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NORSK HYDRO NITROPHOSPHATE PROCESS[1]

by

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SUMMARY

[illegible]

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The process is entirely based on nitric acid digestion of rock phosphate and does not require sulphuric acid or sulphates.

Up to [illegible] per cent of the calcium content of the digestion liquor can be removed as calcium nitrate by crystallization and filtration at low temperatures in very reliable and efficient equipment. The high degree of calcium removal results in three very important advantages:

The water solubility of the phosphorus content of the product can be increased from the usual [illegible] per cent to about [illegible] per cent.

The nutrient content of the products is very high.

None of the usual NPK-formulations, based on potassium chloride, are liable to self-sustaining decomposition.

The mother liquor from the filtration is neutralized with ammonia, and the neutral liquor is evaporated to a water content of [illegible] per cent. When making NPK-fertilizers the evaporated NP-melt is mixed with potassium chloride (or sulphate). Micro-nutrients can also be added. The NP-melt or NPK-mixture is then prilled, cooled and coated. A dryer is not necessary. Compared with other granulation methods the prilling process has several advantages as to operation, product quality and economy. Single prill towers

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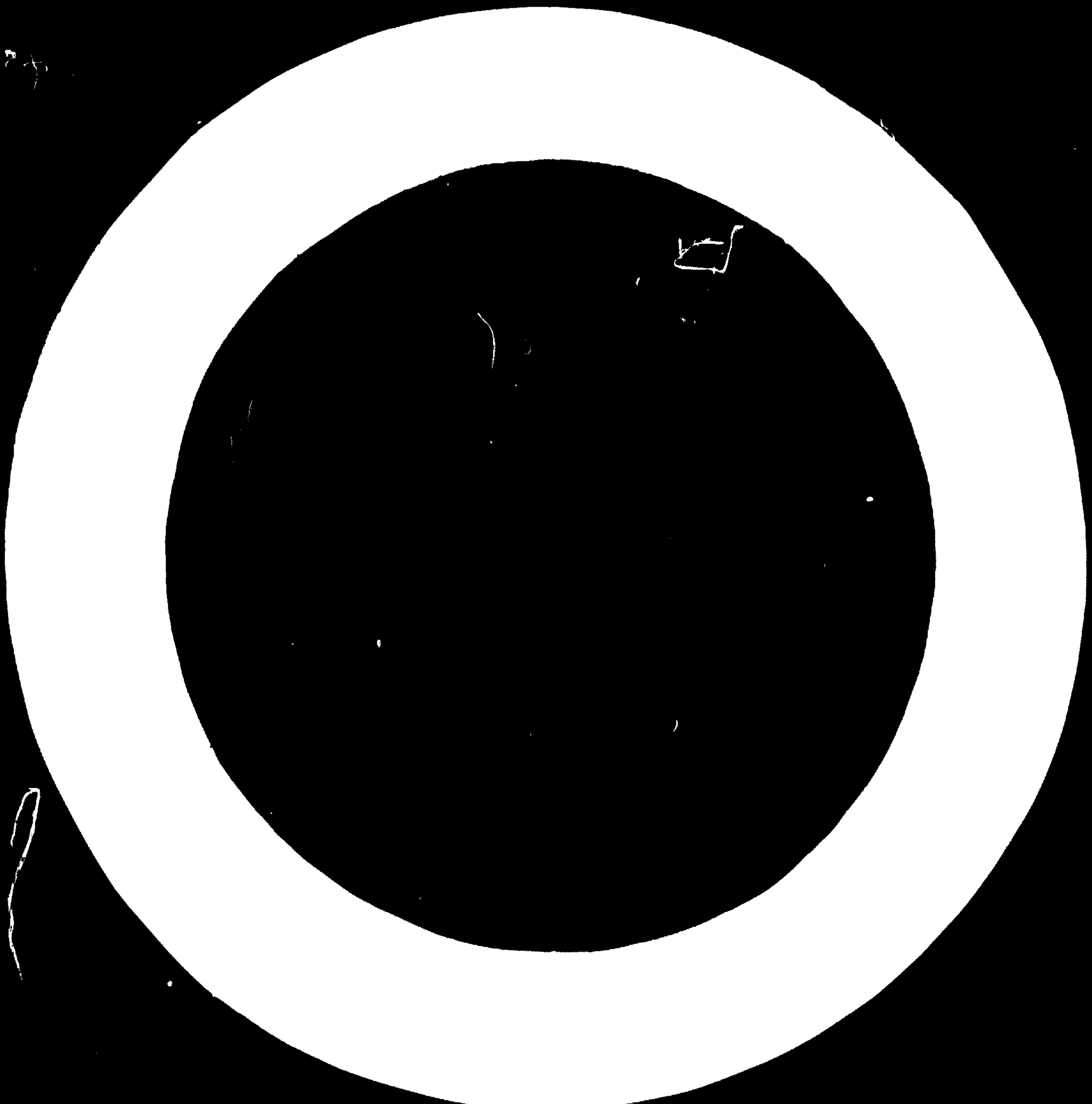

with capacities from 500 to more than 2000 metric tons of NP/NPK-fertilizer per day have been constructed.

The by-product of calcium nitrate is normally converted to an ammonium nitrate solution by means of ammonia and carbon dioxide. Depending on the ratio between N and P_2O_5 in the product, more or less of this solution is fed back to the nitrophosphate process as a source of nitrogen to the NP/NPK-product. Any excess of ammonium nitrate solution can be processed to ammonium nitrate and/or ammonium nitrate limestone fertilizer.

Based on more than thirty years' production experience Norsk Hydro has made many improvements concerning equipment, instrumentation, process and product control etc., and this is utilized in the company's three plants in Norway, where the capacity is more than one million tons of products per year. The process has proved to be very flexible as to raw materials and product formulations. The storage properties and the agronomic effect of th products are very satisfactory.

The Norsk Hydro process has for some years been offered on the world market, and the paper gives information regarding new plants utilizing the process. Recentl a plant for 800 tons per day was put in operation in the United States. Another plant with a capacity of 2200 metric tons per day is being built in Hungary. In Romania four new plants will have a total capacity of more than 10,000 tons per day. In these countries they have very strict regulations concerning pollution of air and water, and the process is well fitted to meet those regulations. When the new plants have been started up, the total capacity of plants using the Norsk Hydro nitrophosphate process will be more than 5 million tons of NP- and NPK-fertilizer per year.

CONTENTS

I. INTRODUCTION

1. For obvious reasons there is a growing tendency among farmers to apply complex fertilizers, i.e. fertilizers containing two or three of the main plant nutrients N, P and K. There are many kinds of such fertilizers, nitrophosphates being one of them.

2. The Norsk Hydro nitrophosphate process is based on the Odda method, which was invented in Norway in 1928 by Erling Johnson. The rock phosphate is dissolved in nitric acid, and no sulphuric acid, sulphates or phosphoric acid is needed.

3. For more than thirty years the Odda method has been utilized, especially in Europe, for the production of large amounts of NP- and NPK-fertilizer. Until a few years ago the water solubility of the phosphorous content of the product (WSP) was only 30-40 percent. This was considered satisfactory in the countries where the product was used. But as is well known probably most other countries want a much higher water solubility.

4. Norsk Hydro has made many important improvements of the process, still utilizing the original Odda method. These improvements have not only lead to a technically and economically advanced process, but also to more concentrated products with higher content of watersoluble phosphorous and improved physical properties.

5. During the four years the Norsk Hydro process has been offered on the world market a capacity of about 4.5 million metric tons per year has been or is being installed in different countries. Together with the company's own production the total capacity of plants using this process will shortly be about 6 million metric tons per year.

II. THE PROCESS

6. In this paper we will concentrate on some of the main features of the process. As a background a survey of the whole

process will first be given. The process and the operating experience acquired with it are described in more detail elsewhere (1,2).

a. Survey

7. A simplified flow-sheet is shown in the appendix.

8. The rock phosphate is dissolved in 58-60% nitric acid. The heat evolved raises the temperature 40-50^{o}C, depending on rock phosphate properties. Calcium is removed from the solution as $Ca(NO_3)_2 \cdot 4H_2O$, by crystallization and subsequent filtration on rotary tandem filters. The crystals are washed with nitric acid and some water in the second filtration stage. The wash acid is returned to the rock digestion step.

9. The mother liquor is then neutralized with ammonia gas. Ammonium nitrate solution is added to obtain the required N/P_2O_5-ratio in the product. The water content of the neutralized liquor is reduced to about 0.5% by evaporation. The NP-melt is mixed with recycled fines, and if required also with potassium salt and other additives. The mixture is then prilled in an air-cooled tower. The prills are cooled, screened and coated with a conditioning agent before leaving the plant as finished NP- or NPK-fertilizer. Oversize is crushed and returned to the screens. The fines are recycled to the mixer.

10. The calcium nitrate from the filter is melted and can be converted to ammonium nitrate solution and calcium carbonate with ammonia and carbon dioxide. Some of the ammonium nitrate produced can be fed back to the nitrophosphate process as a nitrogen source, the amount being dependent on the N/P_2O_5-ratio in the product. The ammonium nitrate solution can also be made into AN-prills for fertilizer or explosives or into ammonium nitrate limestone fertilizer (ANL), utilizing the calcium carbonate which is produced in the conversion process.

11. Norsk Hydro has its own modern processes for the conversion of calcium nitrate and production of AN- and ANL-products.

These processes are also licenced and used in other countries. They are not described in this paper.

12. The calcium nitrate can also, if required, be processed into a calcium nitrate fertilizer containing 15.5% nitrogen. This fertilizer contains some ammonium nitrate and water of crystallization. Under normal conditions the storage properties are very good, and Norsk Hydro produces about one million tons of it per year.

b. Some special features of the nitrophosphate process

13. For many years a close cooperation has taken place between the people running the company's three NP/NPK-plants and a rather big group of specialists from research and development. Ideas and suggestions have been flowing in both directions, and experiments have been carried out in laboratory, pilot plants and on full scale in the plants. In this way each step in the process has been improved and optimized, both with regard to the equipment itself and the way of operating it. Instrumentation and process and product control have played an important part in the development. It is not possible to deal with all of these aspects in a brief paper, and we therefore have to restrict ourselves to some selected points.

Crystallization of calcium nitrate:

14. The main purpose of removing calcium from the digestion liquor is to prevent formation of insoluble calcium phosphates (apatite) during neutralization with ammonia and to increase the water solubility of the phosphorous content of the product. A low Ca/P-ratio in the mother liquor will give a high solubility, i.e. high content of ammonium phosphates.

15. The Ca/P-weight ratio in the digestion liquor is normally 2.2 - 2.6, depending on type of rock phosphate used. Common practice in the Odda method has been to cool the digestion liquor to 15 - 20°C, resulting in a Ca/P-ratio in the mother liquor of 0.8 - 1.1 and 25 - 40% WSP.

16. Norsk Hydro has developed a method and equipment for reduction of the Ca/P-ratio to 0.3 - 0.4 by crystallization of calcium nitrate. This method has been in successful operation for 4 - 5 years. It is advantageous for many reasons. Some of them are:

- The water solubility of the P-content increases to about 85 percent.
- The concentration of nutrients in the product increases.
- Many nitrophosphates containing potassium chloride are liable to self-sustaining decomposition. This liability is very substantially decreased and for normal formulations it is eliminated (3).
- The increased removal of calcium nitrate from the liquor makes it possible to formulate products with much lower N/P-ratio than before.
- The reduced content of solids ($CaHPO_4$) in the NP-melt to be prilled facilitates the prilling operation.

17. Norsk Hydro was the first company, and is probably still the only one, to practice this extreme removal commercially.

18. If required, the Norsk Hydro process can of course also be operated at a higher Ca/P-ratio.

19. To attain 80 - 85% WSP it is necessary to cool the digestion liquor to about minus 5°C, the exact temperature being dependent on kind and amount of impurities present.

20. The crystallization is carried out in a number of batch type tank crystallizers with internal cooling coils. The crystallizers are filled, cooled and emptied one after another in a certain cyclus. This gives a continuous flow of cooled suspension from the crystallizer battery and a continuous flow of cooling medium into it. The cooling medium is most often a circulating ammonia solution, but other liquids can also be used. In some places water can be used for part of the cooling. The

heat removed can be used for evaporation of liquid ammonia, which in turn can be used in the neutralization section.

21. The carefully designed equipment for crystallization, and the selected operating instructions ensure high heat transfer coefficients, and the capacity per unit crystallizer volume is consequently very high. The calcium nitrate crystals are coarse (about 1 mm) and uniform in size. This is important for the subsequent filtration.

Separation of calcium nitrate crystals from mother liquor:

22. Most companies practicing the original Odda method use centrifuges for this separation. Norsk Hydro uses rotating tandem filters of the company's own design. The coarse and uniformly sized crystals and the special design result in a very high filtration rate. Solid impurities in the suspension do not affect the rate. The content of mother liquor in the washed crystals is very low. The filters are very reliable in operation and require very little maintenance.

Evaporation of neutralized NP-liquor:

23. The water content is reduced to 0.5% at about 180°C and at a low pressure. To prevent crystallization of ammonium phosphate, clogging etc. it is necessary to have a thorough knowledge of the chemical and physical properties of the liquor. Norsk Hydro uses equipment of their own design. The availability of the plant is very high. The instrumentation and process control allow the evaporation section to operate automatically with very little supervision. No potassium chloride is added to the liquor before evaporation. This is to avoid any possibility of thermal decomposition.

Mixing of NP-melt with potassium salt and possibly other additives:

24. The potassium source can be either K_2SO_4 or KCl. When mixing KCl with a hot nitrophosphate melt the viscosity of the mixture has, due to chemical reactions, a strong tendency to

increase to such a degree that prilling is impossible. Norsk Hydro has carried out very much theoretical and practical research and development work to suppress these reactions. These efforts have resulted in equipment and way of operation which allow addition of very large amounts of KCl without increasing the viscosity too much. The mixer gives a very efficient distribution of the potassium salt in the NP-melt. The equipment is simple and inexpensive.

Prilling:

25. The NP-melt or NPK-mixture is formed into "drops" in the top of the prill tower by means of a rotating perforated prill bucket which is specifically designed to prevent clogging and to give an even distribution of the prills in the air-cooled tower. From time to time the bucket has to be cleaned. It is then replaced by a fresh bucket. The change of buckets is done very quickly by means of a special device.

26. The solidified prills are removed from the tower with a rotating tower bottom or a rotating scraper. The amount of off-size (÷1 +4 mm) is low, normally below 10%.

27. The advantages of the prilling process are for example high capacity in one train, low recycle rates and hold up in the equipment, no need for drying of the product, low investment and maintenance cost. The prilling process is especially advantageous for high capacity plants but can be used economically for small plants too, for instance down to about 500 metric tons per day. Normal pug mill/drum granulation can also be used in Norsk Hydro's process, but normally prilling is preferred.

28. It is very easy to control the product composition, because of the process itself and the low hold up. Also the size of the prills is easily and quickly controlled.

29. When nitrophosphates containing KCl is granulated in normal pug mills and rotating drum granulators, the large amount of fertilizer material in the equipment rather often starts to decompose ("fire"). This does not happen in the prilling

process, because the temperature and composition etc. are much better controlled and the retention time at high temperature is very low.

30. In one of the Norsk Hydro plants more than 2000 tons of NPK-fertilizer is produced in one prilling tower per day.

Pollution control:

31. The process is well suited for efficient pollution control, and procedures and equipment have been worked out to minimize the amounts of liquid and gaseous effluents. In new plants under construction these amounts are quite negligible and well below even very strict demands.

III. RAW MATERIAL FLEXIBILITY

32. The nitrophosphate process requires rock phosphate, nitric acid, ammonia, KCl and/or K_2SO_4 and a conditioning agent. Ammonia and carbon dioxide are needed for the conversion of calcium nitrate to ammonium nitrate. Off-gases from urea-plants can often be used for this purpose. The recovery of N, P_2O_5 and K_2O is in the range of 97 - 99%.

33. With the exception of rock phosphate it should not be necessary to give any special comments on these raw materials. Normal qualities are used, with no extraordinary requirements.

34. Different types of rock phosphates can be used in Norsk Hydro's plants, from Kola, various parts of Africa and U.S.A., Israel etc.

35. It is normally advantageous to use rocks which are not too low in concentration. The cost of transportation per ton of P_2O_5 is lower, the amount of impurities to the process is decreased etc. Poor rocks most often have a high calcium content and therefore require more nitric acid for digestion, the crystallizer load and calcium nitrate production are increased etc.

36. Norsk Hydro has special research people for investigating the

usefulness of new types of rock phosphates in laboratory and pilot plants. Before making the final conclusion it is often necessary to try the rock on a full technical scale in one of the plants.

IV. PRODUCTS. QUALITY AND GRADE FLEXIBILITY.

37. The minimum $N:P_2O_5$ ratio in the NP/NPK product is determined by the ratio between nitric acid and rock phosphate (P_2O_5) fed to the digestion step and by the degree of calcium nitrate removal in the crystallization step.

38. For most rock phosphates and for products with 80 - 85% WSP the minimum $N:P_2O_5$ ratio in the product is about 0.6. By addition of ammonium nitrate to the process the $N:P_2O_5$ ratio can be increased to any level.

39. If all the calcium nitrate from the filtration step is converted to ammonium nitrate and returned to the nitrophosphate process, the $N:P_2O_5$ ratio will be about 2:1 in a product with 80 - 85% WSP (somewhat dependent on Ca/P_2O_5 in rock).

40. The maximum $K_2O:P_2O_5$ ratio is to some degree dependent on $N:P_2O_5$ ratio but can be very high, for instance more than 2:1.

41. More than thirty different formulations have been produced commercially in Norsk Hydro's plants. Examples of possible formulations and concentrations are 17-17-17, 22-11-11, 13-13-26, 23-23-0, 15-20-15.

42. The storage properties of the products are very satisfactory, both in bulk and bags. The bulk density is high, 1.1 - 1.2 kg per dm^3. The product is not dusty.

43. A lot of agricultural experiments in different countries have shown that the effect of the products is very good both with regard to N, P and K, fully comparable with the best of single nutrient fertilizers.

V. PROCESS ECONOMICS

44. It is rather complicated to make a comparative cost calculation between different NP/NPK-processes, with differe[illegible] raw materials, may be different nutrient concentrations, so[illegible] of them making more than one fertilizer simultaneously etc. Still more complic ted is it to calculate the total cost when th fertilizer has been applied to the fields. The cost calculations may also give different results for different location of the plants, availability of raw materials, transportation cost etc.

45. However, some calculations have been published (4,5, 6), all of them concluding that the economy of the Odda method is very favourable, even with very low sulphur prices.

46. More detailed information regarding investment cost, raw material and utility consumption etc. can be obtained from Norsk Hydro's licensees.

VI. NORSK HYDRO'S NITROPHOSPHATE PROCESS ON THE WORLD MARKET

47. Norsk Hydro started its first NP/NPK-plant in Norway in 1936. The company now has three plants in operation in Norway. Total capacity is 1.2 - 1.4 million metric tons per year, somewhat dependent on the formulation of the products. Two of the plants have prill towers, the third pugmill/drum-granulation.

48. Four years ago the company started licensing of its fertilizer processes on the world market. The know-how is offered through Humphreys & Glasgow, England, Lurgi Gesellschaft, Germany and Wellman-Power Gas U.S.A. All these companies are working with no geographical limitation.

49. Till now the following plants are in operation or under construction outside Norway.

a) One plant in North Carolina, U.S.A. with a capacity of 900 short tons of NP/NPK per day. Products with about 80% WSP can be produced. A plant for conversion of calcium nitrate into ammonium nitrate solution is included.

b) One plant under construction in Hungary. The maximum capacity is about 2200 metric tons of NPK per day. The water solubility (WSP) 80 - 85%. The calcium nitrate is converted to ammonium nitrate solution. The amount of ammonium nitrate being used as a nitrogen source in the NPK-plant is dependent on formulation of the product. The excess of ammonium nitrate will be processed into ammonium nitrate limestone fertilizer in an appurtenant plant. In this plant the calcium nitrate from the filters also can be processed into calcium nitrate fertilizer, when wanted.

c) Four NP and NPK-plants under construction in Roumania. The capacity of each of the plants is about 2700 metric tons per day. Water solubility is 85%. Conversion plants for calcium nitrate into ammonium nitrate solution are included.

50. When these plants have been started up the total production capacity of plants using Norsk Hydro's nitrophosphate process will be about 6 million metric tons of NP and NPK per year.

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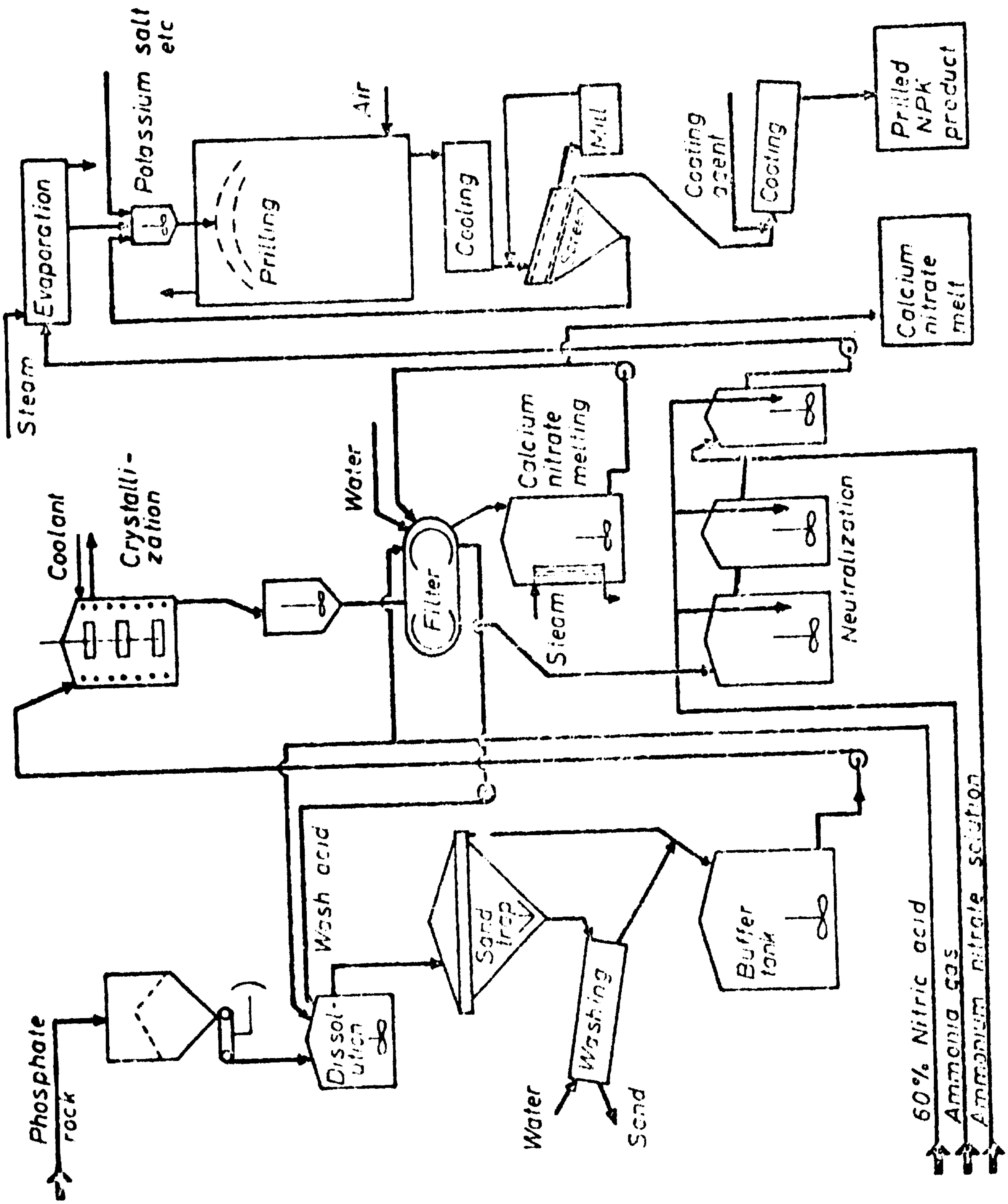

FIG 1. THE NORSK HYDRO NPK PROCESS.

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