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FLEXIBILITY OF THE BASF NITROPHOSPHATE PROCESS[1]

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SUMMARY

BASF has developed the nitrophosphate process to a highly flexible process: meaning the flexibility in NP(K) qualities and in design. The examples for different NP products demonstrate, how the production of NPs and straight N-fertilizers are coupled. At the same time the water soluble fraction of P_2O_5 can still be adjusted to varying requirements. The lime produced is usually used in agriculture or building industry. An additional small AN synthesis helps in smoothing the CAN production and allows production of NPs with high nitrogen content.

The developed design alternatives allow a process layout according to environmental regulations or restrictions. The emissions can be reduced with simultaneous nutrient recovery. A design with only gaseous effluents is possible. This does not affect the flexibility in the production.

RESUME

BASF a développé le procédé d'attaque nitrique pour en faire un procédé très souple, c'est-à-dire une souplesse au point de vue des qualités de NP(K) et dans la conception. Les exemples pour différentes formules NP montrent comment on associe la production d'engrais NPs et N simple. En même temps, la fraction de P_2O_5 *soluble dans l'eau peut être encore ajustée aux exigences. La chaux produite est habituellement utilisée en agriculture ou dans la construction. Une petite synthèse supplémentaire de AN aide en régularisant la production de CAN et permet d'avoir des formules NP riches en azote.*

Les alternatives de conception développées permettent d'adapter la structure du procédé aux réglementations de l'environnement ou leurs restrictions. Les émissions peuvent être réduites avec récupération simultanée des nutriments. Un plan avec effluents gazeux seulement est possible. Ceci n'affecte pas la souplesse du procédé.

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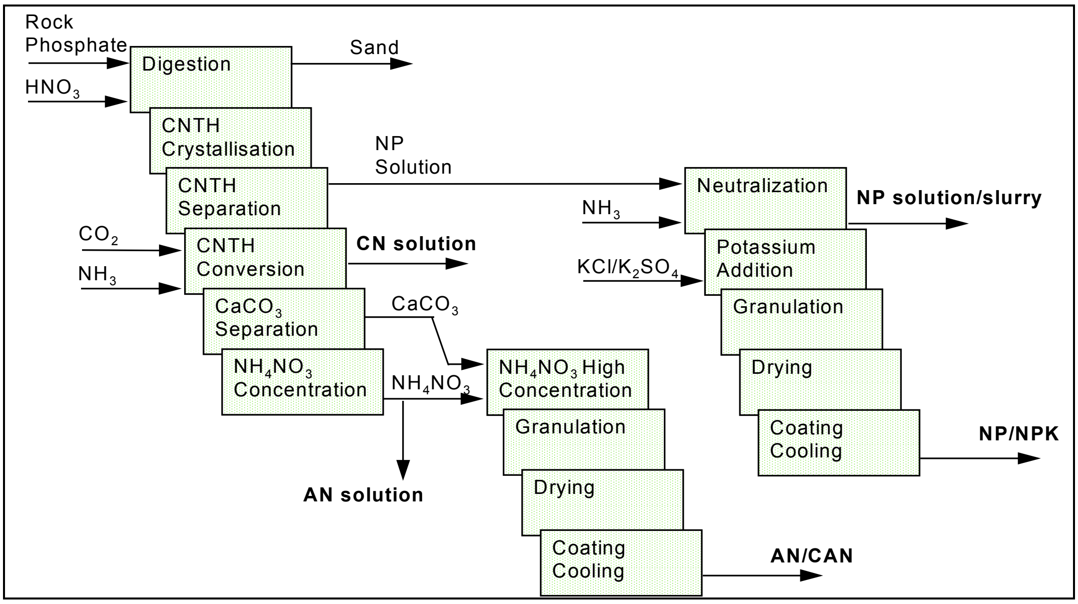
Introduction

Regional differences in fertilizing practice (different crops, soils) require a wide variety of high analysis fertilizers. From single N- to multi-nutrient NPKs this range can be covered by the BASF nitrophosphate process. It offers the advantage of a simultaneous production of NP or NPK multi-nutrient fertilizers and straight N-fertilizers.

Figure 1 - Basic scheme of the BASF nitrophosphate process



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[1] *Flexibilité du procédé BASF d'acide nitrique*

The rock phosphate (Figure 1) is digested in nitric acid and insolubles, mostly sand, are separated. Calcium nitrate tetrahydrate (CNTH) is then crystallized by cooling the solution down to approximately 0°C with optimized energy efficiency. Calcium nitrate is separated with a filter. This way, the calcium separation does not require sulfuric acid; no gypsum is produced.

The resulting solution is the nitro-phosphoric acid or NP-solution. This is neutralized with ammonia and excess water is evaporated to obtain the so called NP-melt. After the addition of potassium the melt is ready for granulation, drying and finishing.

CNTH is further processed with ammonium carbonate, which is synthesized from carbon dioxide and ammonia. The conversion reaction with calcium nitrate leads to calcium carbonate, lime, which precipitates, and to ammonium nitrate. The lime is then separated and the ammonium nitrate solution is concentrated. Both can either be sold as products or can be combined in a further granulation line to calcium ammonium nitrate fertilizer, CAN. The lime does not need to be dried for this procedure.

Raw materials needed are rock phosphate, nitric acid, ammonia and carbon dioxide.

The process offers the possibility of extracting a wide variety of liquid and granular products (Table 1):

- granular NP/NPK fertilizers
- granular straight nitrogen fertilizers (AN, CAN)
- liquid straight nitrogen solutions (calcium nitrate, ammonium nitrate)
- liquid NP/NPK suspensions

Table 1 - Product Range from Nitrophosphate Process

	NP-fertilizer, granular	**NPK, granular**
	examples	examples
N : $P_2O_5 > 1$	27+13	24+8+8, 20+10+10
N : $P_2O_5 = 1$	18+18 up to 22+22	15+15+15, 12+12+17
N : $P_2O_5 < 1$	17+27	10+15+20, 8+12+24
	N-fertilizer, granular	
ammonium nitrate	up to 33,5% N	
CAN	23 % to 27% N	
	solutions	
NP	examples: suspension for example 14+17 with 30% water	
ammonium nitrate	from process directly: 40 - 94% N usable for example for UAN solutions	
calcium nitrate	from process directly: crystal CNTH 15% N, 13% CaO with 35% water usable for example for solutions	
	else	
lime	wet or dry for soil pH adjustment, for building industry	

Raw Material and Product Mass Balances (examples)

The correlation between the NP(K) and the straight N-fertilizer production is demonstrated for some typical NP grades in terms of overall mass balances. The main parameters determining the product ratio is the CaO:P_2O_5-value. The examples are calculated for 1 MT of P_2O_5 and cover he following cases:

- Example 1 (Figure 2): **low CaO:P_2O_5-value**
  NP 17-27, which requires a low CaO:P_2O_5-value to achieve a N:P_2O_5-ratio lower than 1. A higher amount of CNTH is crystallized, which results in larger quantities of ammonium nitrate and lime.

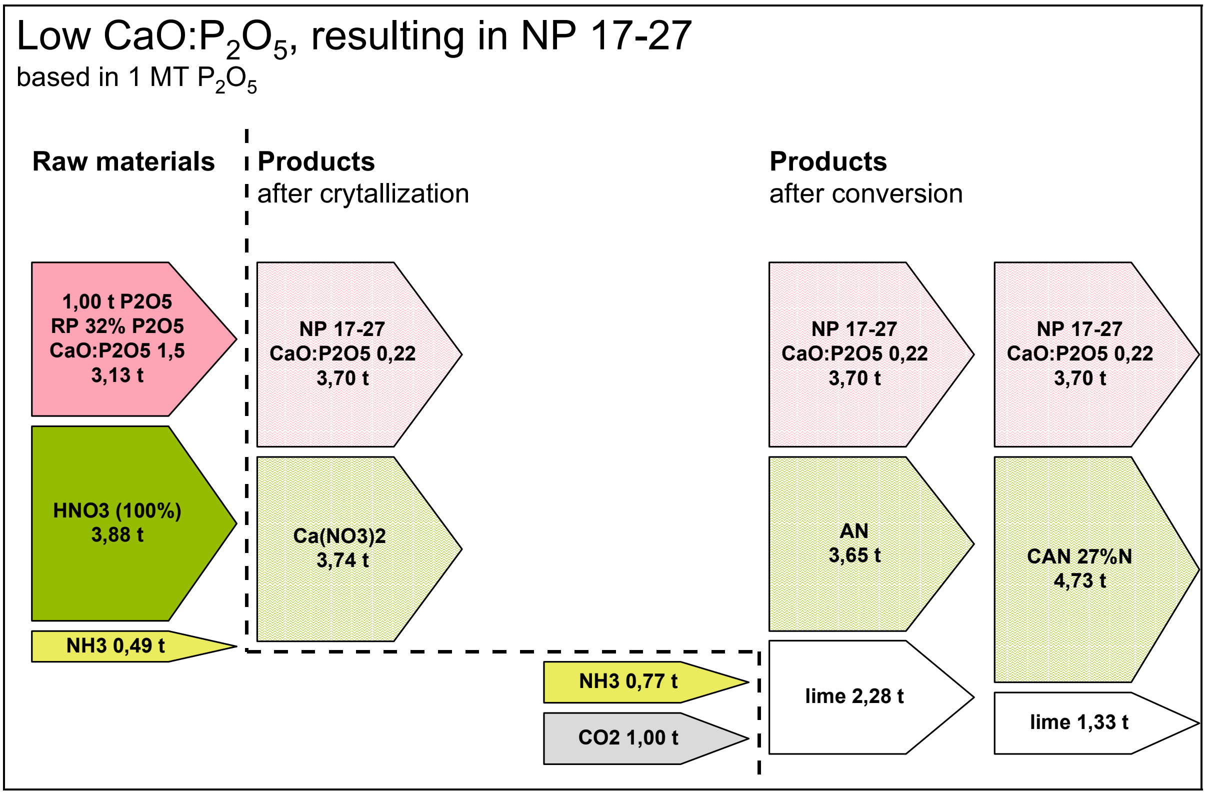
- Example 2 (Figure 3): **high $CaO:P_2O_5$-value**
  NP 20-20, which requires a higher $CaO:P_2O_5$-value to achieve a $N:P_2O_5$-ratio equal to 1. A lower amount of CNTH is crystallized, which results in lower quantities of ammonium nitrate and lime.

- Example 3 (Figure 4): **adjustment of $CaO:P_2O_5$-value**
  NP 20-20 with low $CaO:P_2O_5$-value. To adjust the water solubility of P_2O_5 for special demands, a NP 20-20 can be produced with low $CaO:P_2O_5$-value. To adjust the proper nutrient ratio, part of the ammonium nitrate from the conversion must be added to the NP-intermediate product. Also a small amount of filler is required to adjust the total nutrient content. A higher amount of CNTH is crystallized, which results in higher quantities of ammonium nitrate and lime.

- Example 4 (Figure 5): **additional AN synthesis**
  NP 20-20 with high $CaO:P_2O_5$-value. To utilize the excess lime an additional ammonium nitrate synthesis allows the production of extra CAN. As the examples 1...3 show, there is usually an excess of lime from the conversion. To make the CAN unit basically independent from the fluctuations resulting from different NP production, an ammonium nitrate synthesis is added to always keep the CAN production close to full capacity.

The rock phosphate is always totally dissolved in nitric acid. Therefore the overall N: P_2O_5-ratio for the nitrophosphate process is given by this condition (overall N: P_2O_5-ratio approximately 2). In average this ratio is applied for most crops, which are supplied with a starting dose of N, P_2O_5 and K_2O and a second dressing later with only N. So in average the nitrophosphate process covers the agronomical requirements.

Figure 2 - Example 1 for mass balance

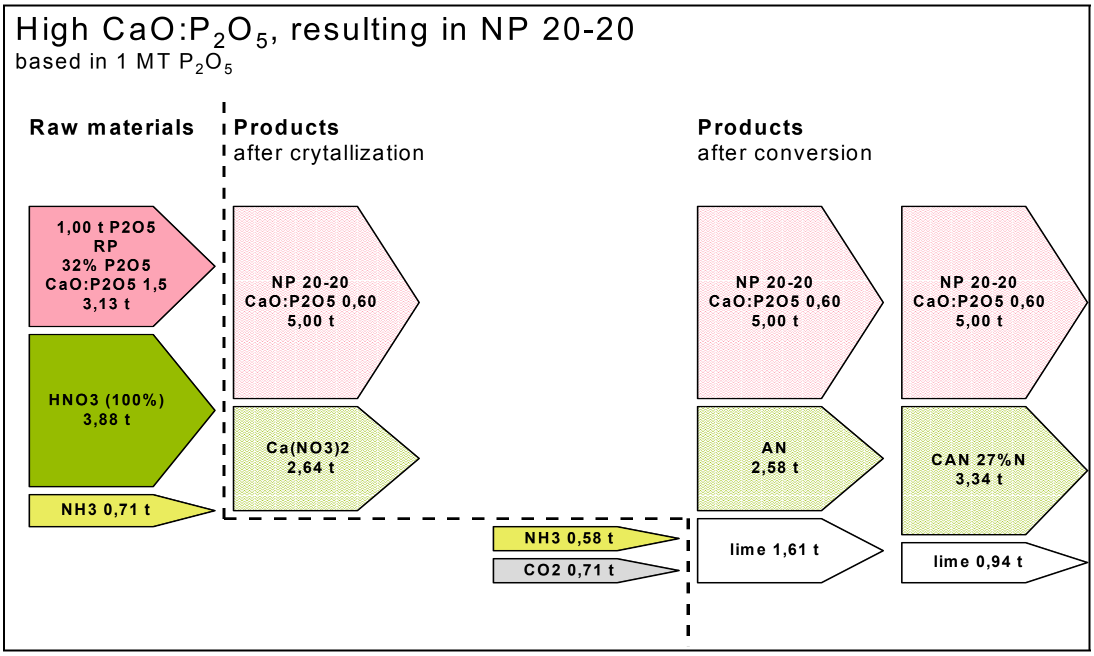


Example 1: low $CaO:P_2O_5$-value
Example 1 (Figure 2) shows the mass balance for an NP 17-27. The $CaO:P_2O_5$-value in the final product is 0,22, which is almost the lowest economically feasible in the crystallization step. Neutralizing the NP-solution with ammonia results directly in the product NP 17-27. Adding potassium to NP 17-27, for example MOP, this would lead to NPKs like 15-24-5, 14-22-10 or 11-18-20.

Calcium is separated as calcium nitrate, which is widely used as solution in green house fertigation systems (droplet fertigation). With carbon dioxide and ammonia it can be converted to ammonium nitrate and calcium carbonate, lime. If not used by themselves, they can be granulated to CAN.

With this low CaO:P_2O_5-value a high amount of calcium nitrate is separated, resulting in a high quantity of CAN (giving a product ratio of NP:CAN of 0,78).

Figure 3 - Example 2 for mass balance

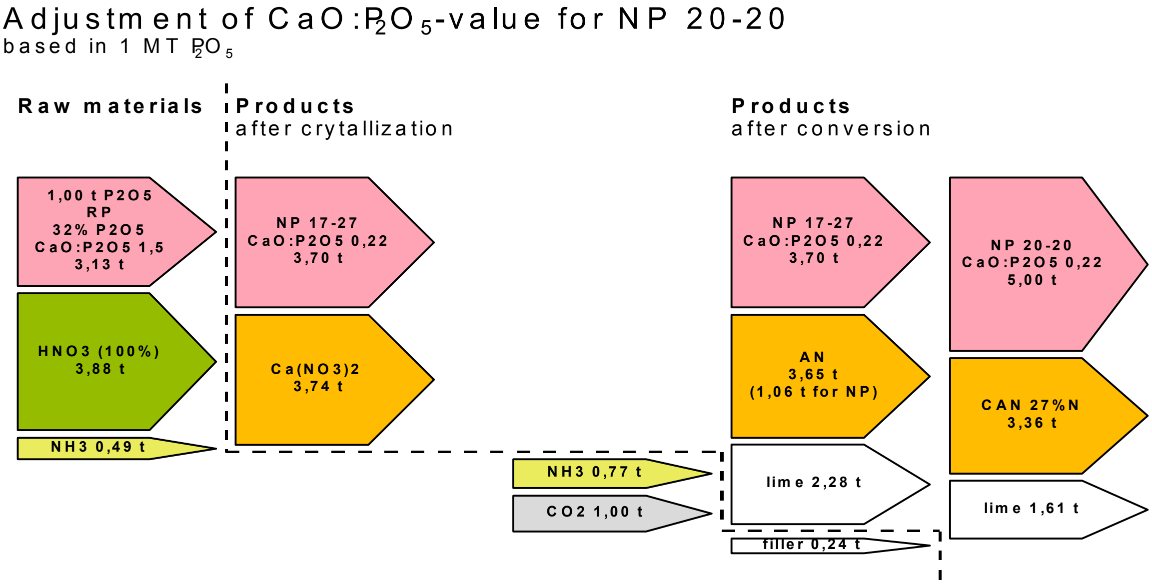


Example 2: high CaO:P_2O_5-value

Example 2 (Figure 3) shows the products for a high CaO:P_2O_5-value of 0,6. The neutralization of the NP-solution results in a product NP 20-20. At the same time the amount of CAN is lower, giving a product ratio NP:CAN of 1,50.

Examples 1 and 2 show the usual range of product ratios NP:CAN directly resulting from crystallization and the CaO:P_2O_5-value achieved in this process step. The amount of calcium, which has to be separated, is calculated backwards from the given overall nutrient content of the fertilizer and the N:P_2O_5-ratio.

Figure 4 - Example 3 for mass balance



Example 3: adjustment of CaO:P_2O_5-value

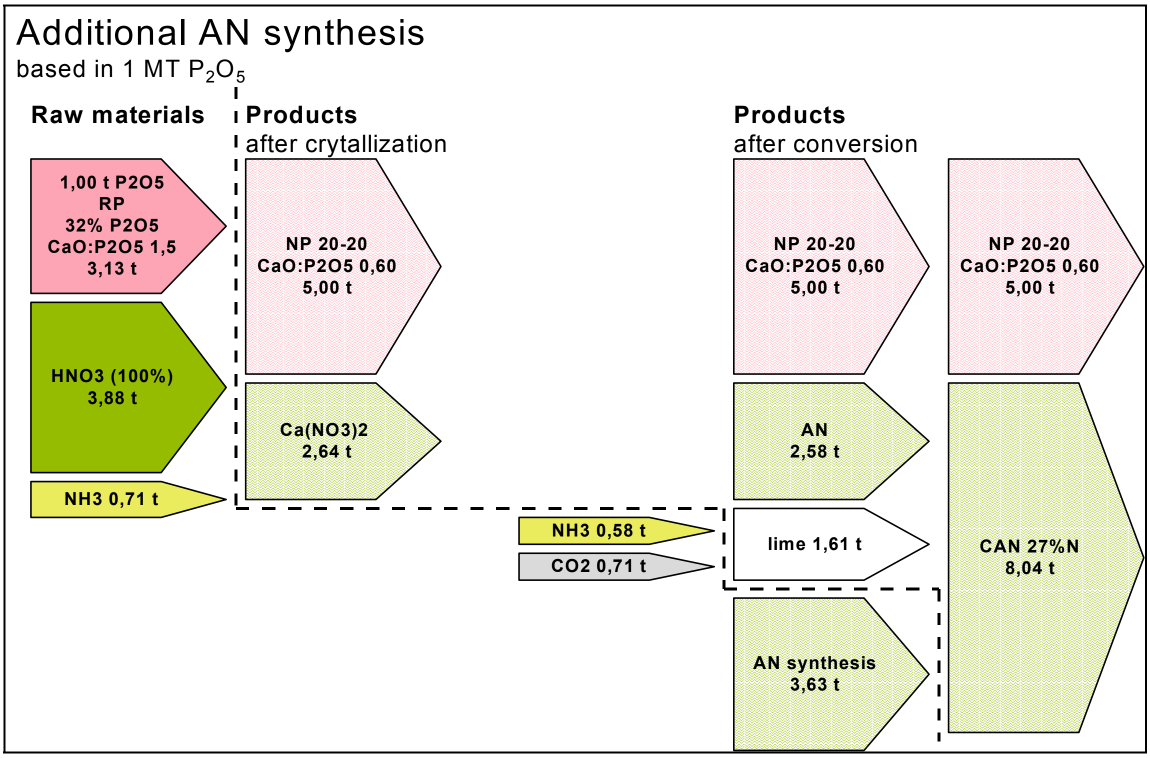
All of the P_2O_5 is citrate soluble, i.e. available for the plants. The fraction of the P_2O_5-content, which is water soluble, is directly coupled to the CaO:P_2O_5-value achieved in the crystallization. A low CaO:P_2O_5-value results in a high fraction of water soluble P_2O_5; a high CaO:P_2O_5-value results in a lower fraction of water soluble P_2O_5.

For special applications, fertilizers with a high fraction of water soluble P_2O_5 are required. To obtain this the crystallization is operated at a low CaO:P_2O_5-value. Example 3 (Figure 4) shows the mass balance for NP 20-20 (compare with example 2) with a high water soluble fraction of P_2O_5. The crystallization is adjusted to a low CaO:P_2O_5-value of 0,22 to remove a high quantity of calcium. To reestablish a N:P_2O_5-ratio of 1, part of the ammonium nitrate from the conversion must be returned to the NP solution. At the same time a small amount of filler has to be added to replace part of the removed calcium. Otherwise the product would be a NP 21-21.

For N:P_2O_5-ratios higher than 1, more ammonium nitrate can be added to the NP solution. With all the available AN the resulting product is a NP 26+13.

This example shows, how the water soluble fraction of P_2O_5 can be adjusted for a given NP product. At the same time the amount of lime increases compared to example 2, since more calcium is separated.

Figure 5 - Example 4 for mass balance



Example 4: additional AN synthesis

As is seen from the few examples above, the different NP grades result in different amounts of AN and lime. Also, if CAN is produced, the quantity of excess lime changes with the NP grade. Usually the excess lime is used for soil pH adjustment or in the building industry.

When designing the nitrophosphate process, there is the possibility of installing an additional AN synthesis to use all the lime for CAN production. Example 4 (Figure 5) shows the mass balance for NP 20-20 (compare with example 2) with extra AN production.

Usually the size of the additional AN synthesis is adjusted to the NP product portfolio in a way, that a constant operation of the CAN unit is always achieved and the amount of excess lime is minimized. The additional AN synthesis is also required to achieve products with N:P_2O_5-ratios higher than 2, for example NPKs 24-8-8 or 15-5-20.

Summary

- **Production Flexibility**

Examples 1 and 2 demonstrate the basic correlation between the ratio of NP and straight N-fertilizer products from the nitrophosphate process. The overall nutrient content and the N:P_2O_5-ratio of the final NP(K) product determine the minimum amount of calcium, which has to be removed as calcium nitrate in the crystallization.

The water soluble fraction of P_2O_5 is correlated to the CaO:P_2O_5-value. If a high water soluble fraction is required, this parameter governs the operation of the crystallisation. The overall nutrient content and the N:P_2O_5-ratio is adjusted by using the AN from conversion and filler in some cases (example 3). This way the water soluble fraction of P_2O_5 can be adjusted independently of the final nutrient content of the NP product.

Finally, a small AN synthesis gives additional flexibility in that it allows the production of NP(K)s with very high N-content and the complete use of all lime for CAN. It also decouples the CAN production from the NP production, which otherwise gives different amounts of AN/lime for changing NP grades. It enables a production of CAN at a constant rate.

The examples shown here are restricted to demonstrate the fundamental process parameters. Of course NP(K)s with other raw materials as for example potassium sulfate or ammonium sulfate to include sulfur as a nutrient are possible. The addition of micronutrients is also widely used.

- **Design Flexibility Concerning the Overall Water Balance (examples)**

The BASF nitrophosphate process is known to be one of the most environmentally friendly processes for fertilizer production. There are no solid wastes. Gaseous effluents are scrubbed according to governmental regulations. Table 2 summarizes the governmental limits and BAT values (Best Available Techniques, EFMA Booklets) for off-gases.

Table 2 - Emission limits according to governmental regulations in different countries

	Dust mg/Nm^3	NH_3 mg/Nm^3	F mg/Nm^3	NO_x mg/Nm^3
Germany	50	50	5	500
Belgium	75	100	5	500 (200 for HNO_3)
England	50	50	10	(200 for HNO_3)
BAT, EFMA	50	50	5	500

Table 3 - Emissions of different processes per MT of P_2O_5

	Commonly used phosphoric acid route		BASF nitrophosphate route	
H_2SO_4	gaseous			
sulfuric acid plant	0.42 - 1.68	kg SO_3		
	5.60 - 33.6	kg SO_2		
H_3PO_4	gaseous			
phosphoric acid plant	0.04 - 0.08	kg F		
	solid			
	5000	kg gypsum		
SSP, TSP	gaseous			
single/triple superphosphate	0,10	kg F		
	0.60 - 5	kg dust		
DAP	gaseous			
diammonium phosphate	1.0 - 4.0	kg dust		
	0.4 - 4.0	kg NH_3		
	liquid			
	0.4 - 3.0	kg N		
NP(K)			gaseous	
BASF nitrophosphate process			2.0	kg NH_3
			1.3	kg NO_x
			0.13	kg F
			2.0	kg dust
			liquid**	
			0.4	kg P_2O_5
			1.0	kg N
			0.3	kg F
			no solids	

* source: Mineral Fertilizer Production and the Environment, UNEP UNIDO IFA, United Nations Publication, Technical report No. 26, 1996

** design without liquid process effluents possible

Another issue in designing a process is the water balance and the question of liquid process effluents. Table 3, taken from the IFA Technical Report No. 26, shows the emissions from different processes based on 1 MT of P_2O_5. The nitrophosphate process usually has liquid effluents, coming from evaporation units as condensates. Mainly, the amount of liquid effluent results from the amount of water, which is introduced into the process with the nitric acid. It usually has a concentration of 58...62%.

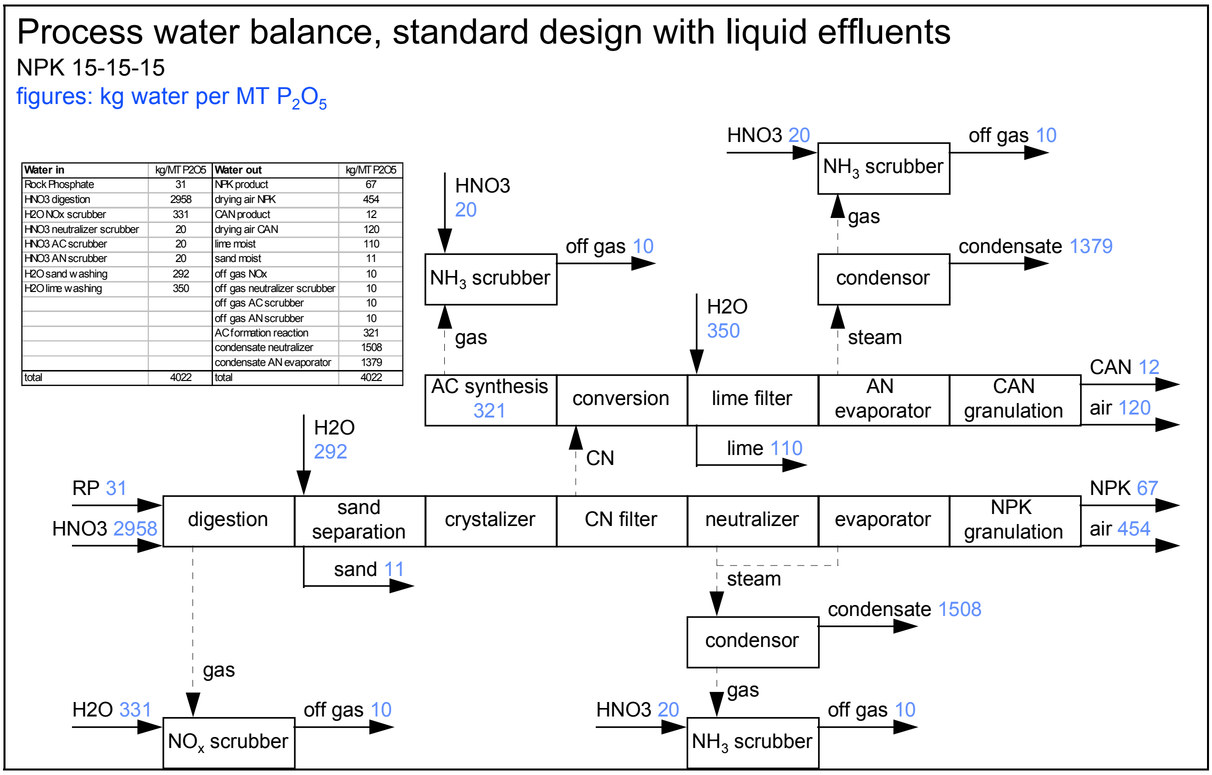
The following two examples focus on the water balance of the nitrophosphate process:

- Example 1 (Figure 6): standard design of the nitrophosphate process with liquid process effluents.
- Example 2 (Figure 7): design of the BASF nitrophosphate process avoiding liquid process effluents.

If the nitrophosphate process is integrated in an existing site, usually a waste water treatment facility is available and sufficient for treating the liquid effluents. Figure 6 shows the water balance for such a process (amount of water calculated in kg per MT of P_2O_5). The main quantity of water input into the process results from the nitric acid. The water is partially evaporated in the NP neutralization/concentration and partially in the AN concentration unit. The condensates are the two sources for liquid effluents.

Smaller amounts of water (most of them also coming with nitric acid) are used in the scrubbing systems.

Figure 6 - Example 1 for process water balance

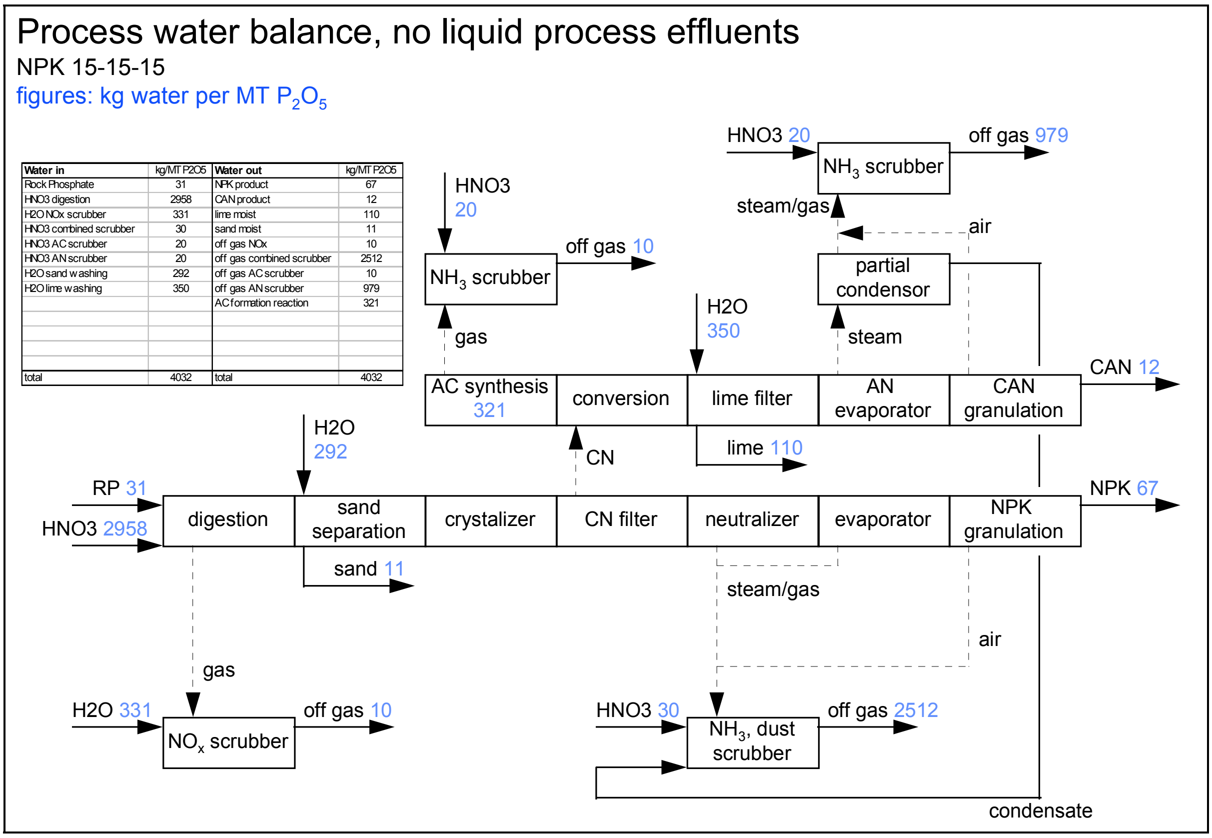


Water in	kg/MT P2O5	Water out	kg/MT P2O5
Rock Phosphate	31	NPK product	67
HNO3 digestion	2958	drying air NPK	454
H2O NOx scrubber	331	CAN product	12
HNO3 neutralizer scrubber	20	drying air CAN	120
HNO3 AC scrubber	20	lime moist	110
HNO3 AN scrubber	20	sand moist	11
H2O sand washing	292	off gas NOx	10
H2O lime washing	350	off gas neutralizer scrubber	10
		off gas AC scrubber	10
		off gas AN scrubber	10
		AC formation reaction	321
		condensate neutralizer	1508
		condensate AN evaporator	1379
total	4022	total	4022

Example 2 (Figure 7) shows the development of the process, which is free of liquid effluents. Instead of condensing the vapors from the NP neutralization/evaporation unit, they are introduced as they are in a scrubber, which at the same time cleans the drying air from the NP granulation unit. The drying air is by far not saturated with water, but comes with approximately 100ºC. The heat content is used to evaporate additional water in the scrubber. As make-up water the condensates from the AN concentration are used.

This way the combined scrubber for the NP vapors and the drying air works as an evaporator for the AN condensates without additional energy requirements. At the same time the main part of the nutrients normally lost in liquid effluents are recovered.

Figure 7 - Example 2 for process water balance, no liquid process effluents



Water in	kg/MT P2O5	Water out	kg/MT P2O5
Rock Phosphate	31	NPK product	67
HNO3 digestion	2958	CAN product	12
H2O NOx scrubber	331	lime moist	110
HNO3 combined scrubber	30	sand moist	11
HNO3 AC scrubber	20	off gas NOx	10
HNO3 AN scrubber	20	off gas combined scrubber	2512
H2O sand washing	292	off gas AC scrubber	10
H2O lime washing	350	off gas AN scrubber	979
		AC formation reaction	321
total	4032	total	4032

Design flexibility

Example 1 of the process water balance shows the design with liquid effluents. They origin from evaporation and condensation units in the process. The liquid effluents can be treated in waste water treatment facilities. In case these are not available or other restrictions prohibit liquid effluents, BASF has developed a design, which is able to avoid any liquid process effluents (example 2). The only emissions have gaseous form. They are scrubbed according to governmental regulations.

Between standard design and no liquid effluent design any intermediate combination is possible. This gives a high degree of freedom in adjusting the process to environmental regulations without losing any flexibility concerning the fertilizer production.