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THE PROFITABLE OPERATION OF NITRIC ACID PLANTS

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1. SUMMARY

As unit costs rise sharply the profitable operation of nitric acid plants becomes more difficult; it is therefore important that manufacturers adapt quickly to technological developments. Some aspects of the profitable use of raw materials, energy, maintenance and labour resources in nitric acid production are therefore examined. Additionally, a high on-stream factor and peak output rates are essential ingredients for profitable operation, and important factors in these areas are discussed.

Fisons has recently developed a number of mathematical models for the conversion, absorption, and platinum recovery parts of the process. These can be integrated into an overall profit model, which is then used to determine the OPTIMUM strategy and MOST PROFITABLE operation for any particular set of circumstances. Examples of the use of the models illustrate the potential economic benefits that arise from use of such techniques.

2. INTRODUCTION

Development of the modern nitric acid process started in the early 1900's with Ostwald's work on the "catalytic oxidation of ammonia with air over a platinum catalyst". The first commercial plant was built around 1920. Since then the basic process has remained the same, although a number of variants are now commercially available; these are the High Pressure, the Medium Pressure, and the Mixed Pressure processes.

Fisons commenced nitric acid manufacture in 1958, and now operates 4 plants (3 high pressure and 1 medium pressure plants) with a total output in excess of 600,000 tpa. Our process development effort initially concentrated on maximizing nitrogen efficiencies, production rates and plant utilizations. However, with these problems largely resolved, the priority switched to the determination of the OPTIMUM conditions and strategy for the MOST PROFITABLE OPERATION.

3. MANUFACTURING COSTS

The starting point in any discussion of profitable operation must be the Manufacturing Cost itself, and a breakdown of typical costs for the main processes is shown in Table 1. Generally speaking manufacturing costs can be reduced by the conventional method of:-

1. Minimizing unit consumptions and costs.
2. Maximizing plant production rate.
3. Maximizing plant utilization.

The superficial cost analysis in Table 1, highlights the major cost items and sets the priorities for examination for the MOST PROFITABLE OPERATION.

TABLE 1 TYPICAL MANUFACTURING COSTS FOR VARIOUS NITRIC ACID PROCESSES

Basis 900 TPD plant, 330 days/annum.

Item	Unit Cost	Range of Costs for Medium, High and Mixed Pressure Processes $/tonne acid (100% acid)
Raw Materials		
Ammonia	188 $/tonne	52.9 - 55.7
Catalyst (after recovery)	15.5 $/gm	1.5 - 2.8
Utilities		
Electricity	0.06 $/kWh	0.2 - 0.6
Cooling Water	0.14 $/tonne	0.4 - 5.0
Demineralised Water	0.35 $/tonne	0.2 - 0.3
Steam	12 $/tonne	credit 3.4 - 6.5
Labour	23,500 $/ annum/man	0.8
Maintenance	5% of Capital	3.3 - 4.0
Depreciation	over 15 years	4.4 - 5.4
Total	-	59.2 - 64.1

4. MINIMISING COSTS

4.1 Raw Materials

4.1.1 Ammonia

Table 1 clearly shows the dominant effect ammonia has on nitric acid manufacturing costs. From an operating point of view the profitable use of ammonia means achievement of high conversion and absorption efficiencies.

4.1.1.1 Conversion Efficiency

The objective here is to convert as much ammonia as possible to nitric oxide, according to the reaction.

$$4\ NH_3 + 5O_2 \qquad 4NO + 6\ H_2O \qquad (1)$$

The two most important items in this context are raw material contamination and the performance of the catalyst pack.

Contamination

The quality of the air and ammonia reaching the gauze must be very pure, so that other factors such as catalyst quantity can be optimised. Typical plant efficiencies vary between 94 -96%: the major reason for low efficiency is the degradation of ammonia to nitrogen before or on the gauze, by reaction with catalyst poisons brought in with the raw materials. The following reaction then applies:

$$4\ NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O \qquad (2)$$

The contaminants also restrict catalyst life by reducing the active surface area and accelerating the premature destruction and loss of catalyst due to localised high temperatures. The poisons associated with ammonia are well known - iron oxides, oil, water, and volatile organics. By far the most serious is iron oxide which enhances reaction 2.

The air supply is another source of contamination by pollutants such as fertilizer dusts, steam, sulphur dioxide etc. These materials act in the same way as either ammonia contaminants, or as agents for the erosion/ corrosion of pipework and equipment within the plant itself, e.g. rusting of iron pipework.

Profitability can only be maintained by achieving high conversion efficiencies consistently. An extensive technical programme is therefore necessary firstly, to identify the type and size of contaminants and secondly, to eliminate them. Obviously the optimum filtration equipment varies from plant to plant as the contaminants change, but a typical system for one of our plants is shown in Table 2.

TABLE 2 TYPICAL FILTRATION SYSTEM

Ammonia	Air	Mixed Gas
1. Liquid - magnetic separators 2. Vapour - special cartridges to retain 97% of particles greater than 1 μm	1. Three stage compressor suction filter to give 99.9% retention of particles greater than 0.5 μm.	1. Special cartridges positioned just before gauze to remove 95% of particles greater than 1 μm.

Once the ideal filtration system is installed regular chemical analysis of the air and ammonia quality is required. A systematic analysis of used gauzes enables monitoring of the filtration efficiency and maintenance of high conversions.

The Catalyst Pack

Having resolved the contamination problem, maximum efficiency is obtained by optimising the operation of the gauze pack itself. The factors here are:

(1) The quantity of catalyst

(2) The proportion of used catalyst

(3) The operating temperature

(4) The campaign length.

The quantity of catalyst installed depends primarily on the type of plant and its throughput. If the catalyst gauzes removed from an efficient plant are examined using scanning electron microscopy, a steady decrease in surface crystallinity is observed between the top and bottom sheets, see Figs. 1-5. Reuse of some of the lower gauzes in the next pack, made up with new material, provides a significant saving in catalyst costs. An improvement in efficiency is also obtained from the optimised crystallinity profile achieved.

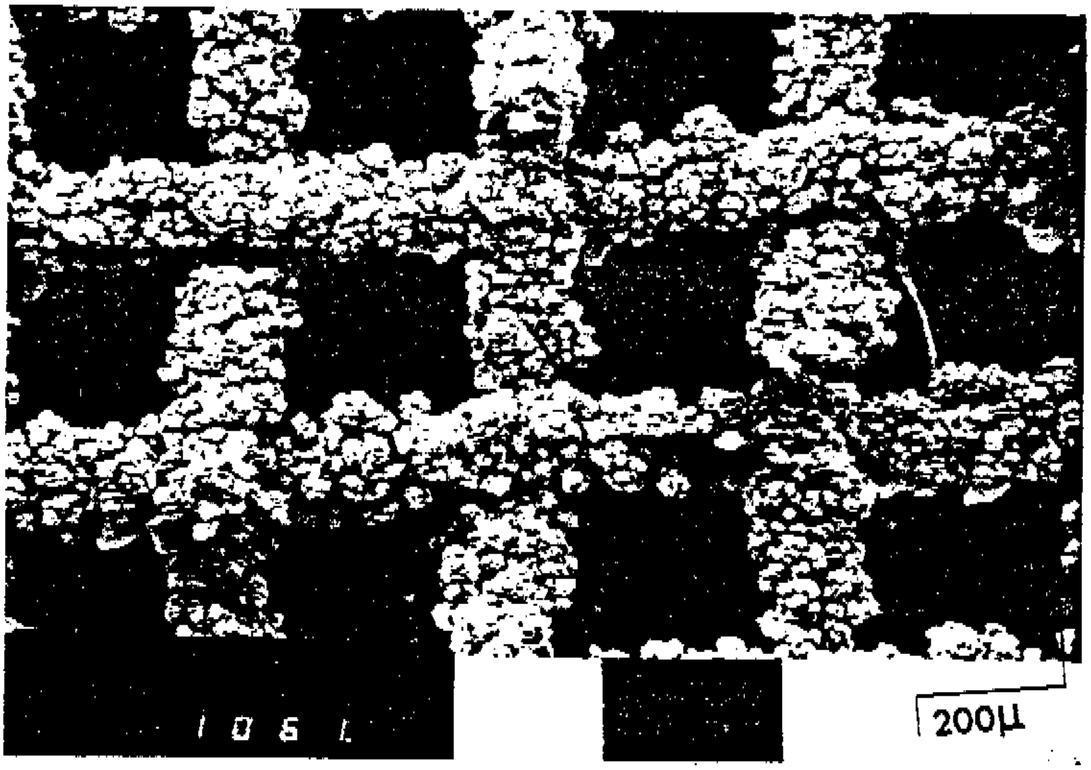

FIGURE 1 Top Sheet of Catalyst Pack

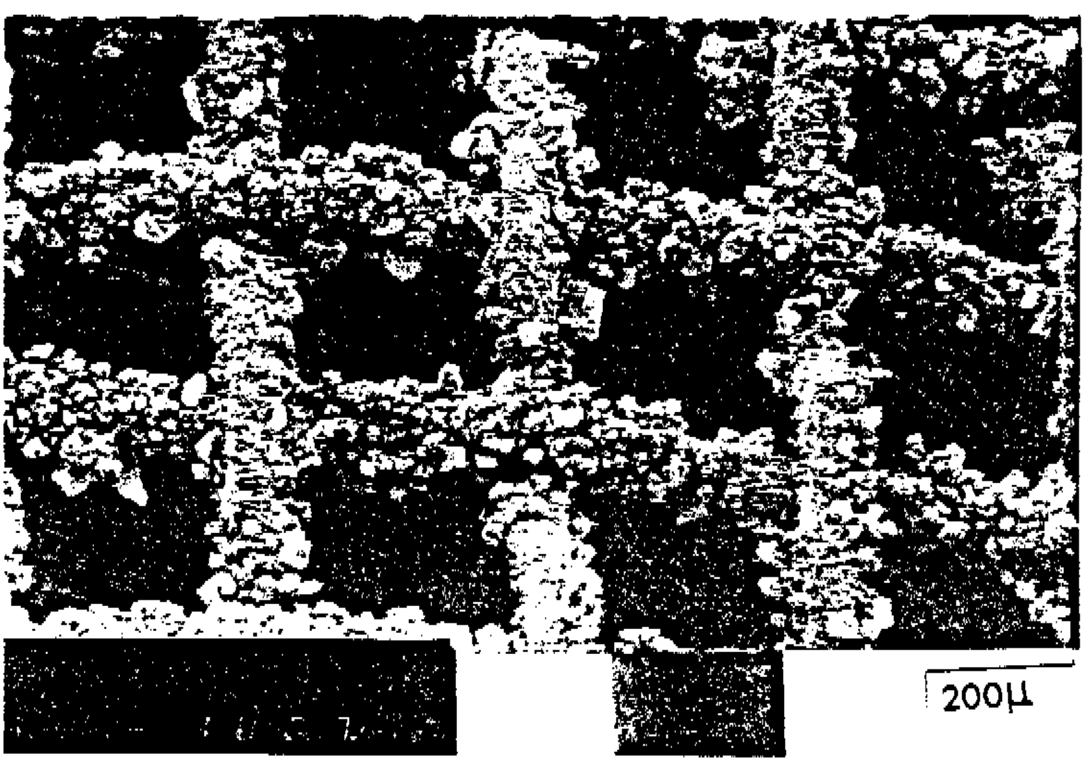

FIGURE 2 Third Sheet of Catalyst Pack

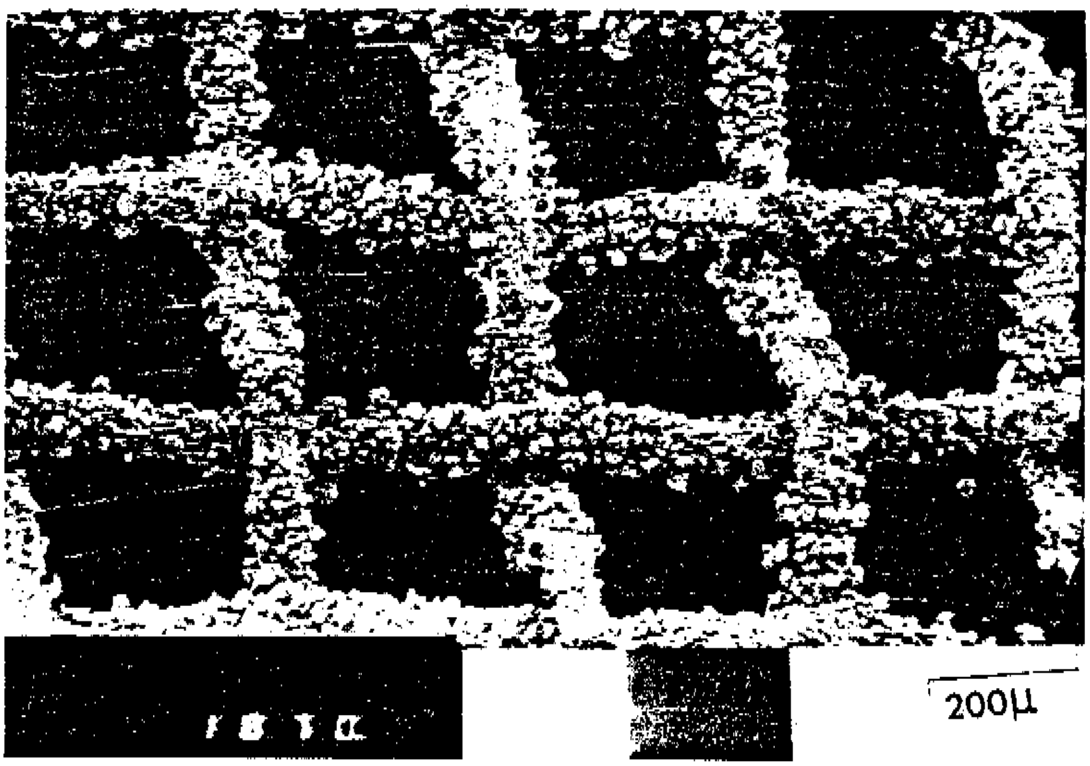

FIGURE 3 Sixth Sheet of Catalyst Pack

FIGURE 4 Fourteenth Sheet of Catalyst Pack

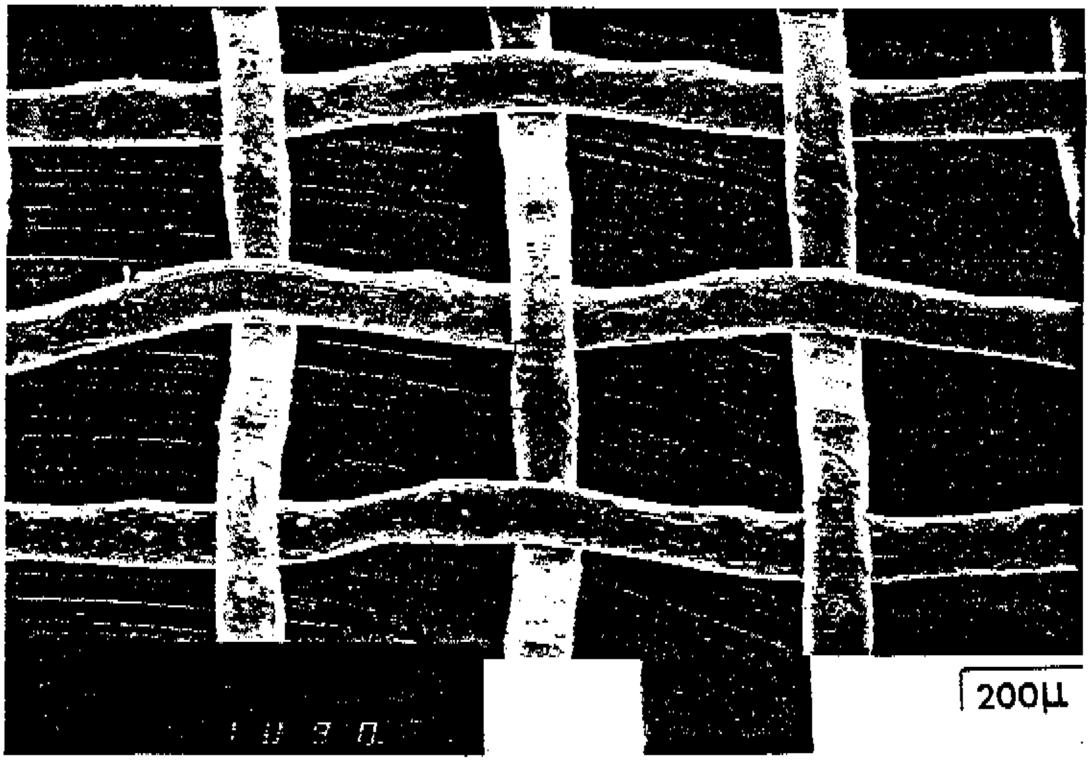

FIGURE 5 Nineteenth Sheet of Catalyst Pack

Gauze temperature is important because an increase improves efficiency although this also leads to greater precious metal losses.

Campaign length is critical and is controlled mainly by the fall-off in efficiency, although inevitably there is a conflict between efficiency loss and longer utilization.

The optimisation of these four factors is difficult and the conversion efficiency model, which will be discussed later, was therefore developed so the MOST PROFITABLE conditions can be readily determined.

4.1.1.2 Absorption Efficiency

The efficiency of the absorption column is essentially fixed by the plant design. However, to achieve a high efficiency close attention is required to the cooling efficiency, the mechanical state of the column internals and the free oxygen level of the tail gas. Inefficient tray performance significantly affects the overall efficiency and ammonia costs. This may be due to poor heat transfer through the cooling coils, or, for example, bad sealing or damage to the trays themselves.

Fisons has recently developed a model for the absorption process. Originally quite simple, it has been progressively refined and a good fit with the working columns is now obtained. The reactions within the column are complex and the model must cover four types of tray - absorption, oxidation, bleach and weak acid addition. Details of the tower geometry and the process conditions are fed to the model which then fits the desired NO_x discharge level by a series of iterative heat and mass balance calculations. Tray efficiencies and other operating factors can therefore be calculated and assessed.

The free oxygen in the tail gas significantly affects the absorption efficiency; the model prediction for this relationship is shown in Fig. 6. Profitable operation stems from selection of the minimum oxygen level required to achieve the desired NO_x discharge, so production rate can be maximised.

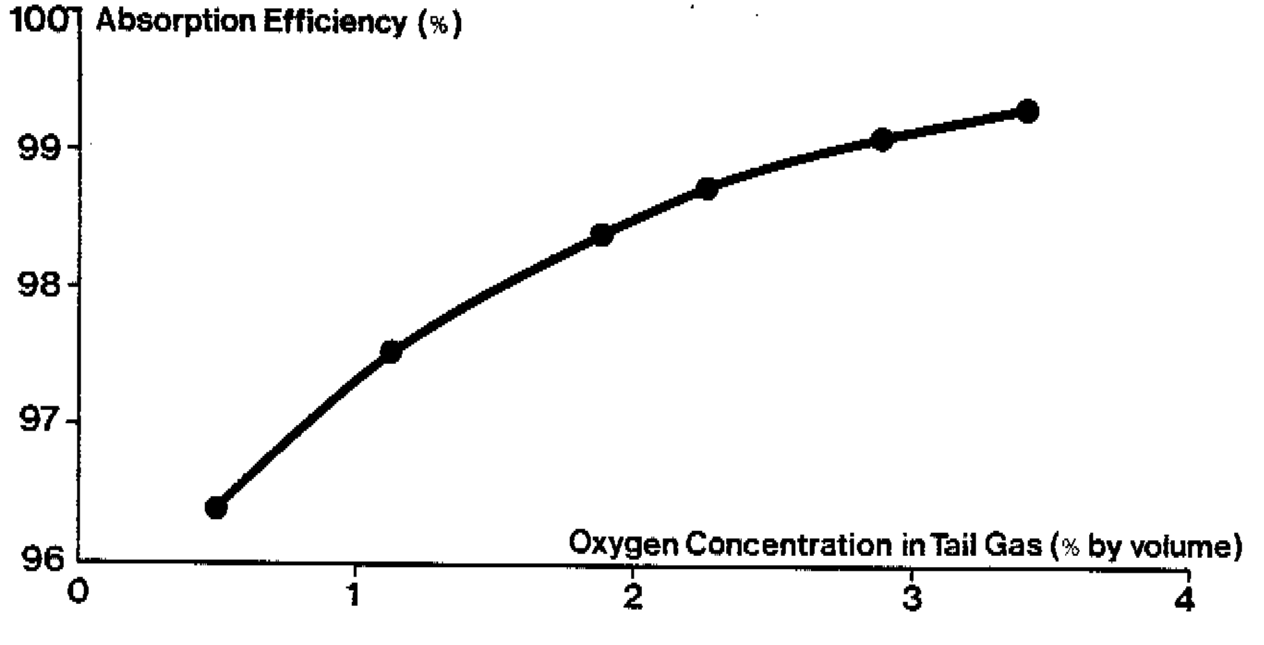

FIGURE 6
CALCULATED RELATIONSHIP BETWEEN ABSORPTION EFFICIENCY & TAIL GAS OXYGEN CONCENTRATION

4.1.2 Platinum/Rhodium Catalyst

It can be seen from Table 1 that the cost of the noble metal lost from the catalyst is significant (around $3 million per annum, before recovery in our case). The losses are dependent on factors such as operating pressure and temperature, the geometry of the converter, and ammonia/air purity. It is usual to adopt some form of platinum recovery - the main methods being:-

(1) Gold/palladium catchment packs

(2) Gaseous phase filtration

(3) Recovery from dusts and scale from equipment and tanks.

The first and second methods incur a pressure penalty and the benefit of the recovered platinum (35-70% of gross loss) must be balanced against the value of the lost acid. The third method is straightforward, and with considerable care and attention to detail, significant recoveries (5-20% of gross loss) are possible.

We have developed a mathematical model to determine the optimum recovery technique to use.

4.2 Utilities

The utility costs, apart from the steam credit in some processes, are not a major cost factor in nitric acid manufacture. In any event costs are minimized by use of good working practices and proven techniques. This involves the implementation of a sound water/steam management policy, which recognizes that no compromise on water treatment and system monitoring is acceptable. In essence, PROFITABLE OPERATION results from vigilance and effective monitoring.

4.3 Labour

The labour requirement for a particular plant is usually determined by local factors and cost reductions in this area are not easy. Recent advances in instrumentation, online analytical equipment and computer control, whilst reducing the need for intensive operator supervision, do not necessarily allow reductions in the labour force. Nevertheless, such developments do enable the plant to be operated consistently at maximum efficiency and hence MAXIMUM PROFITABILITY.

4.4 Maintenance

The main objective of any maintenance scheme must be to maximise the overall operating time at minimum cost. We have been able to progressively reduce our total maintenance expenditure whilst improving plant availability, as is shown in Fig. 7.

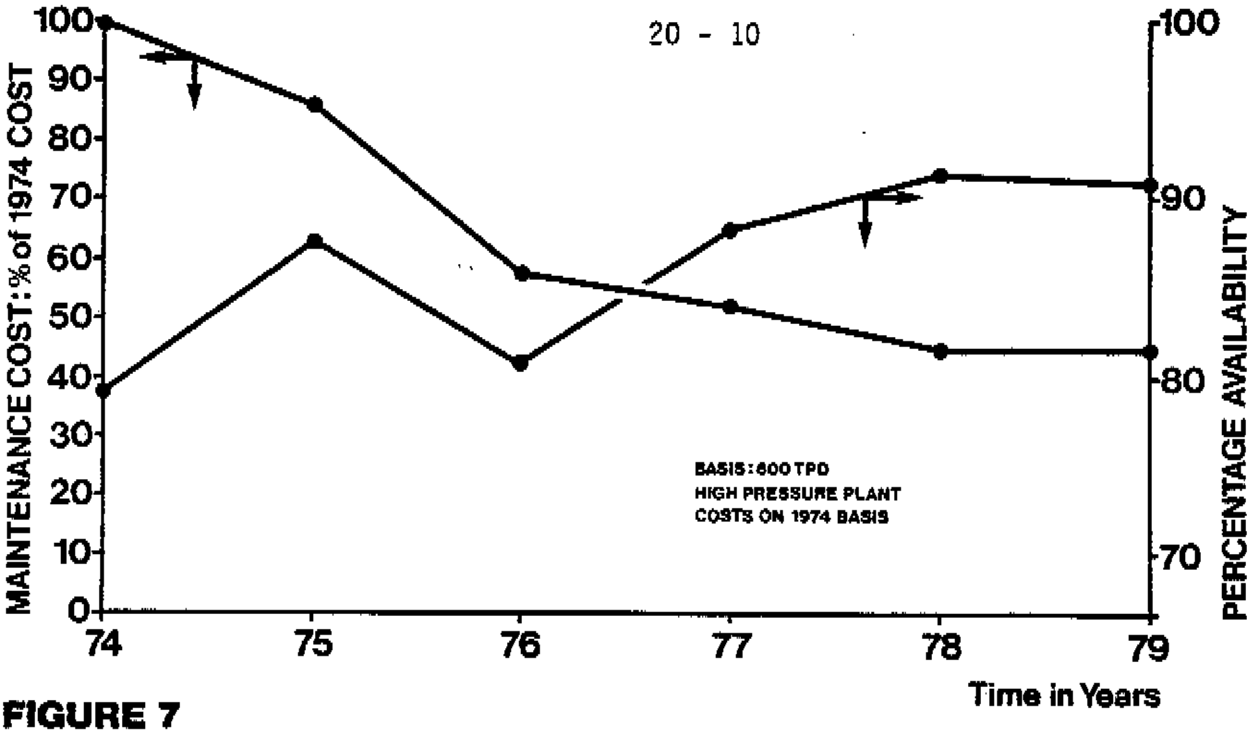

FIGURE 7
MAINTENANCE COSTS & UTILIZATION DATA

We have achieved this by better inspection, planning, and working procedures within the maintenance period. Three types of planned maintenance shutdown are used.

4.4.1 Gauze Changes - Planned Maintenance Shutdown

This is determined by the need to change the gauze and must be preceded by a thorough plant inspection to identify all the maintenance work required. During the shutdown close attention must be paid to the condition of all filtration equipment, to ensure that its performance is maintained throughout the next campaign. Some non-destructive plant testing is often programmed within the shutdown period to provide information for the work programme of subsequent planned shutdowns. Particular attention must be paid to areas where leaks can cause lost time after the ensuing plant start-up.

4.4.2 Major Shutdowns

The timing is dictated by the statutory requirements for pressure vessel inspection and the need for turbo-machinery overhaul, the latter forming the critical path on the shutdown plan. During this shutdown all major vessels are inspected, the opportunity being taken for cleaning to maintain satisfactory heat transfer performance. Extensive use of techniques such as the corrodograph (eddy current techniques) and ultrasonic inspection for the examination of vessel corrosion is made at this time. This information is vital for early identification of possible future problems and for the subsequent planning of replacements.

4.4.3 Planned Replacement Shutdowns

It is possible, by carrying out inspections and using past records, to predict when vessels require replacement. These are phased on a periodic basis and 5 to 10 year plans prepared. These shutdowns are planned so that other work is phased around the replacement task.

5. MAXIMISING PRODUCTION RATE

Profitable operation stems from constantly striving to run at the maximum instantaneous output, efficiently. This can be achieved by close attention to the following areas:-

5.1 Operations

5.1.1 Making Best Use of Raw Materials

We have already discussed the importance of air and ammonia purity: it is also vital to ensure that the maximum air and ammonia flows are used. On the air side, this is achieved by a combination of good maintenance and filtration to keep air compression equipment clean. For example, a small build-up on the compressor blades can easily lead to a 5% reduction in air throughput. Maximum cooling between the compression stages is also important, as is the minimization of pressure restrictions. We have fixed the maximum safe ammonia concentration at 11.5% by volume, but in order to do this good mixing of the gases is essential. Any oxygen which escapes the absorber represents a loss of nitric acid production and the plant should be operated at the minimum oxygen tail gas level commensurate with the required NO_x discharge.

5.1.2 Making Best Use of Cooling Water System

Open recirculatory cooling systems scale-up even with good treatment practices and a loss of heat transfer performance will result in rate reductions. This can be minimized by identifying the optimum cleaning times by regular heat transfer coefficient checks on the main exchangers. Performance can also be improved by the selective use of chilled water in critical items such as the absorption column.

5.1.3 Plant Monitoring

To realise the full production potential of all the items discussed in this report a meaningful data bank of the normal optimised operating condition is required. Operators log sheets can then be utilized to identify problems and potential losses soon after they occur. It is vital, however, that instrumentation is periodically maintained and checked so that comparative information is accurate.

5.2 Removal of Bottlenecks

A maintenance policy of planned replacement of equipment enables production bottlenecks to be systematically removed. This is particularly valuable for eliminating bottlenecks in the compressor and heat exchanger circuits.

6. MAXIMISING UTILIZATION

A high onstream factor is essential for profitable operation. Attention to the following points is necessary

6.1 Design Factors

6.1.1 Operations

Equipment must be run within original design tolerances and mechanical capability. Operation outside the design pressure, temperature and flow can induce premature failures from factors such as vibration, thermal and fatigue stressing and creep.

6.1.2 Exchanger Design

Severe corrosion can occur in heat exchangers, particularly where acid is condensing or reboiling. The exchanger must therefore be carefully sized so that the corrosive conditions occur either in sacrifical vessels of low cost, or where construction materials guarantee a long life. This has led to a more cost effective use of higher grades of stainless steel such as 25 Chromium: 21 Nickel and 25 Chromium: 22 Nickel: 2 Molybdenum, in the localised area where the corrosion occurs.

6.1.3 Flange Joints

In high pressure plants there are several major troublesome flange connections in the exchanger train. This problem is eliminated by initially ensuring the flange design is correct, then by using the best jointing material, and finally by correctly making the joint. The latter requires skill and experience although aids such as Bellvile washers help success.

6.2 Campaign Length

Plant cleanliness, catalyst pack configuration and a planned maintenance system that minimizes unplanned shutdowns are the major factors that improve plant utilization by extending the operating time between gauze changes.

6.3 Spares Policy

Continuity of operation is also protected by employing a sound planned replacement policy. The new vessel must be available before the existing vessel fails completely or the continuous maintenance and consequential loss costs are prohibitive. This aspect is demonstrated graphically in Fig. 8 where the net costs and hence optimum replacement time are determined.

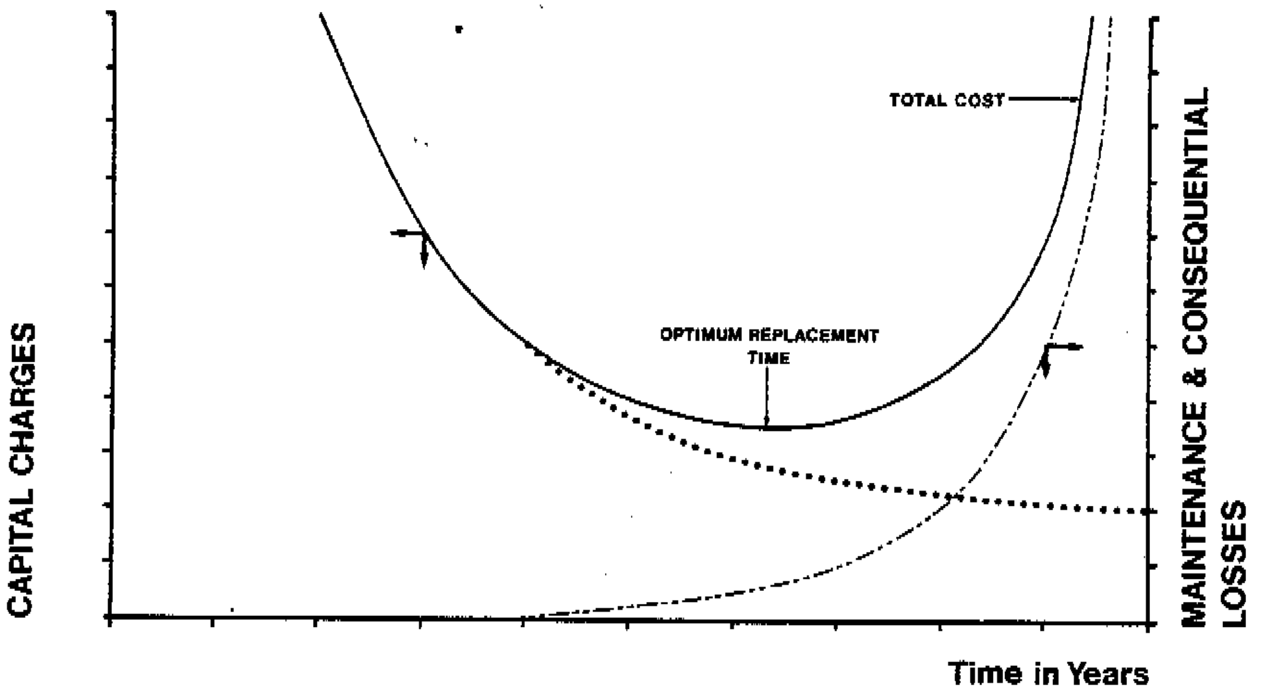

FIGURE 8
ECONOMICS OF SPARES REPLACEMENT

Unfortunately, the situation is not as simple as this as delivery time, material availability, and production requirements must also be considered. Nevertheless the principles are sound and providing inspection and maintenance procedures are good, a meaningful programme of design, procurement and installation can be prepared.

7. MAXIMISING PROFIT

So far the paper has concentrated upon the main operating factors that influence strategy. As we have seen these are often inter-reactive and we must now turn our attention to the question "How can we operate our plants more profitably?" PROFITABILITY is the key work here and it is important to appreciate that this is not necessarily operation at maximum materials efficiency. Our initial approach to the problem led to the development of a number of mathematical models. These can be used either in conjunction or individually to answer specific questions and to determine the optimum set of operating conditions for the case under consideration.

The system uses three models:-

(1) Conversion Efficiency Model

(2) Absorption Efficiency Model

(3) Platinum Recovery Model

The three are then combined in an overall profit model, which is then used to optimise profitably some of the variables in these areas.

7.1 The Conversion Efficiency Model

The model relates the chemico-physico elements of the conversion reaction to variables such as catalyst quantity, campaign length, gauze temperature, ammonia volume etc. It is checked against a series of very precise (±0.1%) conversion efficiency measurements taken throughout a typical run for each plant. An example of the actual and model predicted values is shown in Fig. 9.

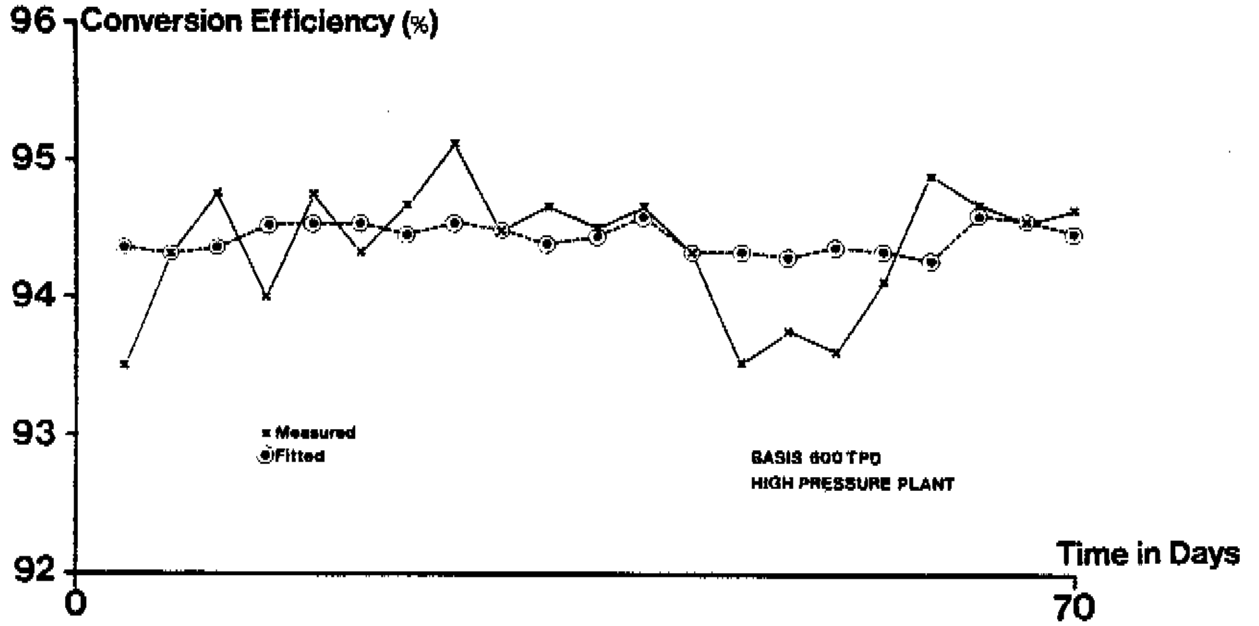

FIGURE 9
COMPARISON BETWEEN ACTUAL & MODEL PREDICTED CONVERSION EFFICIENCY

The model is used to examine many of the parameters that affect the conversion process. For example it can be used to evaluate the effects of changing the number of catalyst sheets in a pack. The model calculates the average conversion efficiency and optimises the campaign length for each case. Other plant operating conditions are also optimised or calculated. The results of such an exercise are shown in Table 5 for one of our plants operating with 20, 21 or 26 catalyst sheets. The optimised values and data are then used in the overall profit model to determine the most profitable conditions to use.

TABLE 5 USE OF CONVERSION EFFICIENCY MODEL

No. of Catalyst Sheets	26	21	20
Campaign Length (Days)	46	72	70
Ammonia/Air Preheat Temperature (^oC)	215	215	235
Ammonia concentration (% v/v)	11.5	11.5	11.5
Catalyst Temperature (^oC)	920	920	944
Oxygen ex Absorber (% v/v)	1.75	1.75	1.75
Absorber Efficiency (%)	98.35	98.35	98.35
NO_x ex Absorber (ppm v)	1960	1960	1960
Bleach Air flow (% of total)	21.6	21.9	21.9
Conversion Efficiency (%)	94.35	94.83	94.85

7.2 The Absorption Column Model

Some of the technical details of the model are discussed in Section 4.1. However, it is important to realise that, with its link into the profit model, is is much more than a simple model for the design of an absorption column. Its real value to us, as an operating company, is that it can assist in the decision making process as well as performing the standard design function. It is invaluable as a trouble-shooting aid where various scenarios can be technically and commercially assessed as the main step in the problem solving process. It can be used to optimise plant operating conditions throughout the year and to advise on factors such as the MOST PROFITABLE time to clean the tray cooling coils.

It can, of course, be used as a design aid for assessment of proposals such as extending columns to improve absorption efficiency, or optimisation of the cooling water distribution to the trays.

7.3 The Platinum Recovery Model

As discussed in Section 4.1, the choice of a recovery system from an economic standpoint involves a balance between the obvious cash benefit from recovery against the costs necessary to achieve it. These costs are derived from the platinum loss and recovery theory, the filter and catchment pack operating performance, the characteristics of the compression set and the overall energy balance for the plant. The link into the profit model enables the technical performance to be translated into a net total profit from following a particular course of action. The model is updated periodically and the overall economics of platinum recovery are rechecked. The optimum solution varies from time to time as relative costs and production requirements change. The results of a recent examination for two of our plants is shown in Table 6.

TABLE 6 PLATINUM RECOVERY STRATEGY

Plant	Capacity TPD	Recovery System	% Recovery	$/annum Annual Profit
A	270	Mechanical Filter	34	25,000
A	270	Catchment Pack	70	Loss
B	500	Mechanical Filter	34	55,000
B	500	Catchment Pack	70	140,000

This shows quite differing conclusions for each plant. The main reason for this is the different plant design characteristics, which lead to different pressure and hence cost penalties. The model checks therefore confirm or otherwise that the system being used at that time, is still the most profitable.

7.4 The Profit Model

The last part of the chain is the overall profit model; this is a standard optimisation program which manipulates the variables in a systematic fashion to find the setting that yields maximum profit. A schematic chart given in Fig. 10 shows some of the qualitative links involved in the overall model. This shows the complex interaction of factors affecting profitability.

If we take the example used in Section 6.1, investigating the effect of the numbers of catalyst sheets in the pack, the overall effect on profit can be calculated. This involves allowing for the cost of the catalyst losses, additional catalyst costs, the value of the additional steam produced, the cost of the ammonia and the value of the acid. The overall results show that an additional profit of $250,000/annum can be obtained with 21 gauzes compared to 26, and $340,000/annum with 20 gauzes compared to 26.

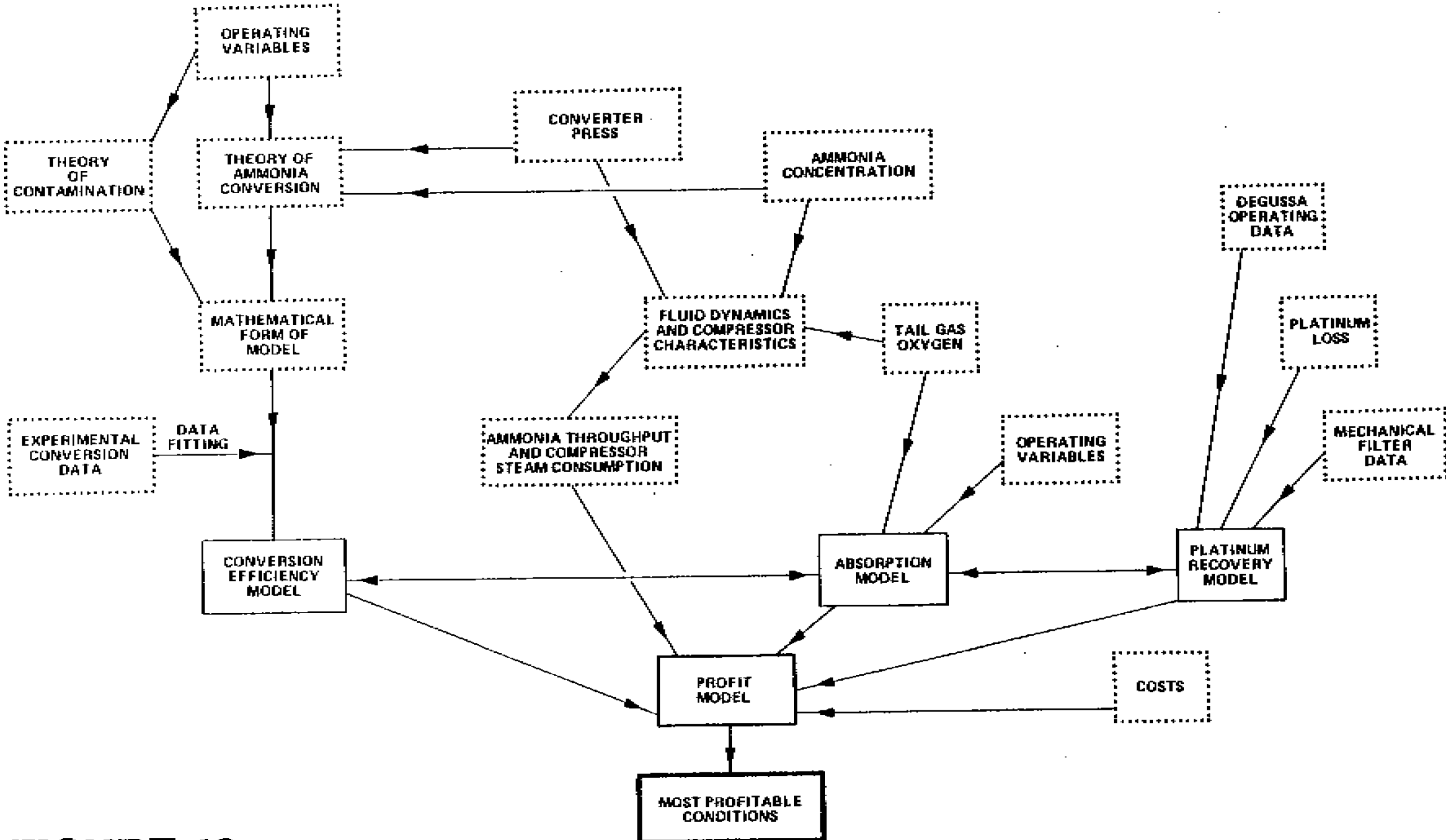

FIGURE 10
SCHEMATIC CHART FOR OVERALL PROFIT MODEL

FIGURE 10

8. CONCLUSIONS

At this point in time, as no major breakthrough in nitric acid technology is expected, and as unit costs rise sharply, profitable operation of plants is all important. The paper identifies most of the factors that affect profitability and the profit modelling techniques offer an opportunity to explore new areas in more detail more accurately.

Although the practical use of these techniques in nitric acid manufacture is relatively new, the development of the mathematics and computer knowledge is well worthwhile and we are now poised to reap the benefits in the forthcoming years.

9. ACKNOWLEDGEMENTS

The authors would like to thank the Directors of Fisons Limited - Fertilizer Division, for permission to publish this paper. Thanks are also due to all in Fisons Limited - Fertilizer Division, whose work has contributed to this paper, especially Dr. P. Pickwell for development of the conversion efficiency, platinum recovery and overall profit models, and Mr. A.J. Garland for his work on the absorption efficiency model.

TA/80/20 The profitable operation of nitric acid plants by J.K. Bradley, M.D. Pask, R.W. Stannard, Fisons Ltd, United Kingdom

DISCUSSION : (Rapporteur J. Eimers, Uhde GmbH, Germany)

Q - Mr. A.C. van KLEEF, UKF, Netherlands

In figure 7, on page 10, you indicate that the availability is over 90% now, which is not bad for a high pressure plant.

Could you explain why it has taken you so long (3-4 years) to achieve that figure, which, in my opinion, is unusual for nitric acid plants.

A - The reason why it took so long time is the extent of equipment replacement. At first, it took some time to find out what was wrong and then we needed time for ordering and delivery.

Q - Mr. L.K. RASSMUSSEN, Superfos, Denmark

On page 20-14, you are talking about very precise conversion efficiency measurements.

Would you please tell how these measurements were made?

A - The precise conversion efficiency measurements are made by taking simultaneous samples of process gases before and after the catalyst. The sample after the gauze is reacted with hydrogen peroxide and then titrated to a pH of 6.1 with 0.1 N sodium hydroxide. The sample from before the gauze is titrated to a pH of 5.55 using 0.1 N sulphuric acid. The proportion of fixed nitrogen after and before the catalyst can be calculated and the ratio gives the conversion efficiency.

Q - Mr. S. LANGE, COFAZ, France

When you change platinum gauzes, do you systematically put on top of the catalyst pack gauzes which have already run one production cycle? If so, did you prove that it was the best operating system?

A - Yes, we do reuse gauze material - this can take two forms - inversion of the pack at the gauze change and making up the new pack with new gauzes, or reuse of individual catalyst sheets after pickling. There is no simple answer to the best practice as this will depend on a number of factors such as:
The cost of ammonia
The physical strength of the used sheet
The plant contamination (pickling does not remove all the impurities)
The cost of new gauzes, and refining and fabrication costs.

We use the platinum model to help predict the optimum, which usually involves some reuse of gauzes.

Q – Mr. A. CLAERBOUT, Société Carbochimique, Belgium

In view of the ammonia pressure drop, is it not preferable to invest in an increased absorption, rather than to destroy NOx?

A – Again, there is no easy answer to the most profitable course of action. Reduction of NOx levels by extended absorption obviously improves overall nitrogen efficiency. However, the cost of the absorption column to achieve low levels (200 ppm NOx) is very high. It is a relatively more attractive proposition for new plants rather than existing ones. Invariably existing plants are boosted at the same time as abating which again affects the economics. The destructive methods, and there are several systems on the market, tend to be relatively cheap in capital cost terms although more expensive in operating costs. The economics of these units are in some cases linked into the overall plant and site energy balances, e.g. the types that incorporate steam generation may be particularly economic on a site with an overall steam deficiency. The optimum decision therefore will vary from site to site.