International Fertilizer Industry Association

IFA Technical Conference

Marrakech, Morocco

28 September-1 October 1998

Date of receipt: 2 June 1998

FLEXIBILITY AND ENVIRONMENTAL PERFORMANCE OF KEMIRA'S MIXED ACID NPK PROCESS[1]

H. Kiiski
Kemira Agro Oy, Finland

SUMMARY

The KEMIRA mixed acid NPK process has demonstrated a high degree of flexibility in the choice of raw materials, grades (formulations), and operating conditions since the process was introduced in the 1970's. The NPK wet process is rather simple and has been combined with the most common granulation techniques such as blunger, drum and spherodiser.

A wide range of not only NPK but also N, NP, NK, and PK products has been made. Combined with advanced process control equipments developed by Kemira and modern automisation systems, the process provides high quality and customised products.

Phosphorous is sourced as a mixture of phosphate rock and phosphoric acid and the P_2O_5 water solubility can be adjusted according to customer needs. Special high quality fertilisers containing Mg, Na, S, and Te's or low chloride products are also produced.

Environmentally, the process is well within the EFMA BAT levels.

RESUME

Le procédé NPK Kemira avec mélange d'acides a montré un degré élevé de flexibilité dans le choix des matières premières, des formules et des conditions opératoires depuis que le procédé a été introduit dans les années 1970. Le procédé humide NPK est assez simple et a été combiné avec les techniques de granulation les plus communes telles que le pétrin, le tambour et le sphérodizer.

Une vaste gamme non seulement de formules NPK, mais aussi d'engrais N, NP et NK a été produite. Combiné avec l'équipement moderne de contrôle de procédé mis au point par Kemira et les systèmes modernes d'automatisation, le procédé fournit des produits de grande qualité et régularité.

Le phosphore est fourni par un mélange de phosphate brut et d'acide phosphorique et la solubilité dans l'eau du P_2O_5 peut être réglée selon les exigences du client. Des engrais spéciaux contenant Mg, Na, S et Te ou des produits peu riches en Cl sont également obtenus avec une grande qualité.

Du point de vue environnement, le procédé est très conforme aux BAT de l'EFMA.

✦ ✦ ✦

1. INTRODUCTION

Kemira NPK process was developed during early 1970's. The patented process was first implemented in Siilinjärvi 1972, followed by replacement of U-tube reactors in Uusikaupunki II 1978. The other Kemira plants in Finland were converted to use the Kemira NPK process quickly after successful implementations. Two licenses were given, one to Superfos (presently Kemira), and RFC in India. The capacities of each plant increased significantly. The fertiliser market situation changed during late 1980's and early 1990's and two of the plants were closed and one converted to feed phosphate production. Clearly the increased capacities were able to supply the domestic need of fertilisers still leaving place for export.

---

[1] *Flexibilité et performance au point de vue environnement du procédé NPK Kemira avec mélange d'acides*

Table 1 - Implementation of Kemira NPK process

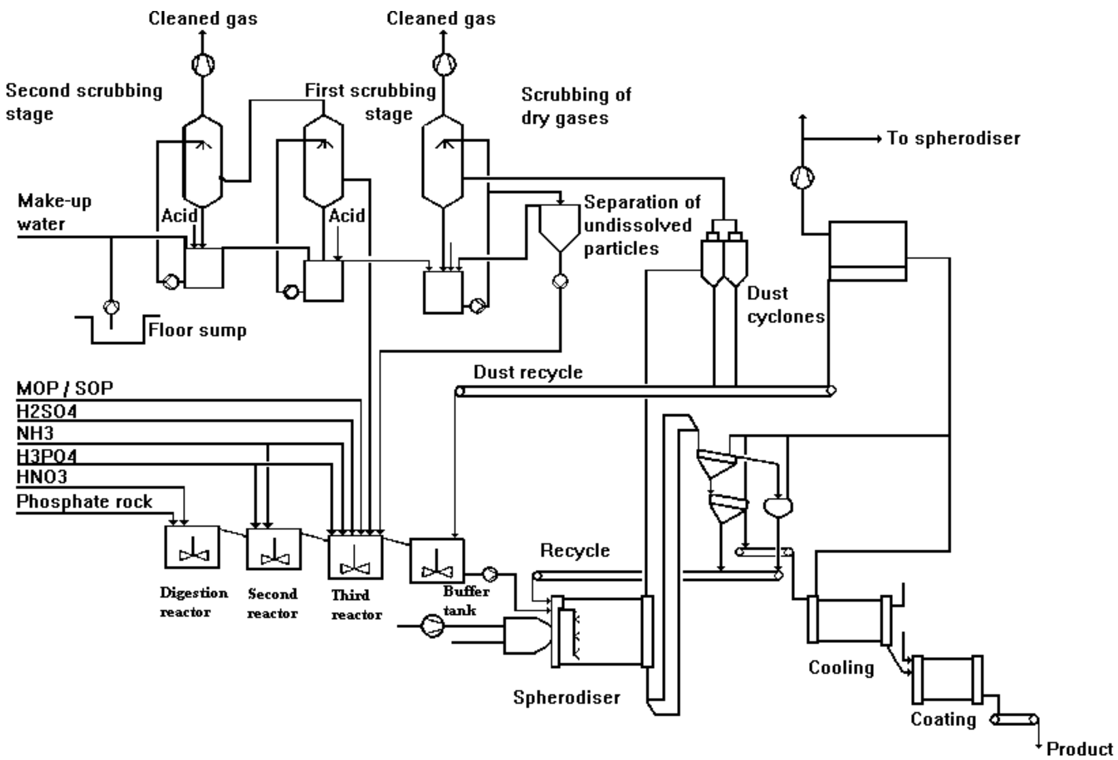
Plant	Nominal capacity	Year	Implementation of Kemira NPK process	Capacity after implementation
Oulu	200	1957	1982	700
Harjavalta	200	1964	1983	700
Uusikaupunki I	300	1965	1984	950
Uusikaupunki II	600	1967	1978	1200
Siilinjärvi	700	1972	1972	1600
Kokkola	400	1970	1981	1250
Fredericia				
India				

This paper is to summarise the experience and development during the last 25 years. After the first implementations several improvements have taken place, mainly in the automisation and control of the process. These improvements are discussed in the following three chapters describing the process, the products that can be made, and how the effects from the process to environment have been minimised. All improvements are a result from an innovative team and the involvement of operators to development work. Their impact can never be underestimated.

2. THE KEMIRA NPK PROCESS

The Kemira NPK process is a mixed acid nitrophosphate, slurry based process producing chemically uniform granular final product. The granulation method may vary between the traditional blunger and drum granulation to spherodiser (granulation-drying) types. The typical PFD (Process Flow Diagram) is shown in Figure 1.

Figure 1 - Process Diagram on the Mixed Acid Process with Rock Digestion



The process can be divided into the following steps:

a. Preparation of slurry from the reacted raw materials
b. Granulation and drying
c. Screening, crushing, and handling of recycle
d. Cooling of the product
e. Coating (anticaking treatment)
f. Nutrient and heat recovery from gas streams

2.1. The reaction section

The reaction section consists of digestion reactor (tank, or 2 U-tube reactors), first and second ammoniation, and buffer tank. The advantages of the arrangement are easy control of raw materials, granulation control, uniform final product quality and full utilisation of neutralisation energy. The reactor operation has closed loop controls with e.g. ammonia feed based on reliable pH measurement.

2.1.1. Digestion reactor

Rock phosphate and nitric acid are added to the first reactor. The reactor design can be based on the classical U- tube, tank reactor, or modified tank reactor with compartments. The reactions (1) and (2) depend on the mole ratio of nitric acid to rock phosphate.

$Ca_5F(PO_4)_3 + 10\ HNO_3 \rightarrow 3H_3PO_4 + 5\ Ca(NO_3)_2 + HF$ (1)

$2Ca_5F(PO_4)_3 + 14HNO_3 \rightarrow 7Ca(NO_3)_2 + 3Ca(H_2PO_4)_2 + 2HF$ (2)

2.1.2. First ammoniation reactor

The overflow from digestion reactor is ammoniated in the first ammoniation to pH between 2,0 and 6,0, depending on the formulation. Phosphoric (reaction 6) and sulphuric acid are dosed also in this reactor. Due to the formation of calcium sulphate a significant improvement in water soluble phosphorous in the final product can be achieved (reactions 3-4). The addition of sulphuric acid must be carefully calculated as excess will react to form ammonium sulphate (reaction 10) and causes dramatic effects to the final product quality (efflorescence, caking, plasticity, etc.). The reactors can also be operated based on potassium sulphate in LC formulations (reaction 5). The reactor dimensions vary between 20 and 40 m^3. The pH is monitored by Kemira developed measurement system, and can be used for closed loop control of ammonia dosage. This ensures a safe, stable and reliable operation with difficult formulations.

$Ca(NO_3)_2{*}4H_2O + H_2SO_4 \rightarrow CaSO_4{*}2H_2O + 2HNO_3 + 2H_2O$ (3)

$Ca(NO_3)_2{*}4H_2O + H_2SO_4 + 2\ NH_3 \rightarrow CaSO_4{*}2H_2O + 2\ NH_4NO_3 + 2H_2O$ (4)

$Ca(NO_3)_2{*}4H_2O + K_2SO_4 \rightarrow CaSO_4{*}2H_2O + 2KNO_3 + 2H_2O$ (5)

$Ca(NO_3)_2{*}4H_2O + 2\ H_3PO_4 + 2\ NH_3 \rightarrow Ca(H_2PO_4)_2 + 2\ NH_4NO_3 + 4H_2O$ (6)

2.1.3. Second ammoniation reactor

The overflow from first ammoniation reactor is ammoniated to pH ca 6.0-6.5 and the remaining solid raw materials are added. The solid raw materials are mainly potash (potassium chloride), micronutrients, etc. (reaction 11). The phosphorous and sulphur content is finally adjusted by the use of phosphoric and sulphuric acid (reactions 8-10). Dust from cyclones and bag filters can also be added at this stage. Again the pH is continuously monitored to ensure good operation. Too high pH would lead to high primary emissions of ammonia.

$Ca(H_2PO_4)_2 + NH_3 \rightarrow CaHPO_4 + NH_4H_2PO_4$ (7)

$H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$ (8)

$H_3PO_4 + 2\ NH_3 \rightarrow (NH_4)_2HPO_4$ (9)

$H_2SO_4 + NH_3 \rightarrow (NH_4)_2SO_4$ (10)

$KCl + NH_4NO_3 \rightarrow KNO_3 + NH_4Cl$ (11)

2.1.4. Buffer tank

Buffer tank acts, as named, to give space for small disturbances in the slurry pumping or capacity fluctuations. Recovered dust from bag filters and cyclones is dissolved before pumping to the granulators.

2.2. Granulation

The slurry in the buffer tank typically contains 10-15% of water with a temperature of 125-135°C. Several types of granulators can be used, the most popular being spherodiser, drum and blunger. The Kemira developed On line moisture analyses are used in closed loop control to stabilise variations with controlled slurry feed to granulator. Another important measurement is the continuous monitoring of granulometry, both from the recycling material, and final product. Typical cycle for analysis is every 5 minutes.

2.3. Screening and recycling

The material outlet of the dryer is screened. Oversize fraction above 5 mm is crushed with crushers (roller, chain, etc.) and recycled to the granulator. The product fraction between 2 and 5 mm goes directly to cooling drum. Part of it is recycled to maintain a stable recycle amount. The undersize fraction is recycled to the granulator. Recycle-to-product ratio depends on the produced grade and can vary from 1:1 to 1:6.

2.4. Cooling

The product fraction is cooled to temperature below 30-40°C in either a rotary or fluidized bed cooler. Fluidized bed cooler has slightly higher operating costs, but demands not so much space and investment as the rotary cooler. The exit gas is cleaned in bag filters and reused as secondary air in the burner.

2.5. Coating

Coating is performed in a rotary drum with either classical coating agents, or by special coating agent specially developed to/by Kemira. Final product is analysed every half-a-hour for its chemical content. Typical parameters are nitrate, and ammoniacal nitrogen, WS- and total phosphorous, WS- or total potassium, and in some cases boron and sulphur. This allows us to produce fertiliser always in the declaration.

2.6. Nutrient recovery

The gas scrubbing will be discussed further under the chapter: Nutrient recovery.

2.7. Process control

Intensive development has been made to implement computer control systems to the production units. These systems allow a stable raw material feeds, stepless production rate regulations, highly sophisticated, quick grade changes and formulation correction. Development in on line measurements has enabled the closed loop control systems to ammonia feeds based on reliable pH measurement, granulator feed control based on continuous moisture analysis, emission controls, etc. Particle size measurement continuously measures the changes in granulometry and a steady operation has been achieved. On line measurement on the nutrient content has allowed laboratories to turn from quality control to quality assurance, no shift work is needed.

3. TYPICAL PRODUCTS

A flexible range of products can be produced by the Kemira NPK process. In the plants the number of different grades produced is between 30 and 50, and close to 100 grade changes were made during the year. The sophisticated grade change procedures make it possible to deliver the right material to the customer at the time it is needed. The range of grades varies from nitrogen fertilisers to PK fertilisers, as follows:

26+ 14 S	15-15-15	12-24-12	0-20-20	25-5-5
CAN	16-16-16	15-20-15	19-0-22	22-2-12
30-10-0	17-17-17	10-20-20	25-0-5	18-9-9
12-12-17	13-13-21	15-5-20	15-20-26	24-6-12

3.1. Formulations

The advantage in the Kemira NPK process is the raw material flexibility. The phosphate content is 100% citrate soluble in the products, and most grades can be produced with different degrees of water soluble phosphorous (rel WS-P_2O_5). To supply the right, requested water solubility has an impact to the cost price by affecting the raw material costs. The sulphuric acid ensures precipitation of calcium sulphate and therefore the high water- solubilities can be achieved. The nitric to sulphuric acid ratio can be changed. Filler is seldomly used as rock phosphate supplies the needed inerts. Most of the NPK formulations can also be low-in-chlorine-types.

The improved emission control in Western Europe has reduced the sulphur quantities entering the soils. This is again a benefit in Kemira NPK process where the relatively cheap sulphuric acid can be used in formulations. The addition of sulphur in form of ammonium sulphate in many pipe reactor processes causes high caking tendencies in the final product due to post reactions, and in some cases makes the granulation troublesome.

3.2. Formulation costs

A comparison between the raw material costs of different processes is made in the Table 2. The comparisons are normally subjected to heavy discussion, therefore the calculations are made as practical as possible[2]. Raw material costs are of key importance in fertiliser manufacturing. The raw material costs are higher than in nitrophosphate processes, but lower than pipe reactor processes. The main disadvantage is the use of phosphoric acid in all mixed acid processes.

The raw material costs on the total production costs is about 75-80%, and the effect should not be under-estimated. The remaining part of the costs can be split to operating costs, fixed costs, return on investment, depreciation and interests. Fixed costs are quite similar in pipe reactor and Kemira NPK processes. Operating costs in the nitrophosphate process are clearly higher due to larger unit with more unit operations. Investment costs depend on the infrastructure. A draft estimate is that the investment costs to Kemira NPK process are ca 20% more than pipe reactor based process, but 50% of the nitrophosphate investment (infrastructure). Maintenance costs naturally depend also on the size of the unit.

---

[2] Based on formulation given in EFMA Booklet; Production of NPK fertilisers by the mixed acid route, 1995.

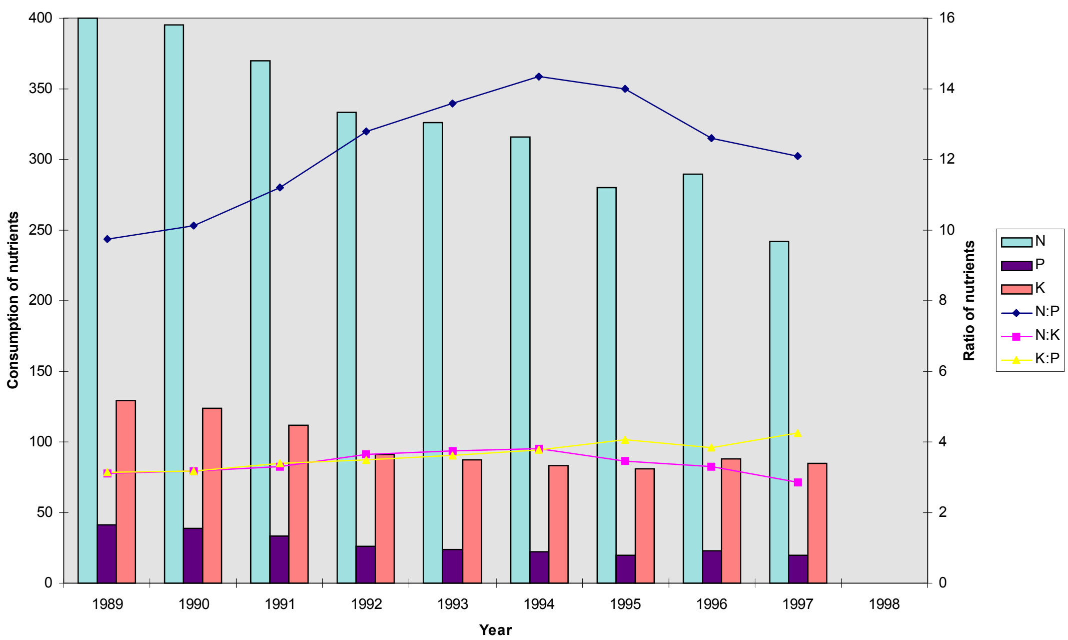
Table 2 - Comparison of the raw material costs for 15-15-15 between different processes

		KEMIRA NPK		PIPE REACTOR		NITROPHOSPHATE
		60%	80%	85%	95%	
Raw materials[3]	Costs[4]					
Phosphate rock	60	151	128	-	-	417[5]
Nitric acid	55	298	282	280	242	105
Ammonia	155	107	111	107	122	155
Phosphoric acid	415	96	104	105	154	-
Sulphuric acid	35	53	76	-	-	-
Potash	115	251	251	250	250	250
SSP[6]	100	-	-	212		-
Filler	20	-	-	-	150	73
Variable costs		112,6	115,08	125,2	127,88	85,03[7]

During the last decade, especially in Europe, the grades have turned more towards low-in-phosphorus types. A typical trends is given in Figure 2 of the change in Danish market. This development further increases the value of Kemira NPK process as the benefit of cheap phosphate from e.g. nitrophosphate process is significantly lower.

The trend towards the V-type final products causes products to turn into class B (self-sustaining-thermal-decomposition). In these fertiliser formulation the proper control of relative water solubility of phosphorous is essential. A typical formulation in the borderline is 22-2-12 (Note! As P and K). The raw material costs are given in Table 3.

Figure 2 - The change in the nutrient consumption in Denmark[8] (as N, P and K) and in the nutrient ratios; N:P, N:K, K:P



[3] Formulations based on reference / 9 /.
[4] Raw material costs based on Fertiliser week, Volume 11, Number 46, 6th of April
[5] All P_2O_5 originating from the rock phosphate
[6] The availibility and price of SSP depends greatly on the local conditions
[7] The removed calcium nitrate (ca 325 kg/t) has to be processed
[8] Ministeriet for fødevarer, Landbrug og Fiskeri, Handelsgødningsstatistik Plantedirektoratet

Table 3 - Cost comparison of 22-2-12 (N-P-K)

		KEMIRA NPK	PIPE REACTOR	NITROPHOSPHATE
Raw materials	Costs[9]			
Phosphate rock	60	51	-	128
Nitric acid	55	452	472	558
Ammonia	155	146	140	134
Phosphoric acid	415	38	64	-
Sulphuric acid	35	46	-	-
Potash	115	241	241	241
SSP		-	-	-
Filler	20	-	49	-
Variable costs		95.65	102.77	86.87

These cost comparisons should be taken as an estimates of the raw material costs in different processes. The formulations costs can be optimised in any of the processes depending on the source of raw materials. One should not forget the other elements in the total costs as presented earlier.

3.3. Quality

The demand for good quality is extremely important in Western Europe, and will increase in other parts of the world as a result of improving economy. The quality of fertiliser is normally defined from the following parameters as:

1. Free flowing
2. Free of dust
3. Uniform size distribution
4. Bulk density
5. Crushing strength
6. Roundness
7. Abrasion
8. Flow rate
9. Spreadability

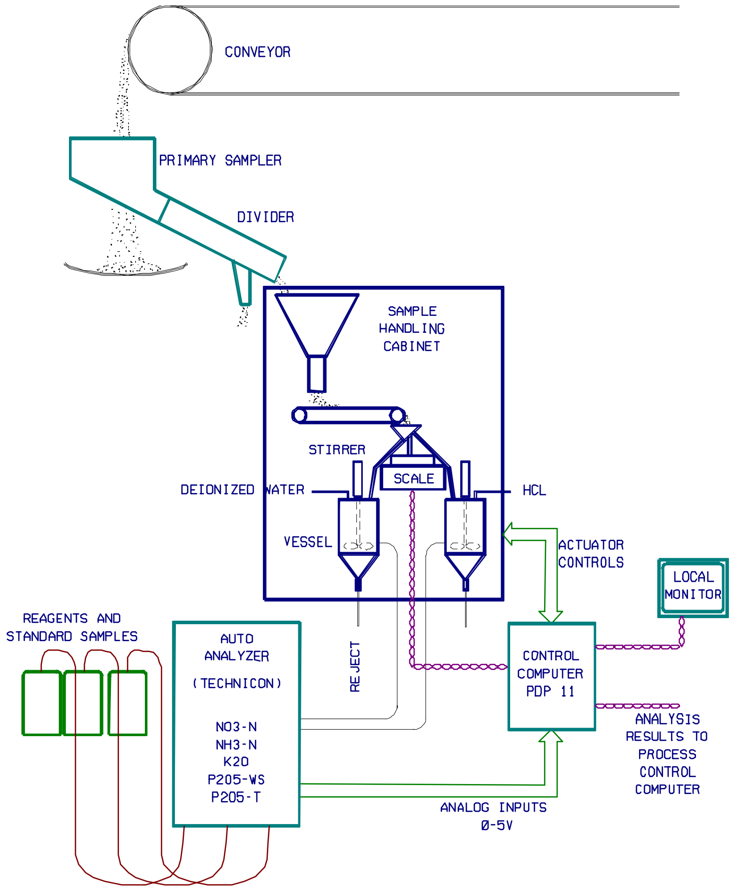
The importance of the parameters is market dependent. During production the physical quality is monitored with quick quality tests, followed by more quantitative measurements in the quality assurance laboratory. All products are ranked and continuous improvement takes place. As the physical tests are not standardised as chemical methods benchmarking is carried out yearly.

The advantages of both nitrophosphate and Kemira NPK process is the uniform chemical composition of the slurry, and therefore uniform composition in the granules. The addition of potash to the reactors ensures full conversion reaction (11). The complete reactions reduce the post reaction risks in the storage.

The chemical composition is controlled by On line NPK analyser. This gives information of the nutrient composition every 30 minutes. Connected to sophisticated control systems it is possible to produce small production campaigns and to supply the customers what is requested.

[9] Raw material costs based on Fertiliser Week, Volume 11, Number 46, 6th of April

Figure 3 - Main components of the On line NPK analyser



.

3.4. Safety

The trends in the market are towards more V-type fertilisers (see Figure 2) known to be sensitive towards self-sustaining thermal decomposition. An advantage in the mixed acid route is the possibility of adjusting the water soluble phosphate by numerous ways and to stay in the safe C-class area. The continuous analysis informs on the possible changes in relative water solubility. Similar risks exist as in any other fertiliser processes.

In the production of NPK fertilisers the mass has a buffer capacity to avoid sudden pH changes due to feed fluctuations. The overflow from reactors reduces the number of pumps, and transfer lines where confinement could cause risks. The production hazards have been evaluated by internal study groups, and after the accident in Terra several Codes Of Practices has been made to Kemira processes related to production of NPK fertilisers, B- class fertilisers, ammonium nitrate solution manufacture, etc.

4. NUTRIENT RECOVERY

Kemira invested during 1980's in several production units to gas scrubbing equipments as a result of company's intensive R&D. The emissions decreased to a level which is below the internationally proposed levels (e.g. BAT). Emissions are controlled with On line instruments which detect also sudden, exceptional disturbances in the process. The main components in analysis are nitrogen component(s) and fluorine. The long term operation of Kemira NPK process in several locations gave an opportunity to make experiments of various technical solutions in practise (large scale). Not only technical experiences, but also extensive R&D was needed to deepen the understanding of the aerosols, related chemical reactions, scrubber performance (efficiencies), etc. The experience has then been taken as a basics in the engineering, and training of employees. Only the best practical solutions were selected. We have used and tested at least the following types of scrubbers:

- spray scrubbers
- spray cyclonic scrubbers
- venturi scrubbers
- floating ball scrubbers
- sieve tray scrubbers
- packed bed scrubbers

A Process Flow Diagram of the nutrient recovery system is indicated in the Figure 1.

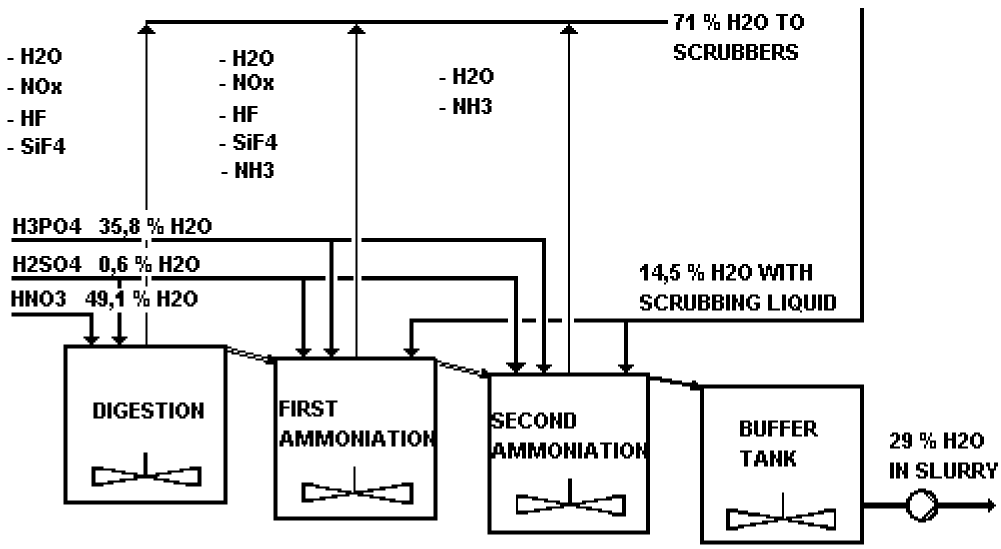
4.1. Reactor gases

Large quantities of water are evaporated from the reactors. Depending on the temperature and grade produced the air quantities are between 30.000 and 60.000 m^3/h. Along water mainly nitrogen oxides, fluorine components and ammonia will enter the wet scrubbing stage.

4.1.1. Water

A significant amount of water enters to the reactors from liquid raw materials, main source being nitric and phosphoric acid. Main part of the water is evaporated due to the heat from neutralising reactions. Typically 70% of water is evaporated. Some 15-20% of water enters to reactors from the scrubbing unit.

Figure 4 - Typical water balance of a NPK fertiliser plant for grade 15-15-15



4.1.2. Treatment of gases from digestion

The gases from digestion reactors are treated separately in a spray tower scrubber to recover NOx and fluorine components. The pH is adjusted by addition of ammonia.

4.1.3. Treatment of gases from ammoniation reactors

The ammoniation reactor gases are scrubbed in several stages of counter-current scrubbing. To obtain the most efficient scrubbing conditions the pH is adjusted with a mixture of HNO_3 and/or H_2SO_4 or H_3PO_4 to ca 3-4. In the first scrubbing stage gases are saturated, in the second stage aerosols are removed in a high pressure venturi. The recovery efficiency is high and cleanest liquid is used in the final stage. In the final stage gases go through a droplet separator.

4.1.4. Solid matter and aerosols

Some of the used solid raw materials, namely phosphate, potash, potassium sulphate, as well as recycled dust may enter to the reactor exit gas stream. Micro-particles (aerosols) are formed from acidic components reacting with ammonia.

4.2. Drying gases

Drying gases from drier (granulator/drier or spherodiser) are led through cyclones before scrubbers. In the scrubbers a variable throat venturi with two stage scrubbing. Again the last stage uses the cleanest liquid. The pH is adjusted to 3-4 to ensure optimal scrubbing conditions. The scrubbing liquor is separated from solids in a settler; overflow being circulated to the process and thickened part to the reactors.

All screens, crushers and conveyor discharge points and de-dusted and this air is cleaned in a bag filter before recycling in the process or discharge into the atmosphere.

4.3. Emissions

The environmental considerations in Kemira will give a good position for several years ahead. The employees are very motivated towards environmental protection, and receive yearly the company's green account. Kemira is today also known as a major producers of water purification chemicals, and has committed to "Responsible Care". One reason for the development was the plant locations close to sea and forest. The harsh climatic conditions and short growing season in the North place high demands on the environmental protection[10].

The development in total emissions does not yet give a right figure on the environmental performance of Kemira's NPK process. To give a clear picture the main emissions are compared to the proposed BAT figures from EFMA. The figures in Table 4 present that the NPK process is well within the typical values.

Table 4 - BAT / Typical values for the emissions in kg/t NPK

	PRS[11]	MIXED ACID WITH ROCK DIGESTION	KEMIRA[12]	NITROPHOSPHATE
NOX-N	-	0.1	0,04[13]	0.2
NH_4-N	0,05	0.1	0.1	0.3
Fluorides	0,005	0.01	0.002	0.02
Dust	0,12	0.2	-	0.3

The range of emissions from the plants operated with Kemira's mixed acid process is presented in Table 5. The figures are presented as kg/ton produced nutrient. The average values are well below the limits, as well as the range of emissions.

Table 5 - The typical emission values and range in Kemira's mixed acid process

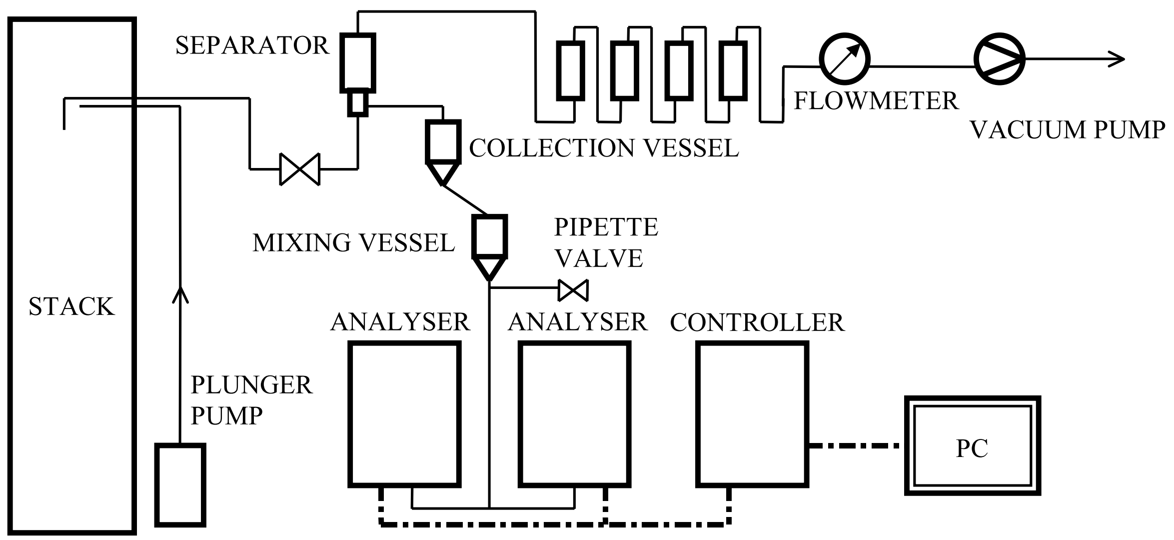
PARAMETER	UNIT	BAT	AVERAGE[14]	RANGE
NH_3-N	kg NH3-N / t N produced	1,33	0.70	0.38-1.20
N to water	kg N/ t N produced	1,33	0.58	0.48-0.64
P to water	kg P / t P produced	-	0,01	0,01-0,02

[10] Kemira started in 1990's to landscape the gypsum pile remained from the phosphoric acid production which was closed in 1980's. Before planting trees mud was taken from the bottom of sea. A couple of years later there was suddenly rare plants, not existing elsewhere in Finland nor Europe. The seeds were from several hundreds years ago and based from wooden sailing ships entering to Uusikaupunki harbour. Due to this the area is now protected, only 200 metres from the fertiliser plant. This represents a real harmony between nature and chemical industry.
[11] Granulation with a Pipe Reactor System
[12] Ref. /5/
[13] As NO_3-N kg/t product including NO_2 kg/t
[14] As an average of KEMIRA's mixed acid plants

To obtain the proposed BAT levels not only a good nutrient recovery system is needed, but also reliable measuring and adjustment devices are needed. The trouble free-pH control and continuous emission monitoring ensures stable operating conditions.

In some countries there are demands on the cadmium content. In a mixed acid NPK process these levels can be kept by sourcing the rock and/or phosphoric acid of low Cd content.

Figure 5 - The schematic of the stack gas emission analyser



5. CONCLUSION

The KEMIRA NPK process has now been operational for 25 years. The basic design is still similar, but with a lot of development in the control and automisation have been made. All the features of a good process are met:

- reliable
- high On Stream Factor
- simple
- ease to operate
- flexible
- economical raw materials
- energy efficiency
- environment

The process has been a key success factor in the turbulent fertiliser market. It has been possible to change the product portfolio to meet customer needs in regular intervals without constraints from the process.

6. REFERENCES

1. Swanström, S., The Kemira NPK process, Phosphorous & Potassium, 145, 1986
2. Lammi, P., Air pollution control in Kemira's NPK fertiliser process, Nitrogen 86, The British Sulphur Corporation, 1986
3. Swanström, S., Kemira's Mixed acid process, IFDC, Workshop on NPK fertilisers, Madras, India, 1988
4. Vuorinen, P., Modernisation of NPK plants, Chemtec+Ort, 1985
5. Sipilä, M., Env , IFA Technical Conference, Amman, Jordan, 1994
6. US Patent 76US-686,536.
7. Hignett, T.P. (Editor), Fertiliser Manual, Vol 15, Martinus Nijhoff / Dr Junk Publishers, The Netherlands, 1985.

8. Best Available Techniques for Pollution Prevention and Control in the European Fertiliser Industry, Booklet No 7 of 8; Production of NPK Fertilisers by the Nitrophosphate route, EFMA, 1995.
9. Best Available Techniques for Pollution Prevention and Control in the European Fertiliser Industry, Booklet No 8 of 8; Production of NPK Fertilisers by the Mixed acid route, EFMA, 1995.
10. Autti, M., Loikkanen, M., Suppanen, P., Economic and technical aspects in some differential NPK processes, IFA, 1976.