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SIMULTANEOUS CALCIUM AND CHLORINE REMOVAL  
IN NPK FERTILISER PRODUCTION

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The object of the research was to find a cheaper way of making chlorine-free NPK fertilisers. The results so far, on a pilot scale, point to a method that make possible the production of chlorine-free NPK fertilisers generally at lower total cost than those of chlorine-containing NPK fertilisers commonly used today.

BACKGROUND

There is a growing interest in chlorine-free NPK fertilisers. From an agricultural point of view the chlorine is unwanted. The trend is towards increasingly concentrated NPK products and in this connection the chlorine is of importance since it is a ballast material. Decomposition problems are attracting increasing attention and here again the chlorine is highly undesirable.

In Denmark no cigarette-burning NPK fertilisers are manufactured. Therefore, it has been necessary to produce some grades (copper-containing grades) without chlorine. Today some 30% of Danish NPK consumption is chlorine-free. The production of these chlorine-free NPK grades is based on imported potassium sulphate, which is much more expensive than the ordinary potassium chloride.

Against this background it was decided to start research to find a cheaper way of producing chlorine-free NPK fertilisers.

BASIC CONSIDERATIONS

Production costs in the phosphate fertiliser industry are linked to the problem of separating the calcium from the phosphorus. Nearly all NPK fertiliser producers use phosphate

rock (calcium phosphates) as a raw material, the removal of the calcium, e.g. as gypsum or calcium nitrate, taking place as a step in NPK production. This implies higher manufacturing investment in NPK production, compared with purchasing other phosphate-containing materials, such as phosphoric acid, which do not have the calcium. However, the higher investment is generally preferable, because of the high prices of the other materials.

To date the situation has not been the same concerning the potassium component of the NPK fertilisers. Here, the preferred raw material is potassium chloride, but the chlorine is generally not separated from the potassium during NPK production. This results in chlorine-containing NPK fertilisers. Thus the demand for chlorine-free NPK fertilisers raises the question of whether it is more profitable to buy a potassium product without chlorine (potassium sulphate or nitrate) or to incorporate chlorine removal as a step in the NPK production process. A number of different methods are known for transforming potassium chloride into potassium sulphate or nitrate, resulting in new investment and new byproducts.

The chlorine problem with regard to potassium corresponds to the calcium problem with regard to phosphorus. The realisation of this fact has led to the two problems being studied together. In the first case it is the cation calcium which has to be removed, whereas in the second case it is the anion chloride that is unwanted. Obviously, if it were possible in one step to react the calcium phosphates with the potassium chloride in such a way that the calcium and the potassium change places, then it would be possible in one step to get rid of both the calcium and the chlorine in the form of calcium chloride.

It is well known that this is not possible by ordinary chemical reactions. However, it might be possible, in the context of NPK production, by reacting phosphate rock with nitric acid, giving a slurry containing calcium, phosphorus and nitrogen, the calcium being cationic. By treating this slurry with a potassium-charged cation exchanger the calcium and the potassium could be made to change places, i.e. the calcium is held by the ion exchanger and a slurry containing potassium, phosphorus and nitrogen is obtained, and this can be worked up in the usual way to yield an NPK fertiliser. By regenerating the calcium-charged ion exchanger with a potassium chloride solution the potassium-charged ion exchanger plus a calcium chloride solution are retrieved.

Thus, if this ion exchange can be carried out in practice, one operation - the ion exchange - replaces two separate operations - the removal of the calcium from the phosphorus and the transformation of the potassium chloride

into chlorine-free material, both of which involve high investment and operating costs.

### THEORETICAL ECONOMIC CONSIDERATIONS

It can be seen that the suggested ion exchange method can compete with the traditional methods of making chlorine-free NPK fertilisers provided that the total costs of the ion exchange procedure are lower than the corresponding total costs of removing calcium in one stage plus those of removing chlorine in another stage. Furthermore, it can also be seen that if the ion exchange can be carried out more cheaply than the traditional removal of a corresponding amount of calcium alone, then the ion exchange method opens up a hitherto unknown possibility of making chlorine-free NPK fertilisers more cheaply than chlorine-containing NPK fertilisers. In the subsequent part of this paper only the latter comparison will be made.

In principle, the question is how the cost of removing one ton of calcium traditionally, e.g. as gypsum in a phosphoric acid plant, compares with the cost of removing one ton of calcium by the ion exchange. If the latter is the lower, then it is cheaper to make chlorine-free NPK fertilisers by ion exchange than to make chlorine-containing NPK fertilisers by traditional methods. The first cost might be estimated by comparing the production costs of phosphoric acid with the price of phosphate rock, and the second cost by estimating the costs of carrying out the ion exchange processes.

In practice, the calculation is not quite as simple as that. The simultaneous removal of chlorine implies the introduction of a corresponding quantity of nitrate ions, which alters the ratio of nitrate to ammonium nitrogen in the end product, thereby influencing the economics (nitric acid being more expensive than ammonia). At the same time the total nutrient content of the end product is increased, which again has an effect on overall economics. Furthermore, the side reactions, e.g. exchange of potassium against hydrogen ions, complicate the situation.

For the sake of clarity, therefore, the calculation will be made in the conventional way for comparing different processes, i.e. by choosing a set of specific grades and comparing the manufacturing costs of these grades.

For simplicity only a 1:1:1 and a 1:1:2 ratio and only a straightforward potassium ion exchange will be considered. This means that only the necessary potassium ions will be introduced by ion exchange, no attention being paid to the possibilities of improving the ion exchange economics by

introducing other cations in parallel with the potassium ions, as suggested in a later section of this paper.

18-18-18 and 14-14-28 grades ( $N-P_2O_5-K_2O$ ) will be considered. Chlorine-containing 18-18-18 and 14-14-28 grades can be produced by the traditional ammonium phosphate nitrate process using phosphoric acid, nitric acid, ammonia and potash as raw materials. Chlorine-free 14-14-28 can be produced by ion exchange based on phosphate rock, nitric acid, ammonia and potash. The phosphate rock is reacted with nitric acid, the nitrophos slurry is treated with a potassium charged ion exchanger, and the ion exchanger is regenerated with a potash solution. Correspondingly, the chlorine-free 18-18-18 can be made by ion exchange based on phosphate rock, phosphoric acid, ammonia and potash, 50% of the  $P_2O_5$  originating from the phosphate rock and 50% from the phosphoric acid. The reason for not using phosphate rock as the only  $P_2O_5$  source for the 18-18-18 grade is that this would result in so much calcium remaining in the end product that a high water-solubility and a high total nutrient content could not be obtained (cf. the section entitled "Flexibility").

The main differences between the products from the two methods are that the ammonium phosphate nitrate based products are chlorine-containing, with about 1/3 of the total nitrogen as nitrate and the water solubility of the  $P_2O_5$  being nearly 100%, whereas the ion exchange based products are chlorine-free, more than 50% of the total nitrogen being nitrate and the water solubility of  $P_2O_5$  being 70-90%.

The theoretical consumption of raw materials per ton of product may be listed as follows :

kg/ton NPK	18-18-18		14-14-28	
	Ion exchange	Ammonium phosphate nitrate	Ion exchange	Ammonium phosphate nitrate
Ammonia, kg $NH_3$	101	146	48	113
Nitric acid, kg $HNO_3$	437	270	452	210
Phosphate rock, kg $P_2O_5$	90		140	
Phosphoric acid, kg $P_2O_5$	90	180		140
Potash, kg 60%	300	300	467	467

Assuming the following raw materials prices, theoretical raw materials costs per ton of product are :

\$/ton NPK	18-18-18		14-14-28	
	Ion exchange	Ammonium phosphate nitrate	Ion exchange	Ammonium phosphate nitrate
Ammonia, \$ 32/ton NH <sub>3</sub>	3.23	4.67	1.54	3.62
Nitric acid, \$ 18/ton HNO <sub>3</sub>	7.86	4.86	8.13	3.78
Phosphate rock, \$ 45/ton P <sub>2</sub> O <sub>5</sub>	4.05		6.30	
Phosphoric acid, \$ 120/ton P <sub>2</sub> O <sub>5</sub>	10.80	21.60		16.80
Potash, \$ 30/ton 60% potash	9.00	9.00	14.00	14.00
Total	34.94	40.13	29.97	38.20
<u>Savings with ion exchange</u>	<u>5.19 \$/ton</u>		<u>8.23 \$/ton</u>	

The prices assumed for ammonia, nitric acid and phosphoric acid are estimated captive-use costs including 20% return on investment.

If all the costs of carrying out an ion exchange process are also calculated, including 20% return on investment, and their totals compared with the relevant above "savings with ion exchange" figure, then which figure is lower indicates the cheaper route.

The costs of carrying out the ion exchange process is a question of possible methods and equipment, and so they will be evaluated below after a discussion of the experimental work.

#### EXPERIMENTAL WORK

Two main problems were encountered in the experimental work, the problem of the stability of the ion exchange resin in the highly aggressive nitrophosphate slurry and the problem of the design of a practicable ion exchange equipment.

The standard cation exchange resins of the sulphonated

styrene-divinylbenzene copolymer type very quickly deteriorate due to osmotic shocks and decrosslinking by oxidation, when used in the hot, concentrated, nitrophosphate slurry. However, some recent resins with a very high divinylbenzene content are more resistant to osmotic shocks and oxidation. We have found that under certain conditions, which can be observed on an industrial scale, it is possible to obtain a long working life for these resins. After reasonable long periods of operation in our pilot plant (more than 30 days, 24 hours per day) under such circumstances there has been no significant reduction either in physical quality or in the useful capacity of the resin.

The problem of practicable ion exchange equipment has been more difficult. The usual fixed-bed arrangement for ion exchange is for dilute solutions only. The useful capacity of the cation exchange resins is between 1 and 1.5 equivalents/liter. Therefore, in processing concentrated solutions the volume of solution to be treated may be only a fraction of the corresponding volume of resin. In this case, the rinsing operation in a conventional fixed-bed arrangement would result in an economically prohibitive dilution of the end product.

Many types of sophisticated equipment have been proposed to improve the economics of ion exchange and enlarge its field of application, and some of these may be successful, especially for processing valuable chemicals (e.g. uranium or rare earths). What was needed in our case was a rugged, reliable apparatus that would permit the processing of large quantities of low cost chemicals with a reasonably low dilution of the end product and a reasonably low consumption of chemicals for regeneration.

The logical line of action is to try to replace the fixed-bed arrangement by a continuous, countercurrent arrangement, the resin moving one way in a loop and the different liquids to be treated moving the other way. This has been done previously, and here again the main problem in our case is that the resin flow rates would be very high compared to the solution flow rates.

Fig. 1, showing the loading section of such a loop, illustrates the problems and at the same time facilitates understanding our solution. The method is not truly continuous, since it is not possible to move the resin and the liquids at the same time. During the flow of liquid, the resin is confined between the valves A and B, the liquid entering through valve 1 and leaving through valve 2. Then the liquid flow is stopped (valves 1 and 2 are closed), valves A and B are opened, and by means of a hydraulic pulse, the whole resin bed is slid down a certain distance in a direction opposite to that of the previous liquid flow.

During this movement of resin, the liquid remaining in the resin bed between valves 1 and 2 when the valves are closed, moves in the same direction as the resin. Moreover, as a result of the hydraulic pulse, the liquid moves faster than the resin, usually by a factor of two to three. So, after closing A and B, but before resuming the liquid-flow, it is necessary to return this liquid to its original position. This is done by means of rinse water, entering through valve 3. At the same time valve 4 is opened, which allows the water introduced together with the resin into the area between 2 and 1 to leave the system. After re-establishment of the position of the liquid, the next liquid-flow step through 1 and 2 may begin. It is important to understand the function of the additional valves 3 and 4, because the possibility of re-establishing the positions of the liquids and of keeping partly concentrated liquids between 3 and 1 as well as between 2 and 4 are necessary in order to maintain reasonably high concentrations in production.

It is possible that this system could operate successfully in many applications. However, in our case we did not find the resin movement to be satisfactory. The nitrophosphate slurry may contain about 10 equivalents of calcium per liter against a useful capacity of the resin of between 1 and 1.5 eqv./liter. Taking into account that the liquids move in the same direction as and faster than the resin during the pulse step, it is easy to see that the movement of the resin and equally, or more so, the position-reestablishing movement of the liquids, would be very considerable compared with the production flow proper. In a large diameter device, such as needed in the present case, this would not only be time-consuming, but it would also require very strict control to ensure a uniform and regular movement of the resin in all parts of the unit and to govern the interfaces between the various solutions being pushed backwards and forwards. Faults in this respect could obviously disturb the process conditions and dilute the product solution. Furthermore, from a resin attrition point of view it is not desirable to move the resin and to operate the valves A and B in the resin bed.

It can be seen that many of these difficulties can be avoided and a less sensitive arrangement obtained if the positions of the liquid inlet and outlet are moved forward stepwise, instead of the corresponding backward movement of the resin. This is indicated in Fig. 2. Again the valves 1 and 2 are open during a production step. Then 1 and 2 are closed, 3 and 4 are opened and the liquid remaining between 1 and 2 is moved to a position between 11 and 22. Now the next production step may start through 11 and 22, and so forth. It can be seen that there is no resin movement and no backward movement of the liquid. The system requires a number of valves and manifolds, and these valves are easily operated automatically according to a chosen programme.



A pilot plant has been erected based on this principle. The operation of this pilot plant has proved it possible to meet the previously mentioned requirements regarding a rugged and reliable apparatus that will permit the processing of low cost chemicals with a reasonably low dilution of end product and with a reasonably low consumption of chemicals for regeneration.

Based on the results obtained in the pilot plant, it has been decided to erect an industrial scale plant designed for 90,000 t. NPK per year. The plant is scheduled to start operation in 1971.

### MANUFACTURING COSTS

By choosing the ion exchange route instead of the ammonium phosphate nitrate route for making 18-18-18 and 14-14-28 there is on one hand, a saving in raw materials as indicated earlier ("Theoretical Economic Considerations"). On the other hand there are the additional costs of running the ion exchange unit (operating plus depreciation costs). Based on pilot plant work, it is possible to get an estimate of the operating costs, the most outstanding being the losses of N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O in the calcium chloride solution, the evaporation costs (mainly due to inevitable dilution of the slurry during the exchange) and the resin consumption.

The following costs may be listed for an ion exchange unit making possible the production of 200,000 tons per year of 18-18-18 or 130,000 tons per year of 14-14-28 :

	18-18-18		14-14-28	
	unit/ton	\$/ton	unit/ton	\$/ton
K <sub>2</sub> O loss	11.5kg	0.58	17.9kg	0.90
P <sub>2</sub> O <sub>5</sub> loss	1.8kg	0.08	2.9kg	0.13
N loss	1.3kg	0.11	2.0kg	0.16
Steam	0.6t.	0.60	0.9t.	0.90
Resin consumption		0.16		0.25
Other operating costs		1.20		1.85
20% return on investment (estimated investment 2 million \$)		2.00		3.10
Total		<u>4.73</u>		<u>7.29</u>
Comparable savings (see "Theor. Econ. Consid.")		5.19		8.23

It should be noted that the costs are interlinked, i.e. it is possible e.g. to reduce the losses by accepting a higher evaporation cost and vice versa. It should also be noted that the costs are subject to confirmation in an industrial scale plant, and that it is very likely that another combination of costs would be more favourable, depending on the results with larger scale operation and also depending on local conditions (local unit costs).

It can be seen that the estimated costs of carrying out ion exchange processes are lower than the estimated savings, even if the differences are relatively small. Taking into account that no attention has been paid to the possibilities of improving the ion exchange economics, such as are suggested in the following section of this paper, we think it is true to say that the results of the work on a pilot scale indicate a method that makes it possible to produce chlorine-free NPK fertilisers generally at lower total cost than those of the chlorine-containing NPK fertilisers commonly used today.

#### FLEXIBILITY

To obtain a high water-solubility, it is necessary to remove most of the calcium from the phosphate rock. If this is done exclusively by substituting potassium for calcium in an ion exchange process, the result will obviously be very poor flexibility regarding the  $P_2O_5:K_2O$  ratio (to a given amount of  $P_2O_5$  in a phosphate rock there corresponds a given amount of Ca, which again corresponds to an equivalent amount of  $K_2O$ ). At the same time the  $N:P_2O_5$  ratio cannot be very much lower than 1:1, whereas any  $N:P_2O_5$  ratio higher than 1:1 can be easily obtained by adding more nitric acid and ammonia.

Some increase in the  $K_2O$  content, say to  $P_2O_5$  ratios between 1:2 and 1:3, may be obtained by allowing for a higher degree of substitution by potassium of hydrogen ions in the nitrophosphate slurry, but at very high  $K_2O:P_2O_5$  ratios it is necessary to use a supplementary source of potassium material. However, considering the NPK fertilisers most commonly used today, the main concern lies in studying the ion exchange process for  $P_2O_5:K_2O$  ratios between 1:1 and 1:2, in which the removal of more calcium than is equivalent to the potassium is of interest. Some comments on this are given below.

Two obvious possibilities for removing more calcium than is equivalent to the potassium are : 1) To remove part of the calcium, using traditional methods and 2) To introduce other cations (e.g. ammonium, sodium or magnesium ions), in parallel with the potassium ions, during the ion exchange.

The first possibility has been used in the 18-18-18 example described earlier in this paper, where a part of the calcium has been removed in the form of gypsum by using phosphoric acid instead of phosphate rock for supplying some of the  $P_2O_5$ . Of course, other well known ways of removing a part of the calcium might be used, such as, for instance, crystallisation of some calcium nitrate before ion exchange or precipitation of remaining calcium after ion exchange.

The second possibility, the introduction of other ions together with the potassium ions, can be realised, for example, by using low grade potash materials containing sodium and/or magnesium in addition to the potassium. This is illustrated by the following example.

The main grade of chlorine-free NPK fertilisers in Denmark today has a  $P_2O_5:K_2O$  ratio of 1:1.7 and a water solubility of  $P_2O_5$  about 75%. At this ratio the removal of calcium exclusively by potassium ion exchange results in a finished product with a lower water solubility than 75%. However, by using 50% potash dissolved in sea water instead of 60% potash dissolved in fresh water it is possible to keep a high water solubility and still use phosphate rock as the only  $P_2O_5$  source. This may further increase the economic advantage of the ion exchange process since the sodium costs nothing and sea water is usually cheaper than fresh water. Furthermore, for some crops, the presence of sodium in the fertiliser is considered to be an advantage.

The introduction of ammonium ions together with the potassium ions is very attractive for grades with a  $N:P_2O_5$  ratio higher than 1:1. To some extent this can be done simply by ammoniating the potash solution. A further possibility would be to dissolve the potassium chloride in an ammonium carbonate solution prepared by absorbing  $NH_3$  and  $CO_2$  in water. A related possibility would be to use a part of the calcium chloride solution for the  $NH_3$  and  $CO_2$  absorption, thereby precipitating the calcium carbonate. After separation a filtrate containing ammonium chloride plus some  $K_2O$  (and  $N$  and  $P_2O_5$ ) is obtained, which would otherwise be lost in the calcium chloride solution. The said ammonium chloride solution may now be used for dissolving the potassium chloride. The potassium:ammonium ratio may be varied and it can be seen that in the extreme case of using no potash at all the result is an NP fertiliser.

## CONCLUSION

Concluding our paper, we mention that patents have been applied for both on the process and on the method and apparatus. Of course, we have encountered quite a number of

problems that are not elucidated in this paper, more problems will be seen during the up-scaling and, naturally, some solutions to problems are considered company know-how. It will be understood that we do not present this paper pretending that we are able to discuss all problems in detail. The intention in presenting the paper can be stated as follows :

In our opinion the trend will be towards chlorine-free NPK fertilisers in the future, and so technical developments will result in cheaper ways of producing these chlorine-free NPK fertilisers. In our paper we have tried to introduce what we think will turn out to be a substantially cheaper way.

DISCUSSION

Mr. K.C. KNUDSEN (Dansk Svovlsyre-og, Denmark) :  
Chlorine is on the way out of NPK fertilisers. From an agricultural point of view as well as from a decomposition point of view the chlorine is clearly undesirable. Furthermore, the trend towards increasingly concentrated NPK products is against the presence of a ballast material such as chlorine in the finished products. Today nearly one third of Danish NPK consumption is chlorine-free.

The production of these chlorine-free NPK grades is based on imported potassium sulphate, which is much more expensive than the ordinary potassium chloride. So the trend towards chlorine-free NPK fertilisers raises the need for cheaper ways of producing these fertilisers. The problem is how to produce chlorine-free NPK fertilisers based on the cheapest potassium raw material (which is potassium chloride), instead of on the more expensive potassium products such as potassium sulphate or potassium nitrate.

Everybody in the phosphate fertiliser industry knows that the problem of producing phosphate fertilisers is a problem of separating calcium from phosphorus. Calcium phosphate is the cheapest phosphate raw material, and therefore the chemistry involved in phosphate fertiliser production is centred on processes for separating calcium from phosphorus. Correspondingly, if you want to make chlorine-free NPK fertilisers based on potassium chloride you need processes for separating chlorine from potassium.

The chlorine problem with regard to potassium corresponds to the calcium problem with regard to phosphorus. The realisation of this fact led us to study the two problems together. Obviously if it were possible in one step to react the calcium phosphate with the potassium chloride in such a way that the two cations (the calcium and the potassium) change places, then it would be possible in one step to get rid of both the calcium and the chlorine in the form of calcium chloride.

This is obviously not possible by ordinary chemical reactions, but it may be done by incorporating an ion exchange process in the NPK production. A nitrophosphate slurry prepared from phosphate rock and nitric acid may be treated with a potassium-charged cation exchanger in such a way that the calcium and the potassium change places, i.e. the ion exchanger becomes calcium-charged instead of potassium-charged and you get a slurry containing potassium, phosphorus and nitrogen instead of calcium, phosphorus and

nitrogen. This slurry may be worked up in the usual way to yield an NPK fertiliser, and the calcium-charged ion exchanger may be regenerated with a potassium chloride solution, which means that the effluent from the regeneration will be a calcium chloride solution.

Now two questions may be raised : Firstly, is it technically possible to carry out this ion exchange process ? Secondly, is it economically attractive ?

As regards the first question (the technical feasibility) it may be stated that the ion exchange technique is very widely used but only for dilute solutions, and so the process and the equipment are adapted for this purpose. What is needed in the present case is a rugged and reliable apparatus that permits the processing of highly concentrated solutions of low cost chemicals with a reasonably low dilution of the end product and a reasonably low consumption of chemicals for regeneration. We did not find any such equipment available and so we had to develop it ourselves.

In our paper we have explained the basic principle of this equipment and illustrated it in a simple diagram.

A pilot-plant has been erected based on the said principle, and the operation of this pilot-plant has proved it possible to meet the requirements.

The second question (regarding the economic attractiveness) requires a comparison of the costs of carrying out the ion exchange procedure with the costs of removing calcium in one stage plus chlorine in another stage by more traditional methods. Here it can be seen that if ion exchange can be carried out more cheaply than the traditional removal of a corresponding amount of calcium alone, then the ion exchange method opens up a possibility of making chlorine-free NPK fertilisers more cheaply than chlorine-containing NPK fertilisers.

Based on the results obtained in the operation of the pilot-plant, we have made some comparisons for 18-18-18 and 14-14-28 grades as described in the paper. Of course the outcome of such comparisons always depends on the chosen unit costs. However, it has become our opinion, based on the pilot-plant work, that generally it will be cheaper to produce chlorine-free NPK fertilisers by ion exchange than to produce the corresponding chlorine-containing NPK fertilisers by traditional means.

On the basis of the results obtained, our company has

decided to erect an industrial scale plant designed for an initial capacity of 90,000 t. NPK per year. The plant is scheduled to start operation in 1971.

In our opinion the future trend will be towards chlorine-free NPK fertilisers, and therefore technical developments will result in cheaper ways of producing these chlorine-free NPK fertilisers. In our paper we have tried to introduce what we think will open up a hitherto unknown possibility of making chlorine-free NPK fertilisers more cheaply compared with the chlorine-containing NPK fertilisers commonly used today.

Mr. P. ROLFSEN (Norsk Hydro) : We have here a description of a new NPK process which contains some significant improvements over the present technology provided that the promising pilot-plant results reported are confirmed in the coming full scale plant. As a representative of a company which for more than 20 years has produced sodium nitrate from calcium nitrate and sea-water by ion-exchange and hence a pioneer in this field I know the difficulties involved and congratulate the lecturer on his excellent work.

The main principle behind this process is the simultaneous extraction of calcium and addition of potassium. This is very elegant, but the speaker touched only lightly on the lack of flexibility which follows such a combination process. The speaker told us that for each mol of calcium oxide removed one mol of potassium oxide comes in. This means that, with a normal phosphate rock ( $\text{CaO}/\text{P}_2\text{O}_5 = 1.5$ ), the product will have a weight ratio  $\text{P}_2\text{O}_5:\text{K}_2\text{O}$  of 1:2.5 if all the calcium is removed, and approximately 1:2 if a  $\text{P}_2\text{O}_5$  water solubility of 75% is recognised as sufficient. Only between these limits is the ion exchange process working under its optimum conditions. I think these process limits should have been mentioned. I am fully aware that the modifications mentioned greatly improve the flexibility of the process, but not without a smaller or greater sacrifice of its economic advantages.

As to the economic aspects of the process, the savings in the two examples given are practically nil (U.S. \$ 0.46 and 1.06/t). Two products from this process are compared here with two products of ammonium nitrate phosphate produced via phosphoric acid exclusively. Phosphoric acid alone represents, however, a relatively expensive source of raw material. If one disregards the fact that, for instance, the Odde process does not fully reach the same nutrient content, its raw materials for the same amount of plant nutrient would give process savings of U.S. \$ 7.70 and

1.80/ton respectively in the two examples, compared with the ion-exchange process. But the speaker in his examples has given no credit for the fact that his products are chlorine-free. If we charge the products used in the comparisons with the increased price for sulphate of potash, this improves the results in the speaker's examples to U.S. \$ 6 and 9.5/ton. For the 18-18-18 grade the Odda raw materials still have an advantage over the ion-exchange materials of about U.S. \$ 1.70/ton, whereas the picture for the 14-14-28 grade is reversed. In the latter case the ion-exchange process has an advantage of U.S. \$ 7.70/ton. In this example we are near the optimum conditions for the process. I cannot comment on the production costs since they are compared with those of another process with which I am not too familiar. However, my conclusions are that this process should have good prospects for compounds where credit is given for the absence of chlorine, and for those near the optimum  $P_2O_5:K_2O$  ratio and for compounds which cannot be made stable with KCl.

My last remark is that I had expected the speaker to comment on the transport and storage situation for this new type of compounds. Here the 14-14-28 grade contains 44%  $KNO_3$  according to the IMCO method of calculation, and the IMCO Dangerous Goods Code accepts only 10%  $KNO_3$  without transport restrictions. This code admittedly only concerns sea transport, but its regulations for fertilisers are being used as pattern for other codes. The problem of changing the IMCO code to accept a higher percentage of  $KNO_3$  was thoroughly discussed at the last meeting of the Working Party in Vienna in January this year. It was decided to take no action.

As I mentioned earlier, this paper is very interesting, and I am tempted to ask a large number of questions, but restrict myself to the following :

1. The consumption of resin for the ion-exchange at 90 cts/t.  $K_2O$  seems to be fairly low. Do you mind telling us for what length of time the trial runs for evaluating the stability of the resin have been carried out ?
2. The concentration of the brine leaving the ion-exchange process is very important for the economics of the process. The steam consumption given seems to be low too; could you in this respect disclose the water content in the brine from the ion-exchange unit for the 14-14-28 grade ?
3. You mentioned the possibility of dissolving the potassium chloride in seawater instead of in washing water, in order to recover some sodium. Can you give any cost indications for the sodium recovered (calculated as sodium chloride) ?



4. We have heard of the great weight the speaker has put on the safety aspects, and that all NPK fertilisers marketed in Denmark are of the thermally stable type or so-called self-extinguishing types. The high  $K_2O$  grades have been hitherto sulphate based and also contain copper. For these grades the maximum chlorine content has to be very low to make the fertiliser self-extinguishing. My question is whether a sufficiently low chlorine content can be reached, especially with the small amounts of washing water you obviously use in view of the low steam consumption ?
5. It might be interesting to know the attitude of the Danish authorities towards the storing and transport of compounds such as 14-14-28 with 44%  $KNO_3$ . Do you anticipate special restrictions ?

Mr. KNUDSEN : You mention that we cannot improve the flexibility as regard the  $K_2O:P_2O_5$  ratio, without a sacrifice of economic advantages. In fact, it is our opinion that the introduction of other ions in parallel with the potassium ions will improve and not reduce the economic advantages. I must admit that we cannot prove this today since much more research work has to be done here to clarify this secondary reaction.

Secondly you ask for a comparison involving your Odda process instead of the phosphoric acid route. In our paper we chose the phosphoric acid route because we wanted to compare it with a process which could give the same total nutrient contents in order to avoid the difficulties of assessing values with different total nutrient contents. With the phosphoric acid route ion exchange gives a saving in phosphoric acid and on the other hand there is the cost of carrying out the ion exchange. In the case of the Odda process and the 14-14-28 example, you have the same raw materials : phosphate rock, ammonia, nitric acid and potassium chloride. It is not surprising, therefore, that you get about the same raw materials costs. The difference is in the processing and not in the raw materials costs. In the Odda process you cool, crystallise and filter, make calcium nitrate and sell it ; if you wish you convert it to another nitrate-containing material which you return to the NPK plant. With the ion exchange route, you convert the calcium nitrate in situ, in the slurry, from calcium nitrate into potassium nitrate, and leave it there. In comparing the two processes, this is the main difference and therefore the question to be answered in determining the cheaper route is as follows :

Is it cheaper to convert the calcium nitrate where it is, in the nitrophosphate slurry, than to take it out of the nitrophosphate slurry, convert it outside, and put it back again? The lower overall cost will be determined by this main difference but there are other differences. If you use potassium chloride instead of potassium nitrate in the Odda process you obviously get a chlorine-containing material and therefore a lower total nutrient content. At the same time, if you succeed in converting the calcium nitrate in the Odda process into potassium nitrate and then put it back again, you do not achieve exactly the same thing as we do with the ion exchange route. There are at least two reasons. Firstly, in the Odda process, you have to operate at a higher acid:rock ratio for crystallisation and filtration, than we need in the ion exchange route. Secondly we have a loss of hydrogen and therefore the neutralisation capacity of the slurry, after the ion exchange, i.e. the ability to absorb ammonia in neutralisation, is lower because of hydrogen loss. Therefore, in the Odda process, you will get a higher minimum N:P<sub>2</sub>O<sub>5</sub> ratio than we do. Thus, if you convert the calcium nitrate into potassium nitrate in the Odda process and put the potassium nitrate back into the slurry, it is questionable whether you could make a 14-14-28, because the higher nitrate content would result in a higher N:P<sub>2</sub>O<sub>5</sub> ratio than 1:1. These are minor considerations and the main difference is whether it is cheaper to convert the calcium nitrate where it is or to take it out and convert it outside. I must admit that, before anything can be proved in this respect, we must prove that it is possible to operate an industrial scale ion exchange plant, in order to gain some operating experience which can be compared with your operating experience.

You mentioned sea transportation problems due to the IMCO codes but this is also included in one of your questions.

Your first question concerned the stability of the resin. As far as I see, you wish to know how long we have evaluated the resin we use since you consider the indicated resin consumption to be fairly low. Our pilot-plant has been operating for more than two years under different conditions and the resin is still in good condition. At the same time, we have made quite a number of laboratory tests for different resins under different conditions and it is true to say that under severe conditions even the best resins have been completely spoilt. In our paper we mentioned a test that was made in a period of 30-40 days. The resin, in the pilot-plant, was very carefully checked as regards total and useful capacity and physical appearance,

both before and after the tests. No detectable losses were found. Based on our experience with the resin over this period we think that the figure we have given for resin consumption is very much on the safe side.

Question 2 : you want to know the water content in the brine coming from the ion exchange unit, considering the steam consumption to be low. In fact, we consider it high and we hope to be able to reduce it. If we were to make the calculation today we would probably put in a slightly lower figure. The water content in the brine is related to all the other costs and the losses from less rinsing relate to lower evaporation costs and vice versa. It is a question of what is an economic level of the water content. Today it is our opinion that an economic level might be about 60-65% water in the brine coming from the ion exchange unit. If you want to calculate the steam consumption based on such a figure, you have to take into account that, in the case of the phosphoric acid route of the paper, a number of factors should be considered. Firstly there is dilution in the ion exchange. Secondly, you have to take into account that, in the ion exchange, you use more nitric acid than with the phosphoric acid route. Thus you bring in more water with the nitric acid. The ion exchange has to pay for that in steam consumption. Thirdly, you get less neutralisation heat, among other things, due to the hydrogen loss. Therefore the ion exchange also has to pay for less evaporation due to the neutralisation. Fourthly you have to take into account that, by using phosphate rock instead of phosphoric acid, you introduce less water. It is therefore somewhat complicated to calculate steam consumption.

Your third question. You want to know if we can give any cost indications for the sodium recovered. The answer is no. Sodium is, in principle, of no cost, but of course it puts a load on the ion exchange unit. It is difficult to calculate how much it influences the total running costs of the ion exchange unit because we can accept a high sodium loss. At the same time the selectivity in the resin, for potassium against sodium, involves the possibility of, so to speak, putting the sodium loss on top of the potassium loss, and it influences the possibility of the proportion of the total capacity which could be useful capacity. It is therefore very complicated to give any indication of what it costs to take up this extra sodium in the ion exchange unit.

Your fourth question concerning the chloride content, how low we could go and if we could go low enough. In the pilot-plant I think we can go as low as desired. Today we think that 0.2-0.5% chloride in the finished product is sufficiently low. It is possible to go lower with more

rinsing on the potassium chloride side. This is, of course, without influencing steam consumption, because steam consumption is on the slurry side, not on the regeneration side.

Question 5 : What do the Danish Authorities say in relation to the high potassium nitrate content ? We have no doubt that the Danish Authorities will require some test to indicate the oxidising capacity. As far as we know, there is no official test today, and, therefore, we have used the two proposed tests, the Fisons and the ICI test. We have used these to test the products we plan to introduce in Denmark. We have found by both tests a lower oxidising capacity than for the calcium ammonium nitrate produced and sold in Denmark today. It may be that we have not paid enough-attention to the problem of IMCO Codes and transportation rules. We shall carry out more tests on this, and I thank you for drawing our attention to this problem.

Mr. ROLFSEN : The speaker seems not to agree with my view that the flexibility of this process was increased at the expense of the process' economic advantages. I am familiar with this process only from the paper. The speaker has put forward two examples. In the one case the saving from the process is \$ 1.70, but when the process is operating under optimum conditions, then there is a saving of \$ 7.70. Thus I must draw the conclusion that if the process is working under optimum conditions, then it is economically very advantageous. But when the process is working under less favourable conditions, as in the 18-18-18 example, then he has not demonstrated any economic advantage.

Mr. KNUDSEN : The flexibility has not in fact very much to do with the examples, because the examples are based on a straightforward potassium ion exchange with no other ions taken in parallel with the potassium. As to the comparison with the Odda process, I do not think it is a question of comparing raw material costs. It is obvious that, in the 18-18-18 example, ion exchange will involve higher raw material costs because some phosphoric acid is used. With the 14-14-28 grade we get the same raw material costs as in the Odda process. We consider the running costs more important because there are two different routes, but we cannot illustrate this today because we do not know the costs on an industrial basis. You know them in the Odda process, and we hope to be able to know them in the future for the ion exchange process.

Mr. MINTACOST (Norsk Hydro) : I have one question. Since the resin seems to be confined within the circular tube, I assume the liquids have to be virtually solid-free. Would you please comment on this.

Mr. KNUDSEN : In fact the liquids are not solid-free. It is not economically possible to operate them completely solid-free. One solid which is of interest is the solid in the nitrophosphate slurry. We intend to take some of the sand out of the nitrophosphate slurry in a kind of a simple sand trap or something like that. It is too difficult and in our opinion too costly to take out all the solids. For several reasons we find it necessary to have a backwash procedure as a step in this circular system, whereby the solids which do not go through the resin and follow the effluents, but which are kept back on the resin, will be washed out of the resin in the backwash step.

Mr. P. MORAILLON (Péchiney-Saint Gobain) : What type of phosphate was used in the trials ? Was this phosphate calcined ?

Mr. KNUDSEN : In the pilot-plant we have, up to now, only used two phosphate rocks, Moroccan and Kola. I think the Moroccan rock was the HN type from Casablanca. Mostly we used Kola phosphate rock. The example given in the paper is based on the assumption that it is Kola phosphate rock. I do not think the HN rock is calcined but I am not very familiar with this aspect.

Mr. A. HORNSOJ MØLLER (Dansk Svovlsyre) : I can say the Rhouribga phosphate is of the ordinary 75 76 BPL type. It is not calcined.

Mr. R.D. YOUNG (T.V.A., U.S.A.) : What are your plans for disposal of the calcium chloride ?

Mr. KNUDSEN : We plan to pump the calcium chloride solution into the sea. We are in a lucky position in that respect because our plant is situated near the sea with a strong current. Today we pump the gypsum into the sea. When we start the ion exchange plant, the gypsum, the calcium sulphate, will be replaced by calcium chloride. If there is any waste problem, then it is possible to neutralise the calcium chloride solution. The secondary reaction, the com-

petition between calcium and hydrogen on the resin, means a loss of hydrogen. Thus when you regenerate with the potassium chloride solution you get a calcium chloride solution containing some hydrogen chloride and it is an acid effluent. You may neutralise this with calcium carbonate to get calcium chloride, which makes the effluent problem easier. It is our opinion that, if you do not want any calcium chloride effluent, it should be possible to produce solid calcium chloride. This product is not interesting in our case, but it might be in others.

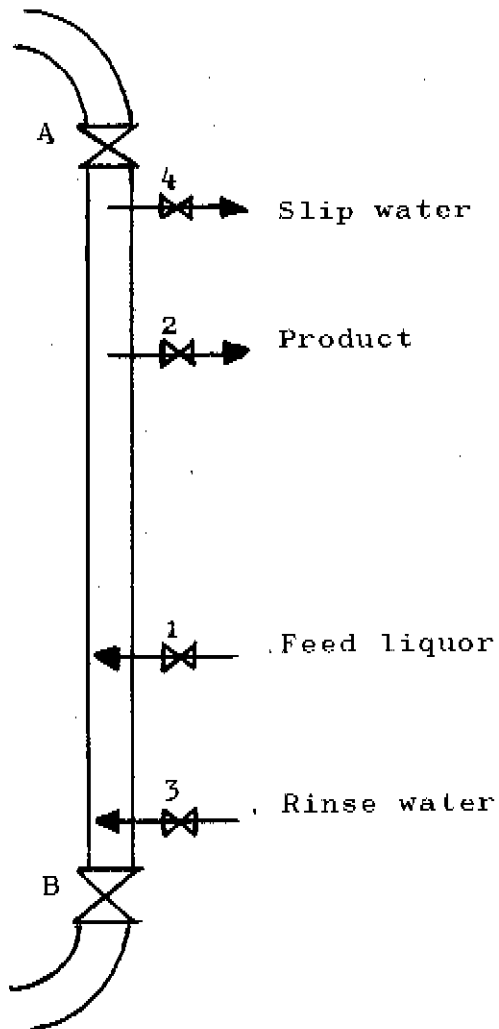


Fig. 1

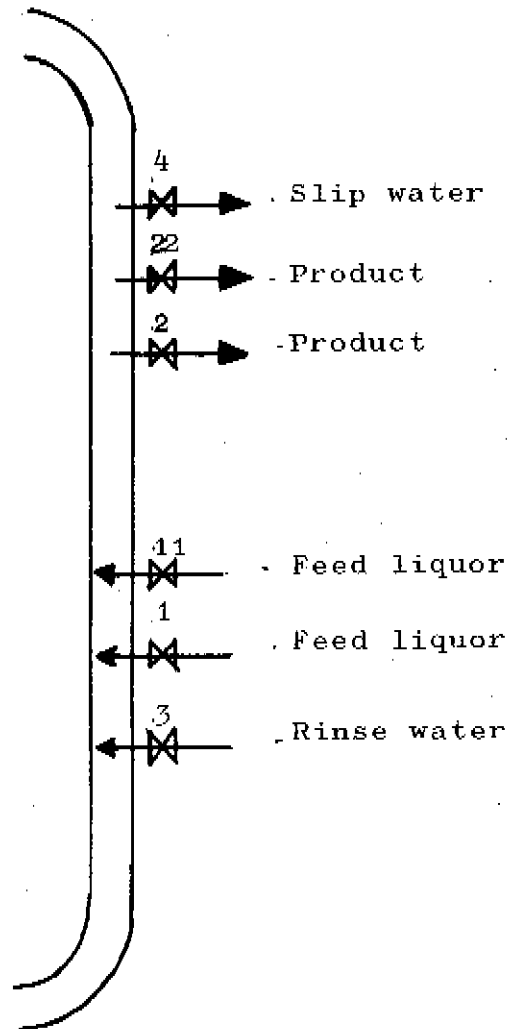


Fig. 2