gross calorific value

     b)   sensible heat

     c)   enthalpy of steam in the gas stream concerned

In view of the energy distribution shown, the objective of revamp engineering should be to keep the heat flow to the cooling water as low as possible to favour the steam generation as recuperative energy, always with respect to given design features. Revamp work on the cooling water side promises the best energy improvement. From the given example the recuperative efficiency can be defined as 42.9%, when steam generation is intended. For other forms of energy, corresponding transformation efficiencies must be calculated.

Improvements with regard to the energy leaving the plant with the tailgas are only possible if the thermal efficiency of the tailgas turbine can be improved.

The energy losses of the nitric acid process consist mainly of vapours from the thermal deaerator and blow-down flash steam as well as the electric energy for the pumps since in this consideration temperature increase for the fluids has been neglected. The energy leaving the plant with the waste water has its origin in the boiler blow down which must be cooled to a permissible discharge temperature by cooling water. Ammoniacal water has no influence on the energy balance.

Revamp engineering for the above-mentioned items is of secondary importance; only detail improvements should be expected.

Having discussed the energy situation at battery limits, a consideration of the process conditions within battery limit should follow.

The process gas temperatures from the catalyst to the outlet of the absorption unit can be summarized to a recalescence curve representing process temperature levels versus transferred heat, see the following

diagram 06 : recalescence curve, heat exchanger train

The blue plot relates to the nitrous gas from the catalyst gauze to the absorption outlet, whereas the red plot represents different process fluids marked and explained in the diagram by legend. The curves allow a comprehensive energy-wise classification of the process. Optimum waste heat utilization is not the only desirable design purpose, but special process features and at least the economic aspect of heat exchanger design must also be considered with the same importance. An evaluation of diagram 06 with regard to how efficiently the waste heat utilization was performed, can be done by analyzing the areas under the curves.

In diagram 06, the conversion efficiency is represented by the area under the red plot divided by area under the blue plot of 49%. The same relation will be obtained if the tailgas temperature is increased by 100 °C. There are some shifts in temperature levels of several items of equipment, but the total relation of the red area divided by blue area remains unchanged. The influence of the tailgas temperature increase can be demonstrated as indicated in the following table 07.

diagram 06 : recalescence curve, heat exchanger train

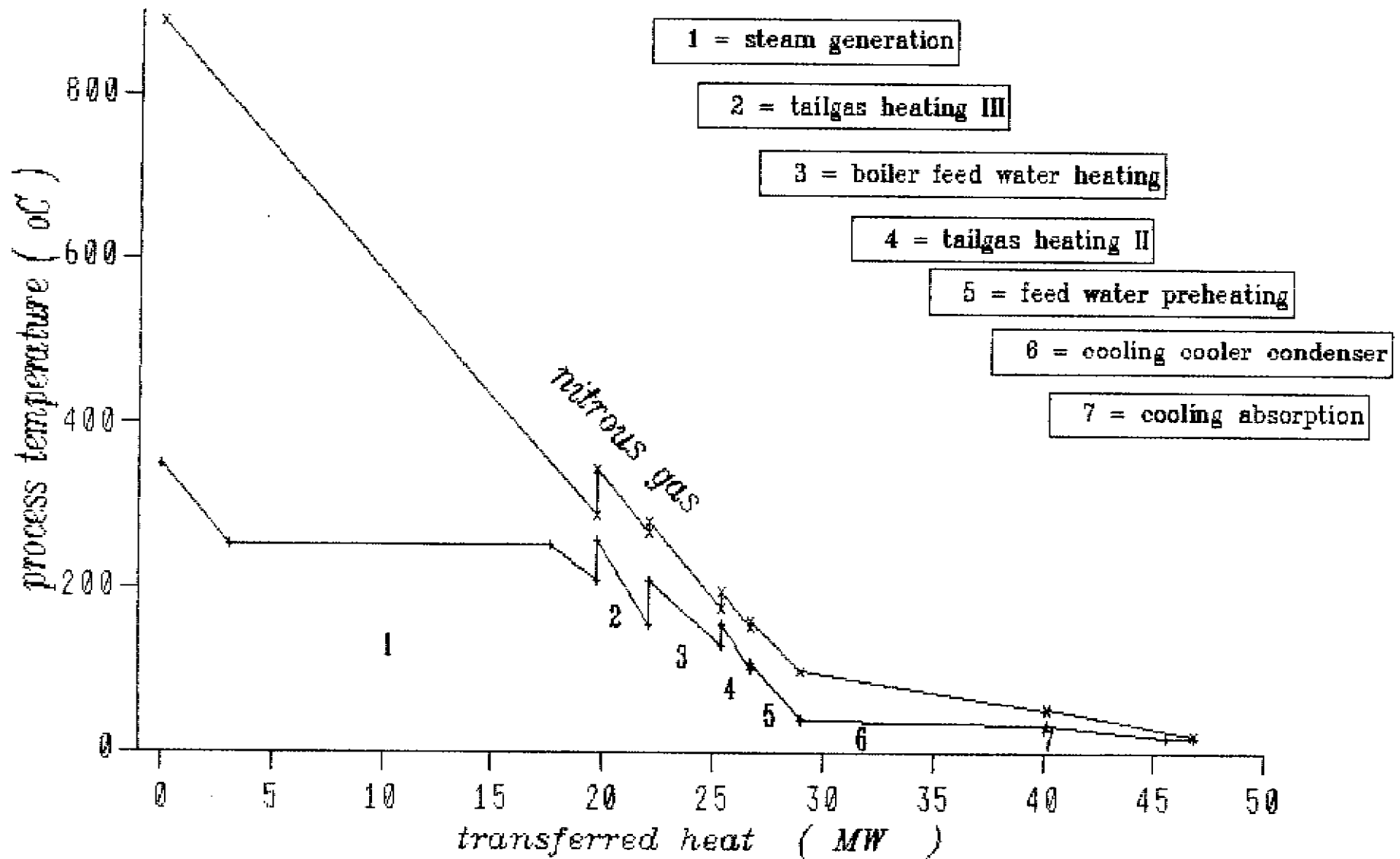1 = steam generation

2 = tailgas heating III

3 = boiler feed water heating

4 = tailgas heating II

5 = feed water preheating

6 = cooling cooler condenser

7 = cooling absorption

nitrous gas

process temperature (oC)

transferred heat   (MW   )

table 07 : nitric acid process - energy output

(%)		(kg/h)	(kW)	
1.5	**nitric acid**	33 605	545	b)
	(47 °C, 5 bar)			
11.0	**tailgas**	83 615	4 101	b + c)
	(184 °C, 1 bar)			
0.4	**waste water**		162	b)
	(60 °C, 1 bar)			
86.0	**combined energy contents**		31 990	b)
1.1	losses		396	
total 100.0		117 220	37 194	

The result of the tailgas temperature increase is that, within the combined energy part, the percentage of the cooling water is raised slightly to 49.6% whereas the steam generation part is reduced to 36.4%. The supposedly better energy recovery in fact leaves the plant at battery limits with the tailgas after passing through the turbine.

These considerations are more important in the design phase than for revamp services. Therefore, an example will now be illustrated giving better energy recovery by application of better heat exchanger material and modified process operation. In a high-pressure plant, combustion pressure = 8 bar abs, the nitrous gas leaving the waste heat boiler is cooled in a tailgas heater and finally in cooler condensers. Due to corrosion problems, the tailgas from the absorption section is first heated by steam to 130 °C before passing through the tailgas heater where it is further heated to the final temperature required for the turbine, which should be the same after revamp. The un-revamped system is shown in

diagram 07 : heat exchanger train, original

The revamp consists of the following:

* replacement of a steam-heated tailgas heater
* additional feed water preheating
* final tailgas temperature upstream of the turbine = constant

The required energy for the tailgas and for the feed water could be taken from the nitrous gas before it enters the cooler condensers. The problem was solved by using corrosion-resistant materials of the specification

C max	Si max	P max	S max	Cr	Ni
0.02	0.3	0.02	0.015	24.5	20.5

with the result that the condensing range of the nitrous gas could be partly used for heat recovery. The extremely corrosive part-evaporation of nitric acid in the tubes, which mainly caused the corrosion problems, has been avoided by designing two smaller tailgas heaters; the first, charged with the cold tailgas from the absorption section, is located directly at the inlet of the cooler condenser, and should always operate with tube wall temperatures below the condensation point, the second with tube wall temperatures above the condensation point. This could be achieved by operating the heat exchangers according to the co-current flow principle.

The result of the revamp with respect to energy recovery is presented in

diagram 08 : heat exchanger train, revamped

and now a yield, with regard to the area units under the curves, of 42.6% compared with 27.9% for the original. In this way, the recuperative part of the combined energy content could be increased. The relationship of cooling water to steam generation has been shifted to steam generation and hence there is less heat flow to the cooling water.

diagram 07 : heat exchanger train, original

1 = tailgas heater
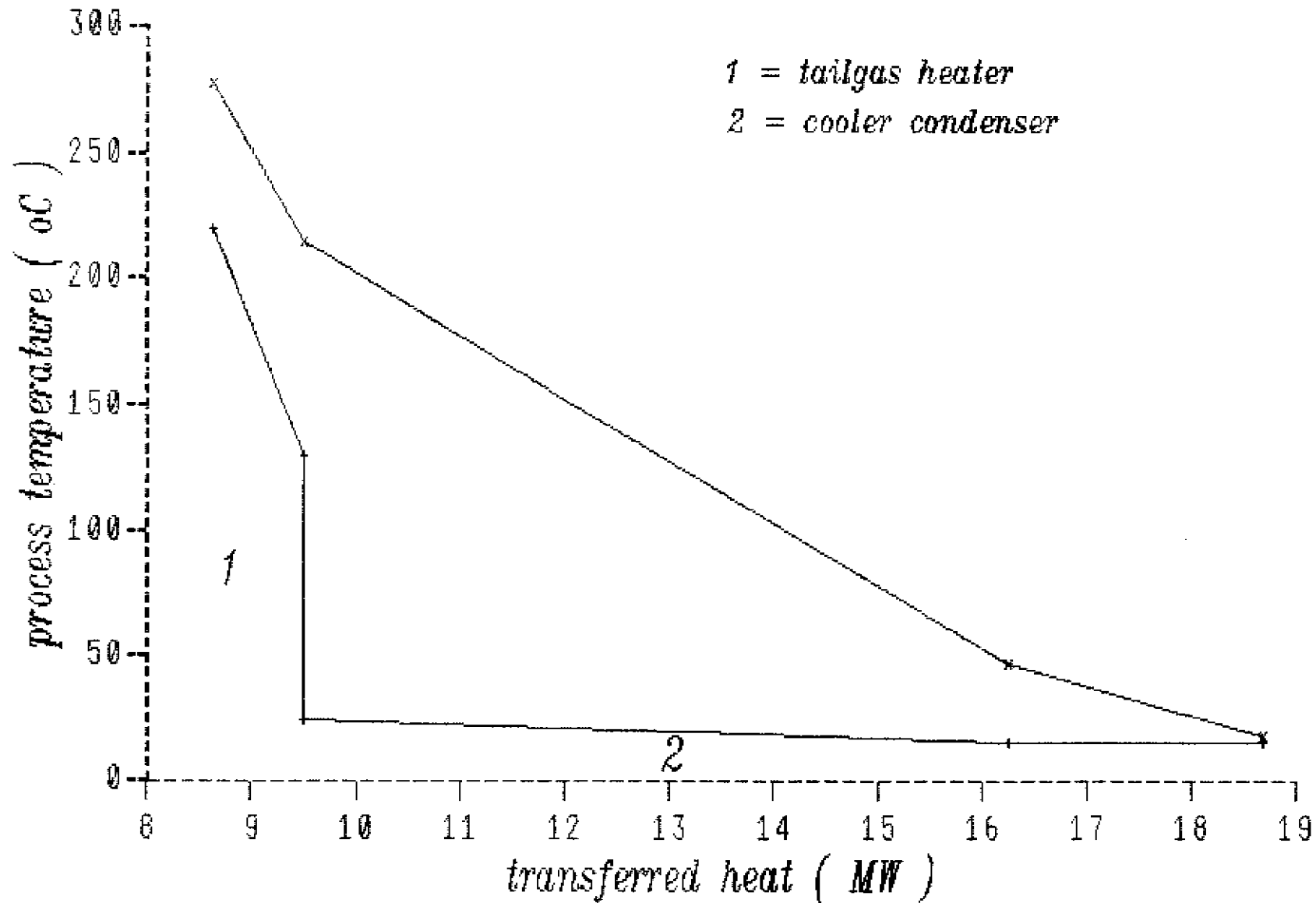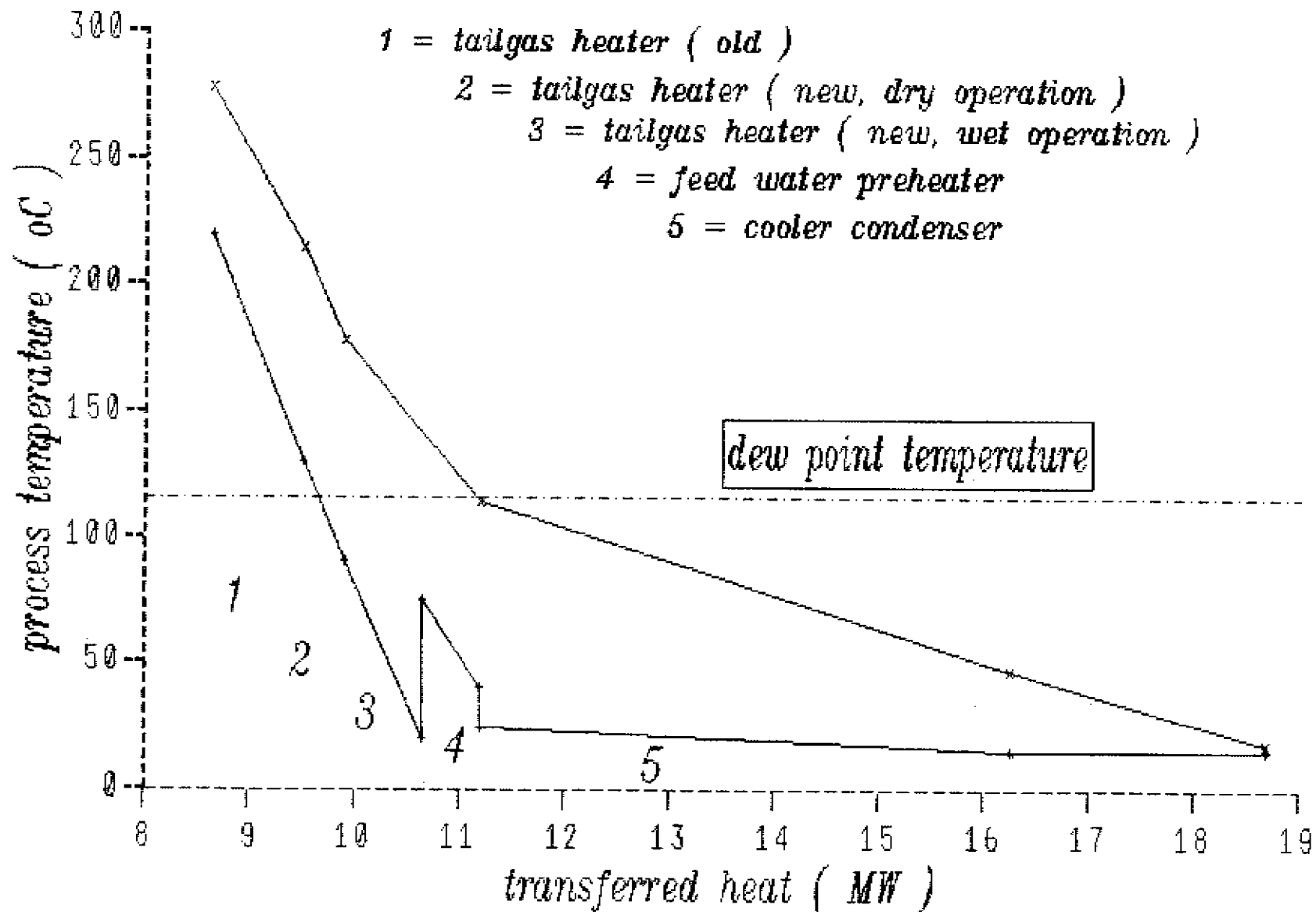2 = cooler condenser

diagram 08 : heat exchanger train, revamped

1 = tailgas heater (old)

2 = tailgas heater (new, dry operation)

3 = tailgas heater (new, wet operation)

4 = feed water preheater

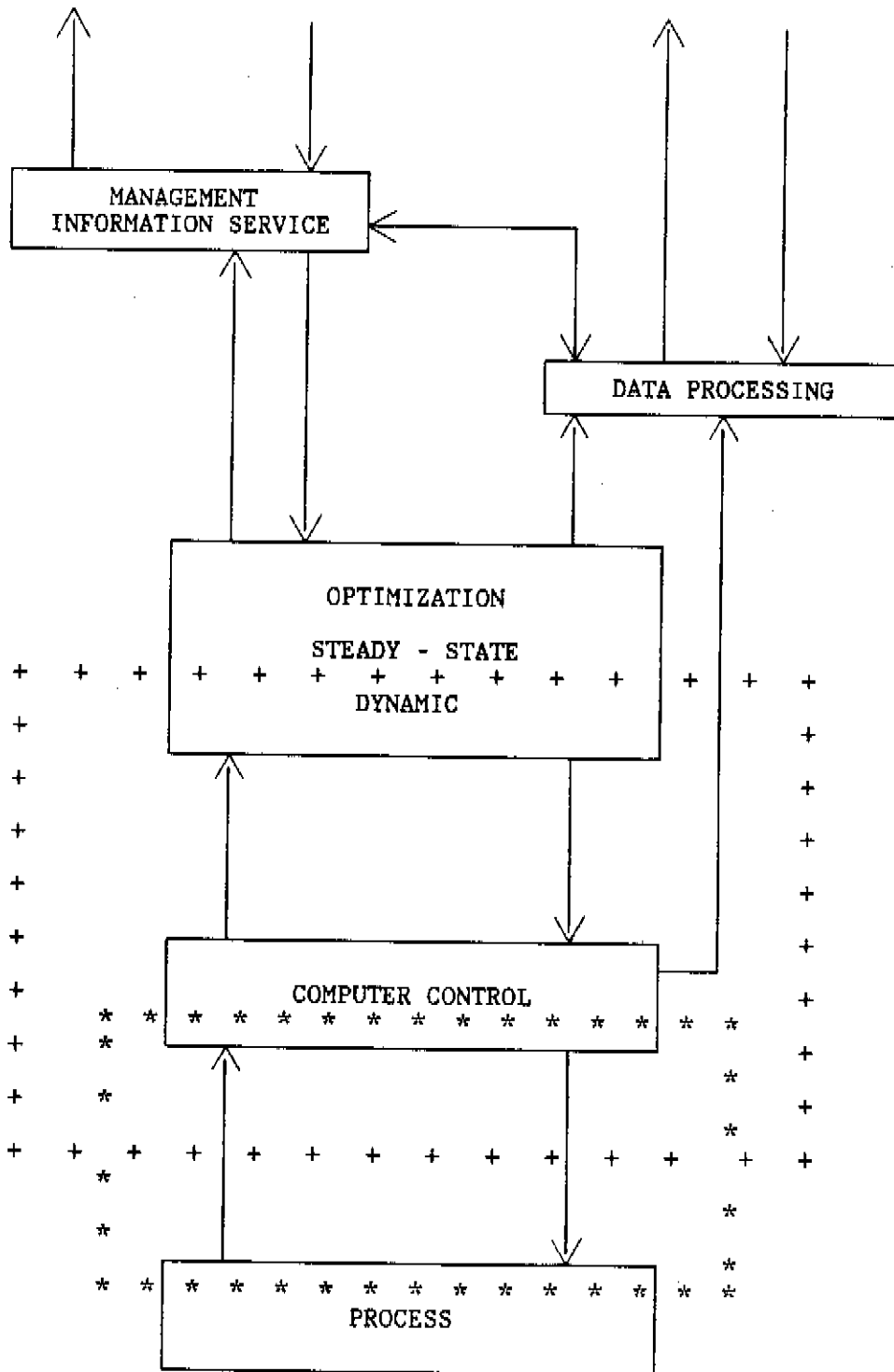5 = cooler condenser

dew point temperature

PROCESS CONTROL

Computerized process control can today help to make profits in, and can model the performance of, plants accurately and cost-effectively. In existing plants, computerized process control is used to reduce operating costs, improve yield and increase throughput. Computerized control can be divided into different levels, the interdependence of which is listed in

diagram 09 : functions of a fully computerized control system

1. unit operation control   means the control of individual items of
equipment, such as ammonia burner,
absorption tower, heat exchanger

2. unit process control   means a combination of individual unit
operations, which must be coordinated
to meet plant requirements

3. plant control   means the concentration of all process
controls at one location, for instance in
a central control room

4. departmental control   means the control of a complete company
division like the fertilizer group; this
control level is not involved directly
with process belongings

5. company control   generally not of interest for process
control, except for some plant inputs
which are initiated from this level

The optimization of the nitric acid process by means of process and absorption calculations with a view to minimizing operating costs can be achieved via a 'Digital Control System' named briefly < DCS > Such a system is also suitable for integration in existing plants, it being possible to compensate the higher investment by improvements in

diagram 9 : functions of a fully computerized control system

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            ┌──────────────────────┐
            │     MANAGEMENT       │
            │ INFORMATION SERVICE  │◄──────────┐
            └──────────────────────┘           │
                                               │
                              ┌────────────────────────────┐
                              │      DATA PROCESSING        │
                              └────────────────────────────┘

            ┌──────────────────────────────┐
            │         OPTIMIZATION         │
  +   +   + │ +   +   +   +   +   +   +   + │  +   +   +
          + │      STEADY - STATE          │          +
          + │                              │          +
          + │         DYNAMIC              │          +
          + └──────────────────────────────┘          +
          +                                            +
          +                                            +
          +        ┌──────────────────────┐            +
          +        │   COMPUTER CONTROL   │            +
        * * │ * * * * * * * * * * * * * * │ * *        +
          + │ *                          │             +
          + │ *                          │            *
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  +   + * + │ +   +   +   +   +   +   +   │ +   +   * * +
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          └──────────────────────────────┘
                     PROCESS
```

* unit operation control *
+ process control +

plant operation. DCS can also tune the process to maximum capacity with output data reflecting the additional cost of this operating option. Improvements and expected operating profits will be listed at the end of this chapter.

The object of the optimization is to keep tailgas NOx within the accepted limits with respect to minimum plant pressure which simultaneously represents minimum energy requirements, whereas the plant load and the actual cooling water temperature are variables. The acid profile in the absorption unit must be controlled as well as the moisture contents of the intake air. Essentially, this outlines the allocation of unit operation control to a skeleton process control.

DCS and the corresponding software available in our company contain algorithms for material transfer of different nitrous gases which are the basis for nitric acid formation on the absorption sieve trays, not only for HNO_3 formation but also for HNO_2. The interspace between the trays is used for the oxidation of NO to NO_2 where the reaction velocity is calculated stepwise and finally integrated.

The reactions are temperature- and pressure-dependent. The composition and temperature of the liquid coming from the next higher tray in the column is estimated first and balanced in the following calculation step together with the gas stream. Finally, 18 equations have to be solved simultaneously. For better control of cpu time, initially only some of the equations are solved either with the gas upstream or with the liquid downstream. The result of the calculation is an acid profile which is presented as the acid concentration on the trays versus the absorption volume. These data are available in respect of each tray for the liquid and gas stream composition and the transferred heat in the absorption unit with the installed cooling area including tray temperatures.

For optimization purposes, the program works more simply because the number of trays in an existing plant is fixed; on the other hand there is enough capacity available to integrate actual plant parameters. The actual calculation for optimization can be described as follows: Based on measured data for ammonia, air conditions and nitrous gas at some key points in the plant, for instance pressure and temperature at the cooler condenser outlet as well as at the head of the absorption column, a flow data list is calculated on a mass basis, while observing fixed input data such as tailgas oxygen and cooling wa-

ter temperature. From the flow data list, initial data are taken for the absorption unit. The calculation of the absorption system is subject to pressure variations and is repeated with respect to certain measured tray temperatures which serve as ancillary data for the program until the desired NOx tailgas concentration is reached. The highlighted data are:

- primary and secondary air flow
- process water make up
- absorption inlet pressure
- the tray for acid condensate feed

and various other data which are useful for plant and process control, and also the complete acid profile. The input of the new rated values can be performed via an external keyboard.

The interrelationship with the second important process part, i.e. the ammonia conversion on the catalyst gauzes, is established by separate program calculations, the results being fed to the mass flow data list.

An optimized ammonia oxidation depends on several variables which can be influenced within certain limits.

- area load of catalyst gauzes
- system pressure upstream of the catalysts
- gauze temperature
- number of gauzes installed
- running period of the catalyst

Increased gauze temperatures as well as frequent shut-downs lead to untimely aging of the catalyst, as the platinum becomes eroded and must be replaced more often which represents a loss in production. The optimization yields the right time for a catalyst change and indicates the quantity of catalyst which should be replaced and gives recommendations with regard to the suitable gauze temperature. Key parameters for the calculation are the costs for ammonia and the catalyst as well as the acid requirements. Significant difficulties within this optimization result from the measurement of conversion efficiency.

UHDE has developed a physical model of the catalyst gauze which allows the determination of platinum losses and conversion efficiency. The results obtained are satisfactory and can be used via DCS.

Finally, some facts should be mentioned regarding the profits expected. These can be subdivided into two groups, one with not directly itemizable benefits and the other with same, expressed directly in terms of money. The first group can be summarized as follows:

- preventive maintenance
- medium-term capacity planning
  change of catalyst
  quantity of new catalyst required
  ammonia consumption
  (each of the above-mentioned items in
  relation to the actual cost situation)
- auxiliary facilities for the training
  of operating personnel
- shortening of start-up periods

For the second group, a rough estimate indicates that the investment costs for DCS can be recovered in two years of operation by a medium-pressure 370 mtpd plant with a catalytic abatement system. The direct profits are:

- savings of ammonia in the abatement system
  due to closer operation at rated value with
  lower oscillation
- oxygen concentration in the tailgas can be
  lowered and this is directly energy saving
- continuously lower NOx emission increases
  the acid production rate and saves ammonia
  at the catalytic abater

- optimized capacity planning lowers production costs compared with constant operation
- preventive maintenance lowers the risk of unexpected shut-downs

CONCLUSIONS

Various options were discussed in this paper with regard to the revamping of nitric acid plants. The question as to whether individual measures or a combination of different measures are to be given preference depends on the objectives specified by the plant owners.

In most cases an evaluation of different technically feasible solutions will produce the desired results, the optimum cost-benefit ratio being obtained by comparing the investment costs required for each particular option with the achievable economic efficiency.

TA/88/13   Nitric acid production, improvements by revamping by W. Freitag, R. Schallert and E. Scheibler, Uhde GmbH, Federal Republic of Germany

DISCUSSION (Rapporteur K. Farmery, ICI Fertilizers, UK)

Q - Mr. P. ORPHANIDES (Duetag, France)

When you say in your paper that the performance reserves of the absorption section of a nitric acid plant is often around 10%, what is the limiting factor ?

Is it:
-absorption efficiency ?
-removal of absorption heat ?
-hydraulic performance ?
-the pressure drop impact due to the rest of the plant ?

A - The main factors are design features like weir heights, the number of holes (i.e. the dry pressure drop), the cooling surface area (which cannot be modified in an existing tower) etc. All limit the extent to which the capacity of an existing plant can be increased. In general, therefore, these limiting features are those which are the most difficult to change - the mechanical design features.

Q - Dr. S.K. MUKHERJEE (KRIBHCO, India)

First a comment. The revamp options for optimisation of a plant in India (800 tpd capacity - 100% acid basis - 53% product strength). have been studied. The plant was built in 1958-59, and has been in operation for nearly 30 years. The revamp option, briefly, is for partial replacement of the absorption section, now 4 bar absolute - single pressure, to high pressure (10 bar-12 bar) in order to obtain:

i/ 68% acid
ii/ 200 ppm NOx emissions against 2500 ppm NOx now
iii/ better ammonia efficiency.

The compression and combustion sections are in good condition and need no technology changes. It seems to be only the absorption section which needs extensive redesign. The project, as described, has been taken forward for implementation. Would Mr. Freitag comment on the project.

My question: will a change of packing improve the absorption capacity of an existing plant where the current packing is normal 35 mm x 35 mm ceramic Raschig rings ?

A - First a comment on the revamp proposal. I know the project quite well. Many options have been considered. All the options involving splitting into parallel streams or adding sieve-tray absorption are expensive. It is hard for me to say from here which would be the best, most reliable solution. A lot of thought and calculation are needed for each option. In addition, the decision has to be made on the basis of payback time, interest rates,etc. However, on balance, I suspect that a complete revamp/replacement of the absorption section is probably the best solution, not adding a sieve-tray tower.

As to your question about changing the packing, I doubt that approach will be profitable.

.../.../...

Q - Mr. G. KONAPHAIS (Norsk Hydro, Norway).

Our experience leads us to conclude that the dew point in nitrous gas is closer to 140° C than 115° C as you indicate in your paper. Will you recommend increased heat recovery in this temperature region when you have had problems with corrosion at the inlet of the cooler condensers in some of the plants you have built ?

A - We know that the inlet nozzle of the cooler condenser in new plants is equipped with a feedwater preheater in advance of both nozzles, so that they have the same temperature as the inlet of the cooler condenser itself. Corrosion in the cooler condenser can be completely prevented, therefore, by adding additional cooling facilities to the inlet portion of the cooler condenser itself.

In this way, we can expect the dew point - whether it is 140° C or 115° C - to be handled in the feedwater preheater, which is designed to handle it.