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*\*In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

UREA AS AN AGENT IN THE DESTRUCTION/RECOVERY OF NO<sub>x</sub>  
IN NITRIC ACID AND NITROPHOSPHATE FERTILIZER PRODUCTION

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### INTRODUCTION

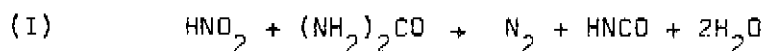
This paper deals with two principally different applications of the liquid phase reaction between urea and nitrous acid in the abatement of nitrogen oxide emission from Norsk Hydro's fertilizer plants at Porsgrunn, Norway.

The first application is the use of this reaction to reduce nitrogen oxides in the tail gases from the nitric acid plants by absorption and reaction, and where the existing facilities in the plants made this choice of process attractive.

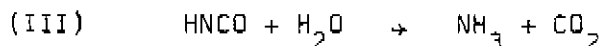
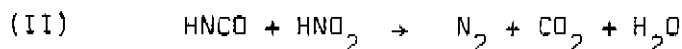
The second application relates to the digestion of phosphate rock in nitric acid in our nitrophosphate plant, where the addition of urea reduces drastically the amount of nitrogen oxides formed.

### REACTIONS OF UREA AND NITROUS ACID

Werner (1) has postulated the following mechanism for the reaction of nitrous acid and acid urea solutions :

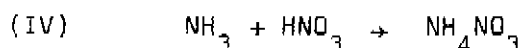


followed by the two simultaneous reactions :

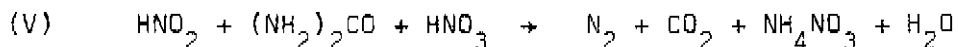


Reaction (I) was considered to be the step determining the rate as (II) and (III) were fast reactions.

In nitric acid solutions the ammonia produced in (III) will form ammonium nitrate :



In our laboratory studies of the reaction under design conditions for nitrogen oxide absorption where the concentration of nitrous acid is low, we have found that the reaction represented by eq. (II) can be neglected compared to (III). The overall reaction will then be :



Kinetic measurements on the reaction showed that under the actual conditions the reaction rate can be represented by the equation :

$$(IV) \quad -\frac{dC_{\text{HNO}_2}}{dt} = k \cdot C_{\text{HNO}_3} \cdot C_{\text{HNO}_2} \cdot C_{\text{urea}}, \text{ where}$$

$$k = 0.25 \text{ l}^2/(\text{mole})^2 \cdot \text{sec. at } 25^\circ \text{ C}$$

## NITROGEN OXIDE ABATEMENT IN TAIL GASES

### Regulations for nitrogen oxide emissions

Until a few years ago any nitric acid plant could be spotted by the yellow-brown plume from the emission stack. However, as public opinion on pollution has become more out-spoken, new and stricter regulations on nitrogen oxide emission are being enforced. In the United Kingdom, for example, the standard for new plants restricts the emissions to 1000 ppmv while the U.S.A. the Environmental Protection Agency has recently published a standard for new plants at 3 lb  $\text{NO}_2$ /t  $\text{HNO}_3$  which corresponds to less than 250 ppmv.

Restrictions are also being made on older plants designed for emissions up to 2-3000 ppmv giving rise to a need for tail gas treatment to meet future regulations.

### Methods for tail gas treatment

Catalytic combustion of nitrogen oxides with hydrogen or hydrocarbons is the most common technique for tail gas treatment today. However, while all  $\text{NO}_2$  is easily reduced to NO (decolorization), it is necessary to consume virtually all the oxygen before the NO is reduced to elementary nitrogen. As temperature restrictions for the catalyst call for more than one stage, or recycling, if the oxygen content exceeds 3 %, this method is not quite suitable for older plants working at considerably higher oxygen values for the tail gas.

It is claimed (2) that a principal concern in the operation of a catalytic reduction unit is the stability of the catalyst (carbon deposit, poisons). There is also some uncertainty that the offgases from the catalytic unit may contain other pollutants (unburned hydrocarbons, etc.) which may give potential problems in the light of possible future restrictions.

A catalytic process using ammonia as fuel is reported (3) to obtain complete reduction of NO without interference by the oxygen present. No experience

with industrial installations is reported.

Absorption on molecular sieves : This method seems very attractive as the adsorbed nitrogen oxides can be returned to the process after desorption. Pilot plant tests are reported (4) to be promising, but experience from technical installations is still lacking. This method seems to have a promising potential in combination with high pressure/high efficiency nitric acid plants in the future.

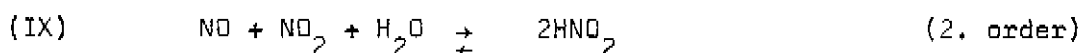
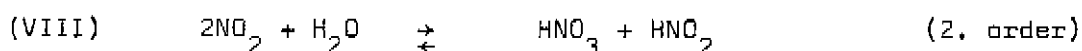
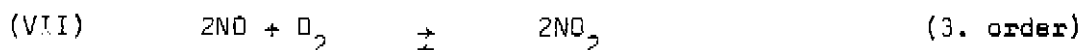
Absorption with chemical reaction : Absorption in alkaline liquids is probably the oldest method for recovering nitrogen oxides from the tail gas by formation of nitrites. The method has the disadvantage of producing a liquid waste stream which is difficult to dispose of.

Ammonia or ammonium carbonate solutions give a product stream that can be converted to ammonium nitrate for utilization. The disadvantages lie in the necessity for low absorption temperatures to suppress mist formation and in the safety hazard presented by unstable ammonium nitrite.

An acid urea solution gives the same high absorption rate as alkaline solutions. It yields ammonium nitrate as a reaction product. The disadvantage of the process is the substantial net loss of nitrogen compounds due to reaction.

#### The chemistry of nitrogen oxide absorption

In nitric acid production nitrogen monoxide from the catalytic combustion of ammonia is considered to react according to the following consecutive reversible reactions :



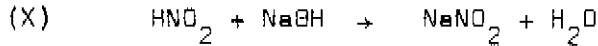
where reaction (IX) during acid production runs from right to left, eq. (IXa), returning NO and NO<sub>2</sub> to the gas phase for renewed oxidation and absorption, and rendering a stationary state concentration of HNO<sub>2</sub>.

The rate of reaction (IX) is considerably higher than of (VII) and (VIII), which in general will represent the rate determining steps for nitric acid production. The rate of reaction increases with decreasing temperature.

In a given nitric acid plant optimal conditions correspond to an optimal oxygen concentration, giving a corresponding state of oxidation (NO<sub>2</sub>/(NO+NO<sub>2</sub>)) in the tail gases. These optimal conditions will depend mainly on the absorption pressure chosen, but also on the absorber construction. For atmospheric units the optimal oxygen content is higher (6-8 %) and the oxidation state lower (0.2-0.3) than for pressurized absorbers (2-4 % O<sub>2</sub> and 0.4-0.5, respectively).

As the apparent overall reaction order will be higher than 2 with respect to pressure, substantial improvements in absorption efficiencies can be achieved only through increased pressures.

When treating nitric acid plant tail gases by absorption the rise in absorption rate is achieved by continuously removing the nitrous acid by reaction. In alkaline liquids nitrite is formed :



and in acid urea solutions the nitrous acid reacts to form nitrogen, carbon dioxide and ammonium nitrate according to eq. (V).

When the concentration of  $\text{HNO}_2$  is being kept sufficiently low, the relatively fast reaction (IX) will run irreversibly from left to right giving a substantial rise in the absorption rate. Also the rate of reaction (VIII) will increase as this reaction also becomes irreversible.

The reaction products from pilot plant tests indicate that more than 90 % of the absorption of nitrogen oxides from tail gases (where  $\text{NO}_2/\text{NO} < 1$ ) can be related to the absorption of equimolar quantities of  $(\text{NO} + \text{NO}_2)$  (reaction (IX)).

As expected, pilot plants tests have shown that absorption rates in alkaline and in acid urea solutions are substantially the same.

#### Technical installations for tail gas treatment

The Norsk Hydro nitric acid plant at Porsgrunn has a total capacity slightly in excess of 500 t N/d. It consists of 3 different absorption plants emitting their tail gases to the atmosphere through a common 100 m high stack. The arrangement is schematically shown in Fig. 1.

The oldest plant is an atmospheric unit consisting of 7 parallel lines (A-G) each having 7 packed towers in series. Except for the last tower in the three lines (A-C) which are built of stainless steel, the absorption towers are constructed in granite. To avoid leakages of acid the granite towers must work at slightly reduced pressure. This plant, now being run at reduced capacity, has an overall absorption efficiency of 98.4 %, giving tail gases containing 6-8 %  $\text{O}_2$  and  $\sim 1500$  ppmv  $\text{NO}_x$  of which 25 % is  $\text{NO}_2$  and 75 %  $\text{NO}$ .

The next plant has medium/low pressure absorption units (3 ata) originally built in the 1950's and later expanded. The absorption efficiency of this plant is  $\sim 98$  %, the tail gas leaving the expansion turbine has a temperature of  $80^\circ \text{C}$ . This gas contains 4 %  $\text{O}_2$  and  $\sim 2000$  ppmv  $\text{NO}_x$  of which 35 % is  $\text{NO}_2$ .

The newest plant is a medium pressure (5 ata) plant having 99 % absorption efficiency. The tail gas contains 3 %  $\text{O}_2$  and 900 ppmv  $\text{NO}_x$  of which 45-50 % is  $\text{NO}_2$ , and leaves the plant at a temperature of  $100^\circ \text{C}$ .

As a result of the stricter regulations foreseen on nitric oxide emission in Norway the Company decided that measures should be taken to reduce this emis-

sion as soon as technologically feasible. Special attention was given to the older plants which were most vulnerable because of the higher specific emission.

Different abatement methods were considered. To assure a visible effect it was evident that all tail gases from the three plants had to be treated, and it seemed impractical to use different methods for the three plants. The high oxygen content and large volumes of tail gases from the atmospheric units ruled out catalytic combustion.

Absorption methods seemed more attractive as they would allow to use the existing equipment and thus to reduce building costs and time. As absorbents both ammoniated liquids and acid urea solutions were considered acceptable, as the ammonium nitrate produced could be utilized in the fertilizer plants on the site.

The use of ammonia would necessitate additional equipment to reduce safety hazards and to secure a sufficiently low temperature to avoid ammonia losses and pollution of the exit gas.

In the autumn of 1973 it was decided to start the construction work necessary to implement urea treatment of the combined tail gas from the three plants. The lay-out chosen will allow future installations for absorption in ammonia if desired. The treatment plant is expected to be in operation in the summer of 1974.

The lay-out of the tail gas treatment plant is given in fig. 2, where it is shown that the last absorption towers of each line of the atmospheric plant are separated on the liquid side from the nitric acid production and utilized for tail gas absorption.

Gas system : Construction changes consist mainly in the rearrangement of gas ducts. The tail gases from the pressure plant will be connected to the three stainless steel towers (A-C) for treatment. To simplify construction work the tail gases from the atmospheric plant will not be distributed evenly between the remaining 4 granite towers. Instead, all the gas from the first four lines (A-D) is taken to the fourth tower (D) while for the last three lines (E-G) the gas duct system will remain unchanged.

In this way the granite absorption towers will operate slightly below, and the three S.5. towers slightly above atmospheric pressure.

The reduced absorption volume in the atmospheric plant will of course lower the absorption efficiency of this nitric acid plant and therefore increase the urea consumption for tail gas treatment.

Liquid system : Each absorption tower will have a separate liquid recirculation system, but will be interconnected with level control to the next tower so that the absorption liquid will flow through the systems from G to A. The major part of the urea feed liquor and the nitric acid is fed to tower G by metering pumps controlled by the liquid level of that tower. To avoid exces-

sive urea concentration leading to precipitation of urea nitrate in the liquid, part of the feed liquids are also fed to tower C.

Overall control of the process is carried out on the last tower (A) in the system. Here pH-control adjusts the concentration of nitric acid to the desired value by administering acid to the towers A and B. Also, a liquid density control system feeds additional water to the same two towers to balance evaporation and control the ammonium nitrate concentration. The discharge of ammonium nitrate product solution is controlled, based on continuous measurement of the urea concentration, thus keeping this concentration at the minimum level necessary for obtaining a reasonable absorption efficiency in tower A.

This control system will keep the urea and nitric acid concentrations within an optimal range of absorption efficiency throughout the towers C to G.

#### Pilot plant investigations

Comprehensive studies of absorption efficiencies and automatic control of the process have been made in a pilot plant using the relevant gas and liquid compositions. In these investigations we have chosen to express the gas load per unit wetted absorption surface ( $m^3$  gas/ $m^2$ , hr) rather than as a function of absorber volume.

The technical absorbers have a volume to surface ratio four times larger than the pilot plant. Although it should be expected that the larger volume will increase the oxidation and thus improve further the absorption efficiency, this is not taken into account by the scale up procedures.

#### Efficiency and economy of the process

Pilot plant and short time full scale tests indicate that the average absorption efficiency of  $NO_2$  will be better than 70 %. We therefore expect to achieve a virtually colorless exit gas, mixed, however, with condensing steam caused by evaporation from the absorption liquid in the absorbers for the pressure plant tail gas (where the temperature will be 30-35° C).

The emission is expected to be reduced by 44 %, i.e. from the present 1525 ppmv to 850 ppmv.

Per metric ton of nitric acid produced (as 100 %) the consumption/recovery of nitrogen will be :

Consumed urea :	7.8 kg/t $HNO_3$
" nitric acid :	8.2 "
Reduced production of nitric acid :	1.2 "
Produced ammonium nitrate :	10.4 "

The net loss of nitrogen, including production loss in the tail gas treating plant, is expected to be 9 kg N/t N produced as acid, equivalent to an efficiency reduction of 0.9 %.

As already mentioned, the full scale process is scheduled to be in operation in the summer of this year. The authors thus expect to be able to give further information on practical performance and experience when presenting this paper.

## SUPPRESSION OF NITROGEN OXIDE FORMATION IN THE NITROPHOSPHATE PROCESS

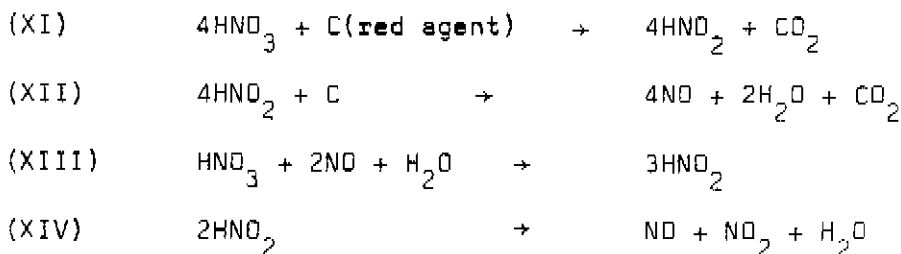
### Process description

Norsk Hydro built its first NPK plant based on the Odda process in the late thirties. Since that time extensive development work has been carried out within the Company to improve production technique and product quality. Today, Norsk Hydro has three NPK plants in operation with a total capacity of about 5000 tons/day, and the prilled NPK product represents the backbone of the Company's fertilizer production.

The Norsk Hydro NPK process has been presented previously and detailed descriptions are available elsewhere (5, 6). To facilitate the understanding of the urea addition scheme, a flowsheet of the process is shown in fig. 3. In short, phosphate rock is digested in 58 %  $\text{HNO}_3$ . The digestion liquor is cooled at about  $-5^\circ \text{C}$ , and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  is crystallized and removed by filtration. The  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  is processed into calcium nitrate fertilizer, or converted to ammonium nitrate and calcium carbonate by the reaction with ammonia and carbon dioxide. The mother liquor from the  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  filtration is neutralized with ammonia, the N/P-ratio is adjusted to the desired value by ammonium nitrate addition, and the water content is reduced to about 0.5 % by superevaporation. The resulting NP-melt is, if desired, mixed with potassium salts and micronutrients and prilled. The product is cooled, screened and conditioned prior to being sent to bulk storage.

### Nitrogen oxide formation

The formation of nitrogen oxides ( $\text{NO} + \text{NO}_2 = \text{NO}_x$ ) in the process results from the reduction of nitric acid when it acts as an oxidizing agent. Reducing agents present in commercial phosphate rocks (sulphides, organic matter etc.) reduce nitric acid via nitrous acid into  $\text{NO}_x$  during rock digestion. The nitrous acid probably serves as an autocatalytic carrier in a chain reaction :



The amount of nitrogen oxides formed in the process is highly dependent on the type of phosphate rock employed. Traditionally, Norsk Hydro has been



using Kola rock which is a high grade rock containing few reducing impurities thus yielding very little  $\text{NO}_x$  during digestion. During the last decade or so, however, the process has been adapted to the use of other lower grade phosphate rocks. Most of these rocks contain considerable amounts of impurities which will reduce nitric acid. This point is illustrated in fig. 4 where the  $\text{NO}_x$  formation during digestion is shown for some commercial phosphate rocks  $\times$  (at zero urea addition in fig. 4).

The increasing use of lower grade phosphate rocks in our NPK plants, which has been a necessity as our production has expanded, has coincided with the adoption of stricter laws and regulations concerning air pollution in Norway. Thus, during the last few years we have spent considerable time and effort for increasing the efficiency of the pollution abatement systems in the plant, such as scrubbing towers etc., and at the same time looked at ways of reducing the emission of undesirable gases from the process itself by altering process conditions, or by chemical means such as urea addition.

#### Experimental studies

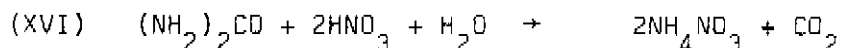
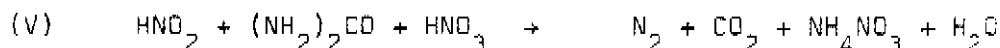
Around 1970 an experimental program was started to study the effect of urea as an inhibitor of nitrogen oxide formation in our nitrophosphate process. As previously discussed in this paper the reactions of urea and nitrous acid are known, and assuming the chain mechanism of nitric acid reduction to be correct, the addition of urea to the phosphate rock digestion would conceivably reduce the degree of nitric acid reduction.

Due to the possibility of adverse effects in the nitrophosphate process itself and in the physical properties of the final product caused by urea addition, extensive studies were carried out in the laboratory and in our nitrophosphate pilot plant. As the results of these studies became available, the experiments were extended into the plants. During the last 2-3 years urea has been used on an experimental basis in the plants. To-day, permanent urea addition equipment have been installed in the two NPK plants at Porsgrunn and urea addition is now done currently.

The results of the experiments are summarized below.

#### Reactions

Our laboratory studies indicate that the following overall reactions take place when urea is added to the digestion liquor :



Any urea remaining after the acid section of the process, i.e. digestion, crystallization and filtration, will probably be hydrolyzed during neutralization and super evaporation. Negligible amounts of urea were found in the final product (< 0.001 %).

### Reduction in NO<sub>x</sub> formation

The best effect of urea addition on NO<sub>x</sub> formation was obtained when urea was added to the first of the two consecutive digestion vessels. This is not very surprising, since for most phosphate rocks, more than 98 % of the rock is digested there. Identical results were obtained using solid urea and aqueous urea solutions.

The effect of urea addition on NO<sub>x</sub> formation is shown in fig. 4. The data shown were obtained during plant experiments of several days duration. Solid urea was fed to the first digestion vessel, and the NO<sub>x</sub> content of the exhaust fumes from the acidic section of the plant was measured upstream the scrubber system.

Fig. 4 shows that urea addition to the digestion drastically reduces the NO<sub>x</sub> formation. It is also evident that the effect depends on the type of phosphate rock used.

There appears to be a threshold value of urea addition below which the urea has only a minor effect on NO<sub>x</sub> formation. By increasing the urea addition beyond this value there is a rapid reduction in the NO<sub>x</sub>-formation. At higher urea addition rates the NO<sub>x</sub> formation seems to converge towards a value of about 2.5 kg NO<sub>x</sub>-N/t P. Whether any deeper significance should be attached to this value is uncertain. The most probable explanation is that this NO<sub>x</sub> is actually made up of nitric acid vapours produced by the process. There is no practical way of distinguishing between the NO<sub>x</sub> and the nitric acid vapours when analyzing the exhaust fumes.

### Properties of the final product

Storage tests of 12 months duration in bulk and bags showed no deleterious effect on the storage properties of the NP and NPK products. Neither was the thermal stability of the products adversely affected. As discussed above, no urea was found in the product at normal addition rates. By simulating overdosage of urea by a factor of 10, the content of organic matter (mainly urea and some biuret) in the product amounted to about 0.02 %. No other organic components could be found.

### Effect on operation

The operation of the plant was not affected by the use of urea when the addition of the urea was done in the prescribed manner, neither was any adverse effects observed in the calcium nitrate and conversion processes.

Precautions had to be taken when starting the addition of urea, especially when using phosphate rocks giving a high rate of nitrogen oxide formation. To avoid too rapid a reaction, resulting in foaming and splashing of the liquor, the urea addition had to be increased successively over a period of 2-3 hrs until the desired level was reached.

As discussed above, both solid urea or an aqueous solution may be used. We found it practical to use solid urea and to interconnect the operation of

the phosphate rock and urea feeds. Scrap urea available on the plant site can well be used.

### Investment and cost

The investments required for the purchase and installation of the necessary equipments for addition of solid urea amounted to about \$30 000 for each plant.

It is very difficult to assess the operating cost of the urea addition scheme exactly. The operating cost is :

$$\begin{aligned}
 \text{Cost} = & \text{ (Labour, utilities, maintenance, capital cost, etc.)} \\
 & + \text{ (urea feed) (price of urea)} \\
 & + \text{ (HNO}_3 \text{ converted to N}_2 \text{ in reactions with urea) (price of HNO}_3\text{)} \\
 & - \text{ (urea recovered as } ^2\text{NH}_4^+ \text{) (price of NH}_4^+\text{)} \\
 & - \text{ (reduction in HNO}_3 \text{ converted to NO}_x \text{) (price of HNO}_3\text{)}
 \end{aligned}$$

Based on careful laboratory studies and our price relations it appears to us that the positive and negative factors are roughly in balance for all the phosphate rocks investigated.

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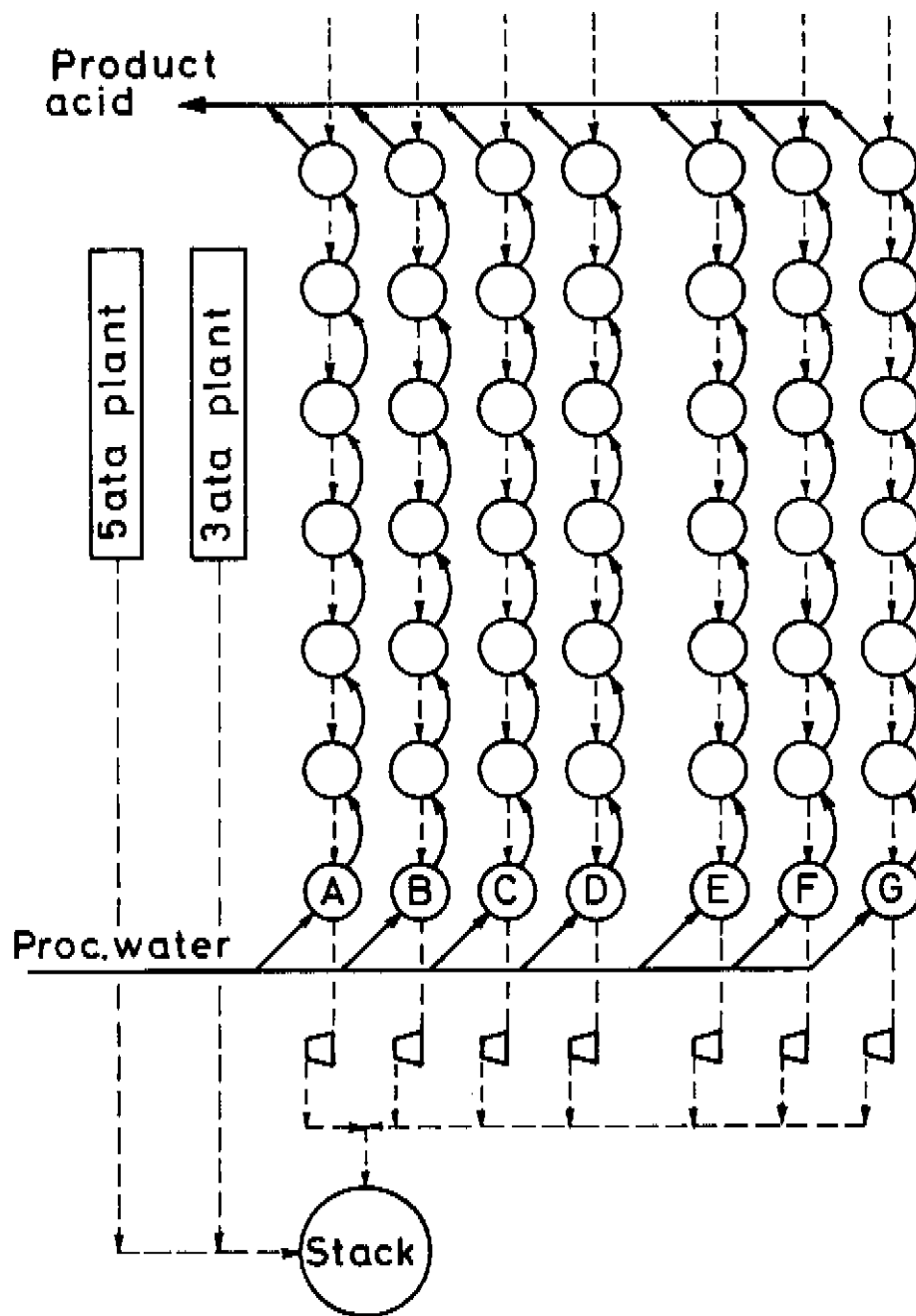


Fig.1. Present nitric acid absorption system.

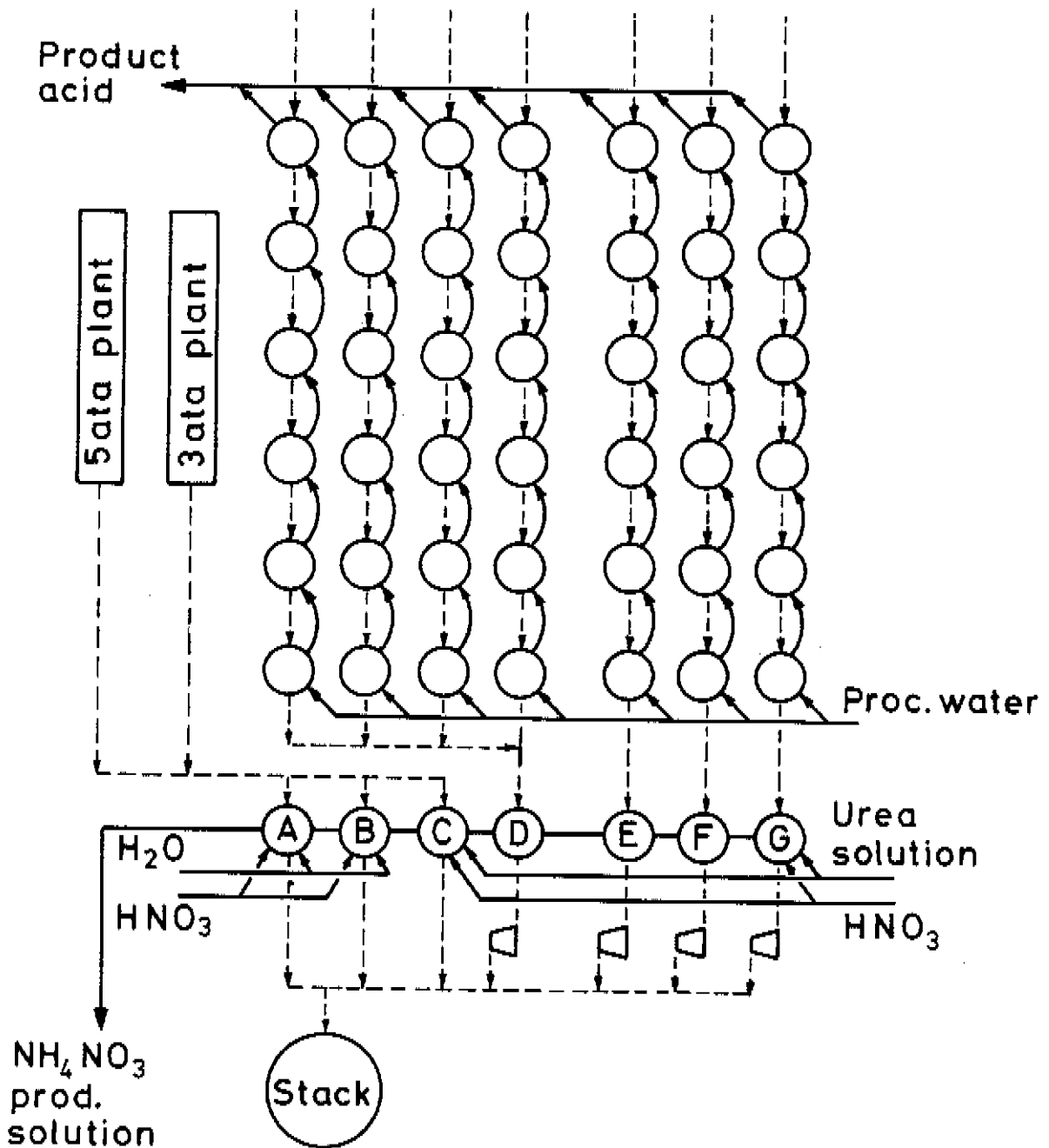


Fig. 2. Nitric acid absorption system with tail gas abatement by acid urea solutions

Fig.3. Schematic diagram of the Norsk Hydro NPK-process

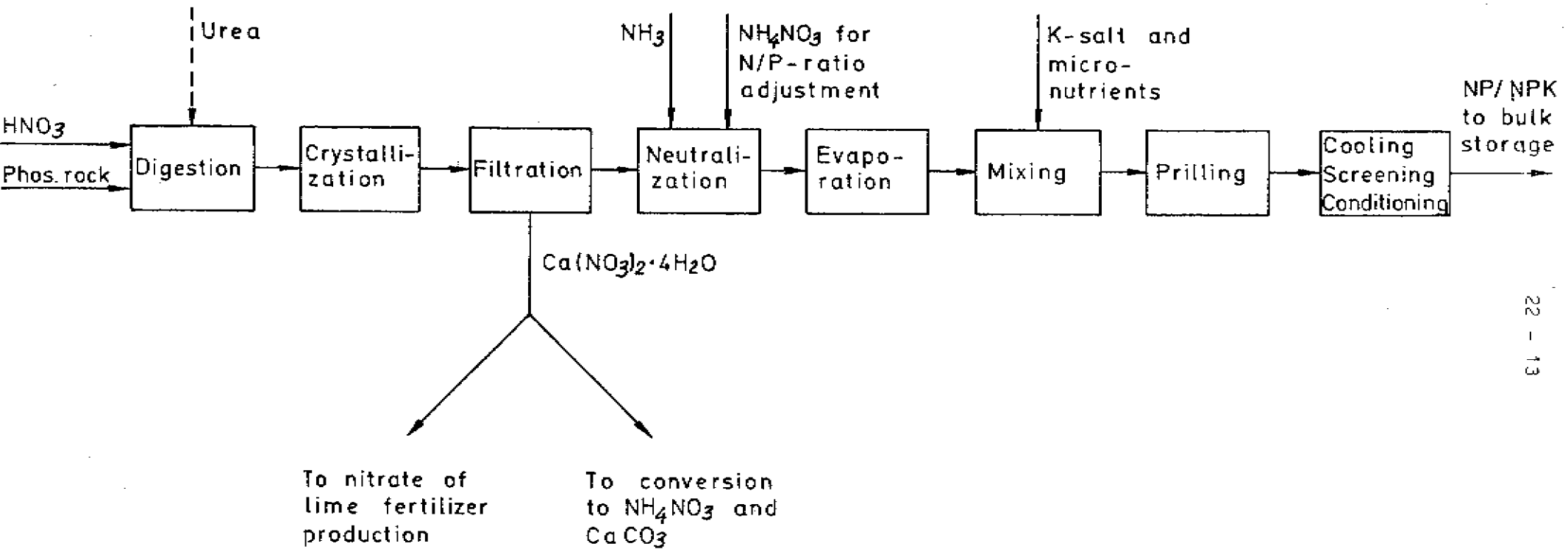
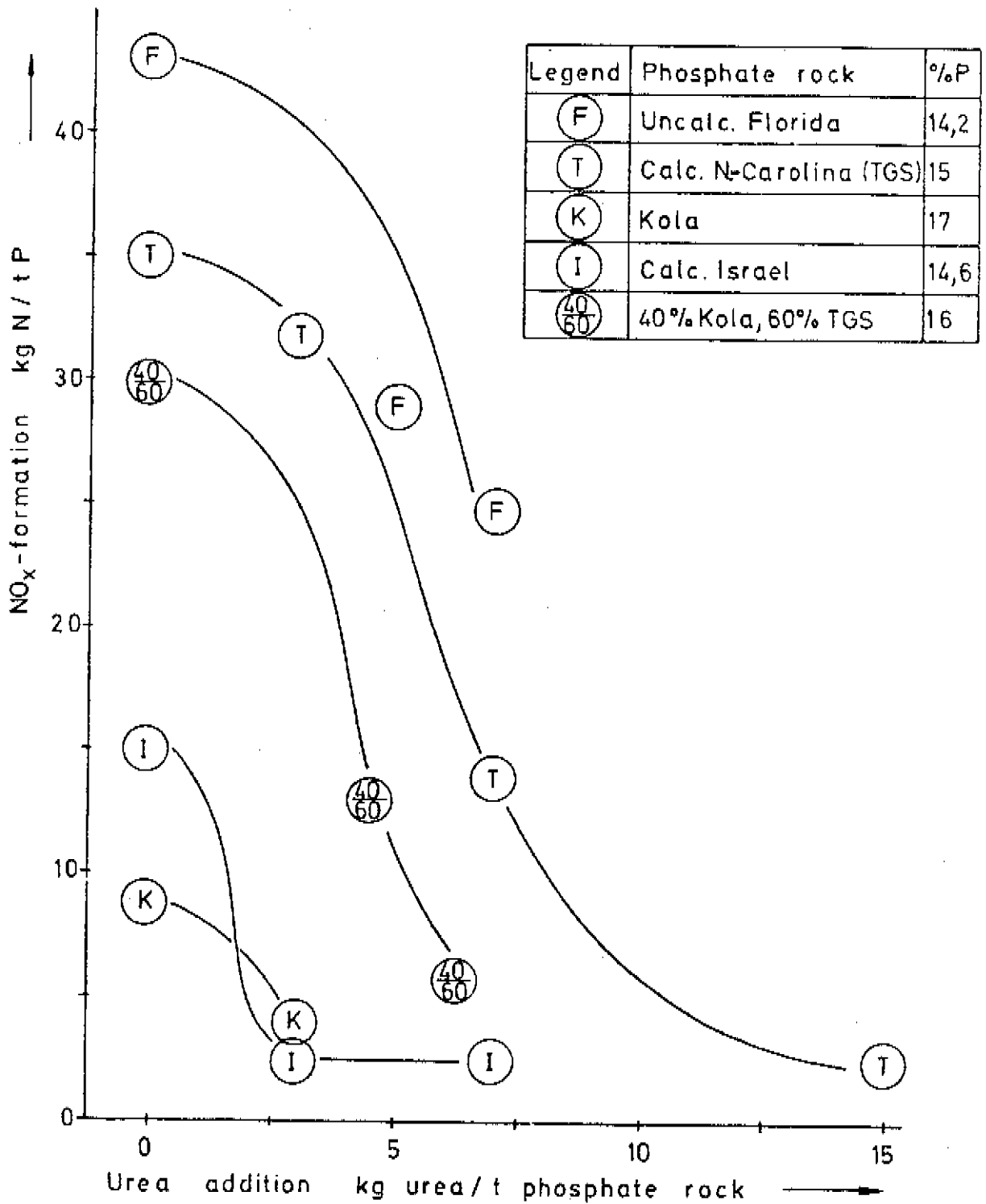


Fig.4. Nitrogen oxide formation in the digestion - crystallization - filtration section as a function of urea addition to the digester.



DISCUSSIONMr. MEJDELL (Norsk Hydro, Norway)

The two processes for abatement of nitrogen oxides presented in our paper deal with two fundamentally different approaches to pollution control : In the treatment of tailgases from the nitric acid plants the improvement is obtained by scrubbing away pollutants from the gas leaving existing plants, in the second example by interfering in the process itself thus reducing the amount of pollutants formed. Both examples, however, have in common that the abatement is achieved by the rapid reactions of nitrous acid with urea in acid solutions.

When scrubbing nitrogen oxides from nitric acid tail gas, the well known mechanism of nitrogen oxide absorption in water, is changed drastically as the removal of nitrous acid will turn the reversible reaction 2 into an irreversible reaction, and also change the direction of reaction 3, which is the faster of the two. In fact, this reaction 3 may count for more than 90% of the absorption.

During the digestion of phosphate rock in nitric acid, there are indications that nitrous acid is the main oxidant for reducing materials in the rock - carbon, sulfides, and so on - that is that reaction 1 is much slower than reaction 2. When the oxidation first is started by reaction 1, the chain reaction of equations 2 and 3 take over, giving off nitrogen oxides by reaction 4. By removing the nitrous acid as soon as it is formed, oxidation will be restricted to the slower reaction 1.

In acid solutions urea is postulated to react with nitrous acid as shown in the next slide.

First, one of the amine groups of urea reacts with nitrous acid to form elementary nitrogen and the unstable isocyanic acid, which in turn reacts according to the next two equations : either by reaction with excess nitrous acid to form more nitrogen and carbon dioxide, or by hydrolysis to produce ammonia and carbon dioxide. In the present application where the concentration of nitrous acid is low and where nitric acid is present, the reaction according to equation 2 is negligible, and ammonium nitrate is formed.

Time does not permit me to go into details on the technical installations that are described in the preprint. Instead I shall use the remaining time to give some information on performance and experience with the two abatement processes.

Solid urea has now for one year been administered to the digestion tanks in our nitrophosphate plants. This has given a pronounced improvement on the emission of nitrogen oxides from the plants, and no adverse effects are encountered in the plant or on the product quality.

The reduction in nitrogen oxide formation and the optimum amounts of urea addition vary with the different phosphate ores used. This should be expected as the kind and amounts of reductants differ from one rock to another.



As small changes in the nitrogen content of concentrated solutions are difficult to determine with sufficient accuracy, the nitrogen balance and thus the cost estimate for the process are uncertain.

### UREA IN NITROPHOSPHATE PROCESS

#### Costs/Savings Balance

<u>Costs :</u>	<u>Savings :</u>
Urea consumption	Reduced $\text{NO}_x$ emission
$\text{HNO}_3$ reacted to $\text{N}_2$	Urea recovered as $\text{NH}_4^+$
Utilities	
Labour	
Maintenance	
Capital costs	

We have, however, the impression that the savings in nitrogen oxide formation and the recovery of ammonium from urea by far outweighs the sum of urea fed to the system and nitrous acid reacted to nitrogen. We expect that the net savings on nitrogen very closely balance the other costs including utilities, labour, maintenance and capital costs.

The tail gas destruction plant has been in operation on part load during two months, and the problems encountered until now have been of trivial nature only. During this time construction and maintenance work in the acid plants have given rise to great variations in the composition of the gas fed to the abatement system. We therefore do not have mass balances accurate enough to justify correction of the balances given in the preprint.

Measurements on the individual towers show absorption efficiencies between 30 and 60% depending on gas loads and compositions. The efficiencies obtained correspond well to what we will expect by alkaline absorption. As an average during the last month the emission has improved from a hypothetical value of 1800 ppm to 1000 ppm. I use the term "hypothetical" as this would be the expected emission value if the atmospheric plant had not been deprived of its 7th. row of absorption towers. The average inlet concentration to the destruction plant thus was 150 ppm higher, or 1950 ppm.

#### ESTIMATED NITROGEN BALANCE IN $\text{NO}_x$ DESTRUCTION PROCESS

	kg/t $\text{HNO}_3$	kg N/t $\text{HNO}_3$	
		consumed	Recovered
Reduced prod. of $\text{HNO}_3$	0.25	0.06	
Consumed urea	9.14	4.27	
Consumed $\text{HNO}_3$	9.35	2.08	
Produced $\text{NH}_4\text{NO}_3$	12.19		4.27
Balance : Loss of N			2.14

This loss of Nitrogen corresponds to a reduction of the Ammonia Combustion Efficiency by 0.9%.

The direct operating cost for the destruction plant can best be illustrated by the estimated nitrogen balance shown on this table, and that corresponds well to our present experience.

The reduced production of nitric acid relates to the 7 towers taken out of acid production. The consumption of urea and the production of ammonium nitrate are based on the assumption that 95% of the nitrogen oxides are absorbed as  $N_2O_3$ , the remaining 5% as  $N_2O_4$ , and further, that each mole of nitrous acid formed reacts with one mole of urea, producing one mole of ammonium nitrate from the nitric acid present and the ammonia formed. The net loss of nitrogen is equivalent to a reduction of 0.9% in the ammonia combustion efficiency.

By utilizing existing absorption towers in the plant this abatement method could be introduced with low investment costs - 0.5 mill. U.S. \$. The advantage of the method is that it does not produce new pollutants either to the air or to the sea. The disadvantage is of course the relatively high operating costs due to nitrogen consumption. However, should nitrogen prices continue to rise as they have done during the last year, only minor changes will be necessary to convert the system to alkaline absorption.

Mr. JOERGER (B.A.S.F., Germany)

In their interesting papers the authors have taken up a problem which is troublesome to all Nitric Acid and Nitrophosphate producers, that is the removal of nitrous gasses, which are an unwanted by-product of the processes referred to.

For the construction of new plants always stricter regulations regarding the  $NO_x$ -emission are being enforced in many countries. But existing plants also are forced more and more to reduce the output of nitrogen oxides. Whilst one is able to plan relevant tail gas treatments for new plants it is difficult to find low-cost and also effective processes for running production.

Mr. Ringbakken and his colleagues have now been able to transfer in an elegant way simple conservative chemistry to chemical big plant and achieved - at least for the Porsgrunn plant - an abatement of  $NO_x$ -emission.

Since many years we in our Company are using urea for the destruction of  $HNO_2$ -traces in nitrate solutions, which are produced by reaction of nitrite solutions in nitric acid. When in 1970 a U.S. Patent (No.3.528797 by A.B. Funk and J.C. Moore) regarding the suppression of evolution of nitrogen oxides resulting from the acidulation of phosphate rock with nitric acid is accomplished by use of urea either in a scrubbing system or by direct addition of urea to the acidulation mixture was published, we in our laboratories and pilot plants took up research on this subject. In the main the theoretical results of the authors of the paper presented have been confirmed. These processes have, however, not been transferred to our plants. A short while ago we have developed a process by which it is possible to convert nitrogen oxides with  $NH_3$  selectively to nitrogen. 250-300°C are needed. This process is very well suited for nitro acid plants operating on medium pressure. The tail gas contains approx. 100 ppm  $VNO_x$ .

Shortly we will equip one of our acid plants with this kind of tail gas treatment.

The abatement of nitrogen oxides to 850 ppmV in the tail gas of nitric acid plants will be, considering the requirements of our authorities (650 ppmV), too small for the future.

We do not believe, that you in Norway will be allowed to emit 850 ppmV much longer.

This brings me up to my first question :

1st question : Is the NO<sub>x</sub>-abatement to 850 ppmV achieved by you as a final state which with you will have to be satisfied or do you see or have further possibilities of development ?

2nd question : When nitrogen oxides are absorbed in water to nitric acid at the end of the absorption process, then, when the oxides are already very diluted the gas-phase-reaction over HNO<sub>2</sub> can be of any importance. And one is almost convinced that in a following absorption in alkaline liquids the formation of nitrite is mainly running over HNO<sub>2</sub> from the gas-phase. Did you touch this problem during your research ? One can assume that the same mechanism applies to the reaction of HNO<sub>2</sub> with urea.

Now to the application of urea at the acidulation of phosphate rocks.

3rd question : Figure 4 shows that phosphate with more organic matter needs a larger addition of urea to get an acceptable tail gas. It would be of interest to know how much urea has to be added when uncalcined Florida phosphate is used to achieve results in the region of 2.5 kg NO<sub>x</sub>-N/tP. Do you actually use the process as developed by you only when using calcined phosphate or phosphate from Kola or also when the phosphates are uncalcined ?

Mr. MEJDELL

I will start with the second question posed. Yes, the mechanism is exactly the same as it is by alkaline absorption that is that the reaction is the one which is important and according to the balances we have made and the urea consumed it is approximately 90% or more of the absorption that is due to this last reaction. Then we naturally come to the first question that is this 850 ppm is a safety value we cannot get below but of course it is a practical limit when we are using atmospheric pressure for the absorption because, as you probably know, the absorption, the reactions are of a second order. So it slows very much down with lower concentrations. But, however, there is quite a big potential improved absorption if you use it on a medium pressure.

Third question concerns whether we use only calcined phosphate and what is happening to that uncalcined phosphates. We are using also uncalcined phosphates mixed with calcined phosphates, mainly a mixture of 40 to 60% or 50-50. And from the graph I showed here which is given in the pre-print you can see an uncalcined phosphate. You need approximately 10 to 15 kg/ton phosphate ore. It might also vary from one plant to the other depending on scale factors. Finally you asked whether we need water scrubbing of the gases from the digestion tanks even if we use urea. Yes of course we do because we have carbon dioxide evolutions and spoilt air coming in saturated with nitric acid vapour and also we have some evolution of fluorine compounds that we also have to wash.

Mr. QUINTON (Fisons Ltd., U.K.)

I have two questions :

1. How concentrated is the ion liquor produced in the absorption process and how you use this liquor ?
2. Is ammonium nitrate formed in the absorption process and, if so, is this a problem ?

Mr. MEJDELL

The ammonium nitrate solution leaving this abatement process is approximately 50% by weight. That is due to the high temperature and the medium pressure as in the plant so that we get an evaporation in the last absorption towers. The formation of ammonium nitrate is no problem at all because we are doing this with an acid solution between 3 and 6% of nitric acid so we have not observed any formation at all. We are using the ammonium nitrate in our NPK plant. So we add it to neutralization or ammonium steps.

Mr. UUSITALO (Kemira Oy, Finland)

We have studied quite a lot over the last 2 years this problem and it was very interesting to hear what you have done and what you have reached, but on the second page in your paper you say that a catalytic process using ammonia as fuel is very little studied and there is no experience on industrial scale today. Our decision is very probable if we are making some decision. So we are going to use this ammonia process and it seems to be most economical and perhaps a little better than what you have told and also we have seen several plants using such system.

Mr. MEJDELL

Is that the catalytical combustion with ammonia you are talking about ?

Mr. UUSITALO

Yes.

Mr. MEJDELL

As far as I know there has been some problems with the catalyst but I really don't know enough about them.

Mr. UUSITALO

In Helsinki 5 weeks ago at the UNIDO' Conference they discussed the same problem there and there were many experts who told that they also had very big difficulties with operating the methane system and the hydrogen system, and, as far as we know, one of the best and most practical systems used is ammonia system and especially a Russian Company process today.

Mr. ALMOUCHAI (Sumitomo Chemical Cy. Japan)

I have a comment.

I wish to mention that Sumitomo has been using urea to decrease  $\text{NO}_x$  from the digestion of phosphate rock and they have obtained similar results<sup>x</sup> as you and another comment concerns what Dr. Uusitalo just mentioned. Sumitomo has a commercial plant with the selective catalytic reduction using ammonia to decompose  $\text{NO}_x$  and Sumitomo has papers in Japanese. If you wish he can send them to you<sup>x</sup>.