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Experiments with  
Pre - neutralisation in the Manufacture  
of Compound Fertilisers

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1. Introduction

The manufacture of compound fertilisers in Finland has increased from negligible amounts 15 years ago to over 50 percent of the total fertiliser production in 1962. The phosphate component of the compound fertilisers is locally manufactured superphosphate and the potassium is added in the form of chloride or sulphate. The nitrogen compounds are also of domestic origin to the extent that our nitrogen industry has been able to produce them. About half of the nitrogen compounds used in compound fertilisers are now produced in Finland. Nearly all of the domestic nitrogen is purchased as so-called nitrogen solution with which it is also possible to ammoniate the superphosphate in the compound fertilisers. The imported raw material has mainly been the double salt ammonium sulphate nitrate ( $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NH}_4\text{NO}_3$ ).<sup>1)</sup> The total nitrogen content of the technical product is 26 per cent, of which one quarter is nitrate nitrogen. The proportion of combined sulphuric acid in the product is about 46 per cent.

When ways of using more nitrogen compounds of local origin in our compound fertilisers were considered, our attention was drawn to the use of a pre-reactor developed in the United States. The pre-reactor makes it possible to neutralise the free ammonia in the nitrogen solution with acids to obtain nitrogen compounds for compound fertilisers. The heat of reaction evaporates excess and detrimental water from the salt mixture. The resulting warm salt melt or slurry of low water content is fed through a distributor in suitable ratios into the other fertiliser components. With the aid of the pre-reactor we are able to increase the consumption of

1) K.D. Jacob: Fertilizer Technology and Resources in the United States, Vol. III, 1953, P. 102

locally produced nitrogen solution and sulphuric acid. In winter the composition of the nitrogen solution is such that when it is neutralised with sulphuric acid, the composition of the produced salt is identical with the imported ammonium sulphate nitrate. The introduction of a pre-reactor will not require us to modify any of the compound fertilisers we are now producing. The results of experiments with a pre-reactor on a pilot plant scale are described in the following. Up to the present the experiments have related to the use of nitrogen solution and sulphuric acid, but we plan to extend these investigations in other directions.

## 11. Raw materials

### 1. Nitrogen solutions.

Owing to our varying climatic conditions the composition of the nitrogen solution is different in winter (winter solution) to that in summer (summer solution). The compositions of the two solutions are shown in Table 1.

TABUL 1

	Winter Solution	Summer Solution
Composition:		
Ammonium nitrate	60.0%	65.9 %
Free Ammonia	24.2 %	16.7 %
Water	15.8 %	17.4 %
Total:	100.0 %	100.0 %
Physical properties:		
Crystallization temperature	- 18°C	+ 6°C
Boiling point (when total vapour pressure of the solution is 760 torrs)	+ 19°C	+ 35°C
Distribution of nitrogen:		
Ammonia nitrogen		
As $\text{NH}_4\text{NO}_3$	10.5 %	11.5 %
Free ammonia	19.9 %	13.8 %
Total:	30.4%	25.3 %
Nitrate nitrogen		
As $\text{NH}_4\text{NO}_3$	10.5 %	11.5 %
Total $\text{NH}_4\text{NO}_3$	40.9 %	36.8 %
Guarantee total nitrogen	41.0 %	36.85%

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TABLE I (Continued)

	Winter Solution	Summer Solution
Distribution of total nitrogen:		
Ammonia nitrogen	74 %	69 %
Nitrate nitrogen	26 %	31 %

An examination of the data in Table I reveals that the percentages of ammonia nitrogen and nitrate nitrogen are the same as in ammonium sulphate nitrate in the winter solution but the nitrate nitrogen content is relatively higher in the summer solution.

Owing to the different compositions of the two nitrogen solutions, the products from the pre-solutions also differ in composition. The difference between the winter and summer solutions is due to the different amounts of ammonia gas added to 80 per cent aqueous ammonium nitrate solution. The winter solution can be changed into the summer solution by removing ammonia gas and the summer solution can be changed into the winter solution by adding 9.8 per cent ammonia by weight. This ammonia deficit in the summer solution can be corrected by introducing ammonia separately into the pre-reactor. Our experiments to date have been carried out using only the winter solution.

## 2. Sulphuric Acid.

The sulphuric acid employed was 93 per cent contact acid which was diluted as required. In some experiments the undiluted acid was employed and water was added separately to the pre-reactor to regulate the temperature.

## 3. Neutralisation of nitrogen solution with sulphuric acid

### a. Winter solution.

100 kgs of winter solution were neutralised by 69.7 kg of 100 per cent sulphuric acid. The calculated composition and nitrogen contents of the dry matter were as follows:

TABLE 2

	Weights	NH <sub>3</sub> -N	NO <sub>3</sub> -N
Composition:			
NH <sub>4</sub> NO <sub>3</sub>	60.0 kg	10.5 kg	10.5 kg
NH <sub>3</sub>	24.2 "	19.9 "	-
H <sub>2</sub> SO <sub>4</sub>	69.7 "	-	-
	<hr/>	<hr/>	<hr/>
Total:	153.9 kg	30.4 kg	10.5 kg
Nitrogen content		19.8 %	6.8 %
Nitrogen ratio		74 %	26 %
Total nitrogen content		26.6 %	

b) Summer solution

100 kg of the summer solution were neutralised by 48.1 kg of 100 per cent sulphuric acid. The composition of the dry matter was as follows:

TABLE 3

	Weights	NH <sub>3</sub> -N	NO <sub>3</sub> -N
Composition:			
NH <sub>4</sub> NO <sub>3</sub>	65.9 kg	11.5 kg	11.5 kg
NH <sub>3</sub>	16.7 "	13.8 "	-
H <sub>2</sub> SO <sub>4</sub>	48.1 "	-	-
	<hr/>	<hr/>	<hr/>
Total:	130.7 kg	25.3 kg	11.5 kg
Nitrogen content		19.4 %	8.8 %
Nitrogen ratio		69 %	31 %
Total nitrogen content		28.2 %	

As already mentioned, the experiments described below relate to the neutralisation of the winter solution with sulphuric acid in the pre-reactor.

III. Equipment

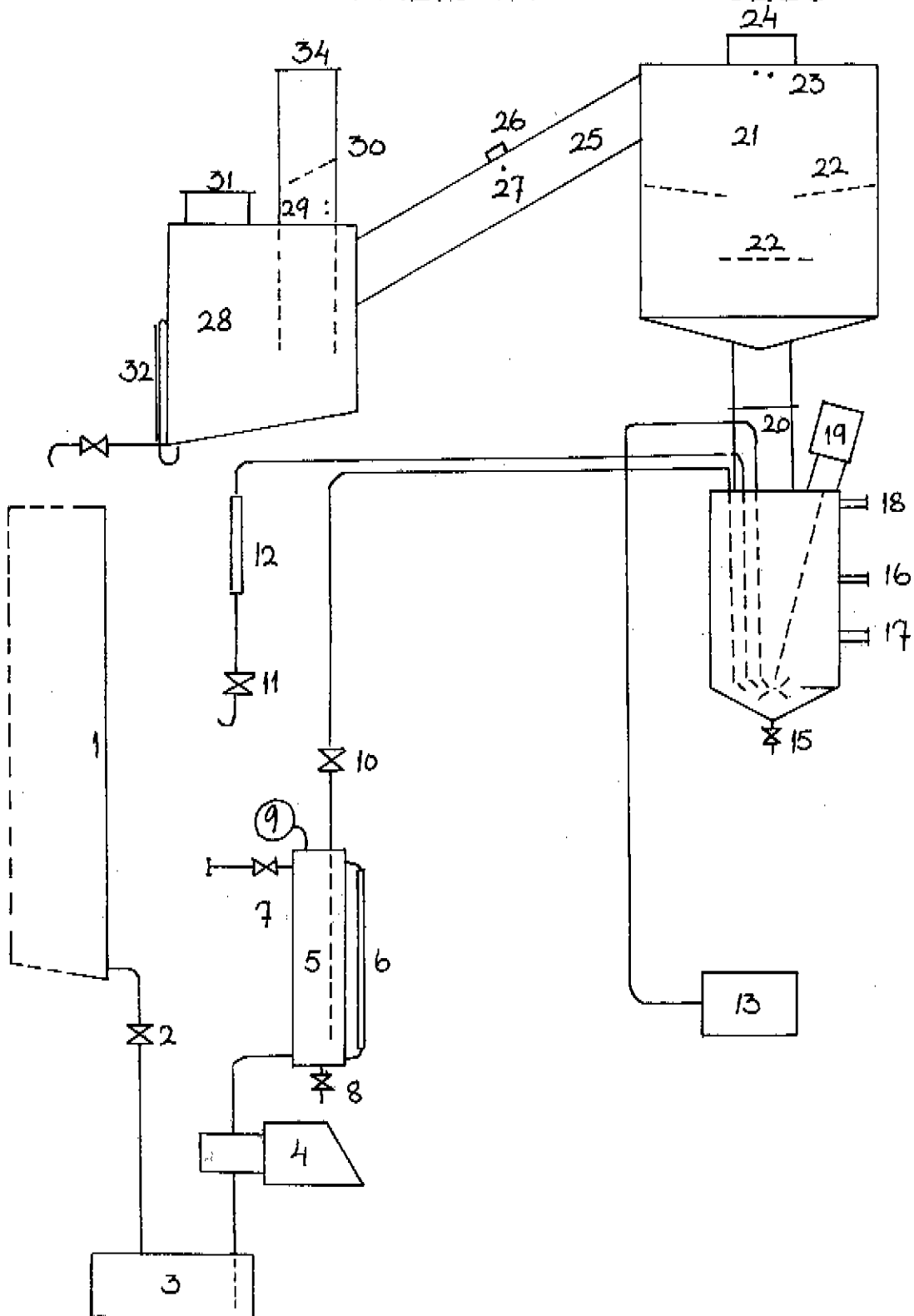
The pre-reactor unit is shown schematically in Fig. 1. The various components of the unit (nos. 1-34) are the following:

1. Three storage tanks for raw materials.

Nitrogen solution tank, volume 1445 l, equipped with cooling coil, mixer, and glass gauge, the latter to follow

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FIGURE 1: SCHEMATIC EQUIPMENT ARRANGEMENT FOR PRENEUTRALISATION PROCESS



and measure liquid consumption.

Sulphuric acid tank, volume 1300 l, equipped with cooling coil and glass gauge. Mixing is effected with compressed air.

Storage tank for water used to regulate temperature, volume 1300 l, equipped with glass gauge.

2. Bottom valves of storage tanks, three of them.
3. Constant-level vessels for nitrogen solution, sulphuric acid and water. The suction heads of the dosing pumps are kept constant by floats and ball valves in these vessels.
4. Dosing pumps, Lova HL 1. The pump for the nitrogen solution delivers 0-185 l/h, the other pump 0-136 l/h.
5. Counter pressure vessels for nitrogen solution, sulphuric acid and water. When the air in the upper part of the vessel is compressed, it produces the counter pressure required by the closing pump and eliminates surges due to the reciprocating movement of the pump cylinder. Dimensions of the vessels are diameter 160 mm and height 700 mm.
6. Glass gauge of counter pressure vessel for following changes in liquid level.
7. Valve for introducing compressed air to replace the air layer during a run.
8. Bottom valve for emptying the counter pressure vessel.
9. Manometer to measure counter pressure.
10. Needle valve to produce and regulate counter pressure.
11. Valve for water used to wash the unit.
12. Rotameter to measure water flow.
13. Temperature gauge.
14. Pre-reactor. Dimensions:
  - outer diameter 400 mm
  - inner diameter 375 mm
  - cross-sectional area of cylindrical part (evaporating surface  $11 \text{ dm}^2$ )
  - height of cylindrical part 620 mm
  - height of conical bottom part 100 mm

The plane where the cylindrical part meets the cone is called the feed plane. Located in this plane are a two-

bladed mixing propellor, a jacketed thermocouple, and the lower ends of 1/4 inch vertical tubes for feeding nitrogen solution, sulphuric acid, water for temperature regulation and water for cleaning the reactor.

15. Discharge valve of pre-reactor. The contents of the pre-reactor can be discharged by means of a double valve either into the mixer vessel (where the pre-solution is mixed with powdered raw materials) or into a drain.

16. Discharge tube 1 (upper). This tube adjusts the volume of liquid in the reactor to 43.5 l and the level of pre-solution to 36 cm.

17. Discharge tube 2 (lower). This tube adjusts the volume of the reactor to 23.5 l and the pre-solution level to 18 cm. The tube can be closed by a plate. When it is open, the discharge tube allows the pre-solution to enter the cone from which the solution flows under its own pressure through a distributor into the mixer.

18. Reserve discharge tube. When either of tube 1 and 2 becomes blocked, the reactor contents may flow through this tube into the mixer or the drain. All three discharge tubes are 1 inch in diameter and 150 mm long.

19. Bauknecht DCF x 1 1/2 mixer, 2870 r.p.m., 2.2 kilowatts, rotating the two-bladed mixing propellor.

20. Connecting tube from pre-reactor to drop separator. Its cross-sectional area is  $2.5 \text{ dm}^2$ , which is 23 per cent of the cross sectional ~~evaporation area of the reactor.~~

21. Drop separator to lower the rate of flow of steam and exhaust gases produced in the pre-solution and to remove spray.

22. Spray removal ring and plate.

23. Openings for thermometer and manometer.

24. Opening for incoming air, diam. 200 mm, equipped with cover.

25. Connecting tube from drop separator to condensate collector.

26. Opening for gas volume measurement.

27. Openings for thermometer and manometer.

28. Condensate collector.

29. Openings for thermometer and manometer.

30. Adjustable damper.



31. Opening for incoming air, diam. 175 mm, equipped with cover
32. Glass gauge.
33. Discharge valve.
34. Connection to washing tower.

The nitrogen solution tank and its ancillary units are of pure sheet aluminium. The other units are of AISI 316 stainless steel. Parts 14, 20, 21 and 25 are insulated by a 5 cm thick layer of mineral wool.

#### IV. Operation of the Pre-reactor

The neutralisation of the free ammonia in the nitrogen solution with sulphuric acid takes place under vigorous mixing in the pre-reactor. The heat of neutralisation raises the produced pre-solution to the boiling temperature. According to previous reports the temperature of the pre-solution must not exceed  $164^{\circ}\text{C}$ , for otherwise the nitrate of the nitrogen solution will begin to decompose. The temperature can be regulated by adding the desirable amount of the water to the reactor. A vigorous evolution of steam occurs when the pre-solution temperature attains its boiling point and water is removed from the pre-solution as steam.

The operation of the reactor can be divided into two stages; the initial or heating stage and the actual run.

During the initial stage the preparation of the pre-solution is begun according to a certain programme. The temperature of the pre-solution (and its moisture content) is adjusted to the desired level. Also the free acid to be left in the solution is adjusted. In our experiments the reactor was brought to operate as follows:

The counter pressure is raised to 2 atm. gauge.

Water (15 l) is added to the reactor to cover the ends of the feed tubes and the mixing propellor.

The mixing motor is switched on.

Nitrogen solution and sulphuric acid are introduced simultaneously at appropriate rates. The reactor gradually fills and the temperature begins to rise. When the level of the solution has risen up to discharge tube, the solution flows out through the latter.

The cooling water is introduced at the end when the programmed temperature has been attained.

The initial stage lasts 45-60 min. During this time, the original pre-solution, which is initially low in nitrogen content, attains its final steady-state composition.

The actual run is a continuation of the initial stage. During the run, as during the initial stage, the rate of flow of the nitrogen solution is held constant. The dosage of water is adjusted to maintain a constant temperature. The proper dosage of sulphuric acid is checked by titrating samples of the pre-solution from time to time.

The reactor operates continuously. The volume of the pre-solution produced is determined by the operating conditions and the dimensions of the reactor. The efficiency may be determined by calculating the weight of the products as a percentage of the weight of the reactants.

When it is wished to terminate the production of the pre-solution, the dosing pumps are stopped and the reactor is emptied through the bottom valve. The reactor is flushed with water after it has been emptied.

## V. Performance of the Experiments

### 1. Pre-treatment of the nitrogen solution.

The composition of the nitrogen solution was checked before each experiment. When its free ammonia content was too low, the required amount of ammonia was added. The average analytical data for the adjusted nitrogen solutions are:

Free ammonia	24.3 %
Total nitrogen	41.2 %
Ammonia nitrogen	30.6 %
Nitrate nitrogen	10.6 %

The rate of flow of the nitrogen solution was checked by following the liquid level in the feed tank and carrying out density determinations. The dosage of nitrogen solution was 120 l/h at full speed and 60 l/h at half speed.

2. Sulphuric acid of 65, 70, 75, 80 and 93 percent was used.

The free acid content of the pre-solution expressed as sulphuric acid was adjusted to 0.3 per cent or 3.3 per cent by varying the acid feed. The first pre-solution will be referred to below as "neutral" and the second as "acid". The acid content was followed by titration at 5 minute intervals. The amount of acid used was calculated from the change in level in the feed tank and the density.

3. The water used to adjust the temperature was determined from the change in the level in the feed tank.

4. The actual run

The initial stage was considered to have ended when the temperature and free acid content had remained constant for 15 minutes. The length of the actual run was 5 hours in all experiments. Samples of the pre-solution were taken at half-hour intervals for analysis in the laboratory. A negative pressure of 0.1 mm water column prevailed in the steam-removal system during the runs. This pressure was maintained by allowing about 170 m<sup>3</sup>/h of air at 22°C to pass into the system through the air inlet of the drop separator. The volume of steam and air-gas mixture removed was about 260 m<sup>3</sup>/h; the temperature of the gases was 63°C on average.

## VI. Experimental

In the first run, the effect of the sulphuric acid concentration on the temperature of the pre-solution was examined without adding water to regulate the temperature (Table 4). Table 5 shows the results when the acid concentration was 70 and 93 per cent. In these runs, attention was paid to the following:

- (1) The preparation of neutral and acid pre-solution.
- (2) The operation of the reactor at full and half speeds with different charges.
- (3) The nitrogen losses. The nitrogen loss is equal to the ratio of the difference between the ingoing and outgoing nitrogen to the ingoing nitrogen as calculated from the analytical data.

Table 4

## Programmed factor levels.

- Sulphuric acid concentration	%	65	70	75	80
- Quality of pre-solution		neutral	neutral	neutral	neutral
- Nitrogen solution feed	l/h	120	120	120	120
- Overflow tube	No.	1	1	1	1
- Charge height	cm.	36	36	36	36
- Temperature	°C			unspecified	
- Number of experiments		4	4	4	4
- Experiment group		A	B	C	D

## Results

## Sulphuric acid concentration

	%	64.9	70.3	75.1	80.0
Reactor temperature	°C	122	126	143	158
Quantities per ton of pre-solution produced					
- Nitrogen solution	kg/ton	591	634	640	660
- Sulphuric acid	"	567	551	526	512
- Water added	"	-	-	-	-
	Total kgs.	1158	1185	1166	1172

## Analytical data for pre-solution

- Water content	%	10.6	7.1	3.1	2.1
- Total nitrogen	%	23.4	24.5	25.7	25.5
- Experiment group		A	B	C	D

Table 5

## Programme

		70						93					
		neutral acid		neutral	neutral			acid			neutral		
- Sulphuric acid cons.	%	120	120	60	120	120	120	120	120	120	120	60	60
- Acidity of pre-solut.		1	1	2	1	1	1	1	1	1	2	2	1
- Feeding rate of N.Solut.1/h		36	36	18	36	36	36	36	36	36	18	18	36
- Discharge tube	cm	free	free	free	120	130	140	120	130	140	130	130	130
- Charge height	cm	5	4	6	5	4	6	3	3	3	3	3	4
- Temperature	°C	E	F	G	H	I	J	K	L	M	N	O	P
- Number of experiments													
- Experiment group													
Experimental results													
- Sulphuric acid cons.	%	70.3	70.2	70.4	92.0	92.2	92.4	92.3	92.2	92.1	91.6	91.5	92.5
- Reactor temperature	°C	126	143	129	124	131	140	121	129	140	131	131	130
Quant./ton of pre-solution produced.													
- Nitrogen solution	kg	634	584	674	629	660	743	507	574	628	728	701	653
- Sulphuric acid	"	551	570	505	413	417	405	416	457	450	375	392	429
- Water	"	-	-	-	197	168	86	290	216	147	119	169	170
Total:	kg	1185	1154	1179	1239	1245	1234	1213	1247	1225	1222	1202	1252
Efficiency	%	84.4	86.7	84.8	80.7	80.3	81.0	82.4	80.2	61.6	61.8	83.2	79.9
Analytical data for pre-solution													
- Water content	%	7.1	6.9	9.7	9.5	6.7	2.3	16.2	7.8	4.6	7.1	6.3	5.9
- Total nitrogen	"	24.5	23.6	24.3	24.2	24.8	26.5	20.9	23.4	24.7	25.4	25.5	25.1
- Nitrate nitrogen	"	6.6	6.1	6.9	6.7	6.9	7.8	5.4	5.0	6.7	7.7	7.7	7.0
- " " "	"	25.9	25.8	28.4	27.7	27.8	29.4	25.8	25.7	27.1	30.2	30.2	27.9
- Free acid (H <sub>2</sub> SO <sub>4</sub> )	"	0.2	3.2	0.3	0.3	0.3	0.3	3.5	3.0	3.1	0.4	0.4	0.5
- pH		3.5	2.4	3.4	3.4	3.3	3.3	2.4	2.4	2.5	3.6	3.4	3.5
- Density		1.51	1.53	1.49	1.49	1.53	1.53	1.47	1.50	1.53	1.49	1.52	1.53
Pre-solution													
- Nitrogen loss	%	5.8	1.7	11.3	5.7	9.8	13.4	0	0.8	4.6	15.3	11.8	6.7
- " solut. required		2.59	2.47	2.77	2.56	2.66	2.80	2.43	2.45	2.54	2.87	2.75	2.60
per kg. of nitrogen	kg.	E	F	G	H	I	J	K	L	M	N	O	P
- Experiment group													

Before examining the results, it may be appropriate to mention the limiting conditions in pre-solution manufacture.

The temperature must not rise to the maximum 164°C, but should remain clearly below this limit.

The pre-solution must have a suitable water content so that it can be fed through the distributor into the dry powdered superphosphate - potassium salt mixture. The minimum water content in our unit is about 7 per cent.

The upper limiting water content is determined by the total water content of the powder mixture and the pre-solution used. The water content should not be so high that the whole mixture becomes a paste. On the contrary, the final mixture must be so dry and fine that it becomes granular with a high yield only on adding granulating water. Our experimental unit was designed on this principle. The phosphate component in Finnish compound fertilisers is superphosphate manufactured from Kola apatite. The water content of the cured superphosphate is about 13 per cent and the free phosphorus pentoxide content about 5 per cent. When the content of this easily plasticizing superphosphate in the powder mixture (to which the pre-solution is added) used to prepare, for example, an 0-13-09 granulate is 72 per cent, the maximum permissible water content in the pre-solution made in our pilot plant is about 10 per cent. It may be pointed out that the water and nitrogen contents of the pre-solution are negatively correlated.

The nitrogen losses should be as small as possible.

Although the main attention was paid in the above experiments to the preparation of the pre-solution, we have also used the pre-solution partly as a nitrogen source in the preparation of a half-ton batch of a 9-13-9 granulate. Of the total nitrogen, 52 per cent was derived from ammoniating nitrogen solution and 48 per cent from the pre-solution; 5 per cent water was used to effect granulation. The dry granulate contained 4 per cent of particles larger than 6 mm, 80 per cent of particles between 1-6 mm, and 16 per cent of particles below 1 mm in diameter.

The results were satisfactory from our point of view. The average composition of the product was:

Moisture	2.0 %
Total nitrogen	9.1 %
Nitrate nitrogen	2.6 %
Free phosphoric acid as $P_2O_5$	0.0 %
Water-soluble $P_2O_5$	7.7 %
Water- and ammonium citrate- soluble $P_2O_5$	9.0 %
Total $P_2O_5$	12.8 %
Potassium as $K_2O$	9.0 %

The average force required to break one granule was 3.6 kg.

## VII. Discussion

### 1. Operation experience

An examination of Tables 4 and 5 reveals a number of interesting details.

The main industrial grades of sulphuric acid, the 70 per cent tower acid and the 93 per cent contact acid, can be used directly without separate dilution in the manufacture of the pre-solution. In our unit the 70 per cent acid could be used as such, but the 93 per cent acid required the addition of water separately to regulate the temperature.

The temperature rise is greater with acid pre-solution than when neutral pre-solution is produced (experiment groups E and F). If the temperature is kept constant, the water added must be varied accordingly (experiment groups H-M).

The nitrogen loss increases with the reactor temperature when both neutral and acid pre-solutions are produced (experiment groups H-J and K-M).

A decrease in the charge volume by one half increases the nitrogen loss (experiment group N) even though the feeding of liquids is halved (experiment groups G and O). A change in the feeding of the nitrogen solution does not essentially alter the nitrogen loss when the charge volume is constant (30 cm; experiment groups I and P).

The nitrogen loss is smaller when acid than when neutral pre-solution is produced.

The proportion of nitrate nitrogen in the pre-solution increases with increasing nitrogen loss. The lost nitrogen is mainly free ammonia which escapes through the pre-solution.

Constant supervision of the temperature of the pre-solution is indispensable. It is difficult to follow the acidity variations with an indicating pH meter because of the high temperature of the pre-solution. We therefore had to follow the acidity variations by titrating samples taken at intervals.

An experienced operator learns to adjust the acidity of the solution by examining the vapours issuing from the reactor. When the solution is close to neutral the vapours look like condensing steam, but as the acidity increases the vapours become more opaque. Fumes can be removed from the exhaust gases in a wash tower.

## 2. Equipment.

The unit operated for the most part according to expectations. Certain details may, however, be stressed on the basis of our experience with the unit:

The boiling of the reaction mixture gives rise to vibration which must be suppressed by suitable means.

The tubes through which the reactants were introduced extend from the top to the bottom of the reactor. In our new full-scale reactor, the tubes enter from the side. Our opinion is that in particular the nitrogen solution should not pass long distances in a hot environment because ammonia tends to vaporize. When the tubes enter from the sides, the reactor must be equipped with baffles to prevent vortex formation; in the pilot unit the feed tubes function as baffles.

The bottom cone of the reactor should not be too high because it favours vortex formation and requires the addition of unnecessary water when the unit is set into operation.

The consumptions of reactants we have followed through a glass gauge in the storage tanks only. Rotameters will be installed in the feed tubes of the larger unit to permit detection of uneven flow.

Particular attention must be paid to the proper functioning of pumps and meters. We have, for example, fitted two manometers



to each of the counter pressure vessels connected to the pumps.

For reasons of safety, an automatic unit should be installed for introducing water into the reactor when the temperature rises too high. Also an alarm should be installed to give a warning when the volume of the charge increases excessively because of blockage of the pipe-lines.

The material from which the reactor and solution and steam pipe-lines were made was AISI 316 stainless steel. It did not corrode except in that part of the sulphuric acid feed line, which was immersed in the hot pre-solution.

#### VIII. Summary

The pilot reactor described has proved suitable for the production of nitrogen-containing components appropriate for manufacturing compound fertilisers not produced in our country. On the basis of our experiments with this unit, we are now erecting a full-scale pre-reactor at our Harjavalta factory. The experiments we have carried out have been limited to a study of the reaction between nitrogen solution and sulphuric acid, but in principle the reactor can be employed in other neutralisation processes.

DISCUSSION

Dr. T. K. VAHERVUORI (Finland) : One of the major developments in the fertiliser industry during the last decade has been the increasing production of compound fertilisers. The relative ratios of the nutrients in the compounds and the incorporation of certain anions and cations must always be adapted to the local conditions relating to soils, crops and climate. Consequently, the fertilisers produced by different manufacturers naturally differ in these respects. When these basic requirements have been clarified, the problem remains for the producer to prepare the products in the most economic manner from the most appropriate raw materials. When seeking the most economic solution, the modern mixed fertiliser industry strives to use the simplest raw materials and to combine certain mixing and granulating operations. One process based on this principle is the use of the so-called pre-reactor, the purpose of which both here and in the U.S.A., where the unit has been mainly developed, is to replace solid nitrogenous components by a solution of reaction products of nitrogen solution and acid. The use of nitrogen solution offers a number of advantages compared with other organic nitrogen compounds previously employed. These advantages are the lower cost of transporting the solutions with their high nitrogen content, and the fewer risks associated with their transport and storage. As in our country the super-phosphate used for the manufacture of compound fertilisers is, in any case, ammoniated with nitrogen solution, the use of the pre-reactor saves us the trouble of transporting and storing the whole series of different nitrogen compounds. The nitrogen in the nitrogen solution is also probably cheaper. The economics of the manufacturing operations can be improved by carrying out the reaction stage in the pre-reactor, so that the heat of reaction and the water content can be used in the granulating and drying stages.

On the basis of the experiments that have been performed, it may be briefly stated that, in the supervision of the continuous operation of the pre-reactor on the production scale, one has to pay attention to only two factors, which control the whole process : the

temperature of the reaction solution and the acidity of the product.

The content of free acid in the pre-solution affects the nitrogen losses, which increase when the free acid content approaches zero. By varying the temperature of the solution, it is possible to control its water content, which in turn determines the tendency of the solution to crystallise and its mobility. The temperature can be regulated by varying the amount of water added to the system. This can be introduced in two ways : either separately or together with the acid. The latter procedure is safer, as its use eliminates any abrupt, undesired changes in temperature which might occur if the flow of water is uninterupted. In our process we intend to use an acid of about 70% concentration. We can then use tower acid as such, and the water content of the product thus obtained corresponds with that found to be most advantageous in our pilot plant experiments.

During the past summer we have completed the construction of the first production scale pre-reactor at our Harjavalta works. Those of you who take part in the visit to Harjavalta will see the unit in operation. The capacity of the pre-reactor corresponds to a production of 23 tons of compound fertiliser per hour. Superphosphate and potash salt are first mixed together in the mixer, and the mixture is ammoniated batchwise in the Sturtevant mixer. The pre-solution is added to the mixture continuously, after which normal granulation and drying are carried out. About half of the nitrogen in our most popular fertiliser, 8-13-9, comes from the solution used for ammoniation, and the remainder originates from the pre-solution.

Finally, with regard to our experiments with the pre-reactor, I should like to say that, considering the raw materials for our compound fertilisers and our nutrient ratios, the unit is evidently quite useful. We intend to have another reactor, as well as a new granulating unit, built at Harjavalta. We shall then be able to make use of the experience gained from the first reactor.

Mr. R. COCTEAU (France) : I have read with much interest the account of the series of experiments carried out by Dr. Vahervuori and Dr. Virtanen. Their observations, which are precisely reported, are interesting. I can only congratulate them upon presenting us with such a complete and detailed report.

If I have correctly understood the introduction to the paper, Finland uses internally produced nitrogenous materials in order to avoid the importation of other nitrogenous materials, either because they are more expensive or because their introduction would present economic difficulties.

I think this is an important point to bear in mind, for, if the aim is to produce concentrated ternary compound fertilisers, there is no great interest in neutralising nitrogenous solutions, called in France "Barrett liquors", by means of sulphuric acid before mixing them with other components. Apart from thus making a large quantity of ammonium sulphate, which is a hindrance to the achievement of a high-grade formulation, one loses the advantage of neutralising the free acidity in the superphosphate. This neutralisation is automatic, since the acidity already exists in the superphosphate. In France, we deliberately engineer a considerable free acidity, for, at the same time, it tends to increase solubilisation in the superphosphate and to give it thixotropic properties which are indispensable to good granulation.

With regard to trials which might be envisaged with another acid, for example phosphoric acid, saturation during the reaction might partially economise on acid concentration, but it would involve an obligation to scrub the effluent gases in order to prevent large nitrogen losses. These losses, which are mentioned in connection with sulphuric acid, are far from being negligible.

I think that the authors must, therefore, be faced with an economic necessity, in view of the raw materials that they are obliged to use.

However, I should like to put three additional questions to them:

1. Do the authors think it will be possible merely by the addition of water to regulate the temperature in a large

- scale installation, involving much larger amounts of materials? Will it not be necessary to link an external refrigeration plant to the pre-reactor?
2. In the pilot plant, the reactor and the pipes for the solutions and the steam were made of stainless steel AISI 316. There was no corrosion, except in the sulphuric acid feed pipe which is immersed in the hot solution. The acid feed is always the most delicate part of the neutraliser and is generally responsible for most of the working stoppages in this kind of apparatus. Are the authors considering the use of any material other than AISI 316 steel for the construction of this acid feed?
  3. Are the authors thinking of using phosphoric acid in this plant to neutralise the ammoniacal solution?

Dr. VAHERVUORI : The first question related to the possible necessity of using a special cooling unit with a production scale reactor. As I mentioned previously, we already have a production scale reactor at Harjavalta : it has been in operation for about a month. According to our experience so far, the water we add to our tower acid is quite adequate for cooling, without the addition of any special unit for this purpose.

The second question related to the steel used in the construction of our reactor and piping. Up to now, the AISI 316 steel has been very satisfactory. Naturally, we expect the sulphuric acid feed pipe to suffer worst from any possible corrosion, but here again we have had no trouble so far.

With regard to the third question, we have not used phosphoric acid so far for neutralising the ammonia solution, but we are planning to do so.

Mr. L. P. HIGGINS (U.S.A.) : With regard to the equipment for recovery of mist evolved from the pre-neutraliser, I presume it recovered entrained material primarily, and I should be interested to know whether it was effective for this purpose, how much of this entrained material was evolved, and whether it

was found to be actually necessary to recover it.

Secondly, I should like to discuss the depth of the pre-neutraliser. The paper states that, as the depth of the solution in the pre-neutraliser was increased, the recovery became better. Would a further increase in the depth of the solution not further improve recovery? Has this aspect been followed up in the large scale unit?

I ask this particularly, because we found in our unit that a depth greater than that indicated in the paper might be best for maximum recovery.

Dr. VAHLERVUORI : In our pilot plant we had no scrubber, only a condenser-separator, and we have followed with the same arrangement in our production scale unit, as can be seen from Figure 1 in the paper. The material flowing through the separator contains ammonium nitrate droplets, but I cannot say what percentage of the nitrogen throughput is recovered in this way because it is fed back into the reactor and comes through with the product.

With regard to the second question, the depth of the pre-neutraliser in our production scale unit is 1700 mm (with the cover 2110 mm). The depth of the solution in the preneutraliser depends on which of the 3 discharge tubes is used. The upper discharge tube corresponds to a depth of solution of 750 mm, the middle one, of 550 mm and the lowest one, 350 mm. The upper tube is normally used.

The recovery improves when the depth of the solution increases, but even that must have a certain upper limit, because the time during which the presolution is in the preneutraliser as well as the evaporation surface have their own importance in the process. We shall strive to obtain an apparatus with as favourable a recovery as possible.

Mr. J. C. FARQUHAR (United Kingdom) : I notice that, in the pilot plant, metering pumps are used. Could Dr. Vahervuori indicate what methods of metering and control are used in the larger plant? Secondly, the level control on the pilot plant is merely overflow. Has this been found satisfactory for the full scale plant? If the reactor level were to surge, simple overflow would cause flooding of material into the granulator.

Dr. VAHERVUORI : We use the same type of feed pumps on our full scale plant as on our pilot plant, although the capacities are naturally different. Similarly, with regard to the second question we use the same type of overflow level control on our full scale plant as that used on our pilot plant. The amount of variation in level is so small as to make no noticeable difference to the product analysis.

Mr. R. ARDOUIN (France) : Firstly, I should like to put two questions to the authors. Do they have a direct draught or an induced draught for the evacuation of steam, gases and dust? Secondly, in order to avoid nitrogen losses, should they not consider above all the position of the ammonia feed in relation to the acid feed ?

I should also like to ask Mr. Hignett, whether, in his I.V.A. ammoniator, he has not been led to suppress the scraper ?

Dr. VAHERVUORI : With regard to the first question, there are certain openings on the upper part of the reactor which enable us to adjust the internal pressure.

Mr. HIGNETT : With regard to Mr. Ardouin's question concerning the scraper in our ammoniator, we find with our system that a scraper is very desirable, because the pre-neutralised solution forms a very hard coating, if it contacts the wall of the drum. It is thus necessary to keep this coating within certain limits, and because of the hardness of the coating, we find that a fixed scraper is not adequate; we use a series of knife blades fixed on a shaft which moves backwards and forwards in a reciprocating motion, thus shaving the coating continuously from the drum. This method has proved quite satisfactory.

Dr. VAHERVUORI : Mr. Ardouin's final question related to the relative position of the feed inlets. It is most important that the nozzles or inlets should be at the same level and as deep as possible within the reactor. The nitrogen feed inlet could even be a little lower than that of the acid, to give the ammonia fumes a better chance of reacting with the acid.