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*In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

THE MANUFACTURE OF COMPOUND FERTILISERS BY THE KAMPKA-NITRO PROCESS

By Dr. F.W. Brandt and Dr. H. Nees
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Germany).

The "Odda-Process" for the reaction of phosphate rock with nitric acid and the related manufacture of an NP or NPK fertiliser together with a straight N fertiliser has been known for some $3\frac{1}{2}$ decades. The process is used by Norwegian, German, Dutch and French fertiliser producers. At least half a million tons of available P2O5, or more than four million tons of NP and NPK fertilisers, are annually manufactured by this process. Co-products of it are either calcium nitrate (15.5% N and 27% CaO) or calcium ammonium nitrate (22% N).

The "Kampka-Nitro" Process, developed by Chemische Fabrik Kalk G.m.b.H., Cologne, is a further development of the Odda-Process.[*] The Odda-Process and the Kampka-Nitro Process belong to the group of so-called wet processes for the manufacture of compound fertilisers.

It has often been reported[**] that the production costs of available P2O5 obtained by a wet process using only nitric acid in the reaction are lower than in the case of processes in which additional sulphuric and/or phosphoric acid are used. This cost reduction is chiefly caused by the saving in sulphur. Following the recent heavy increases in sulphur prices and the appearance of a sulphur shortage, processes which are independent of this raw material deserve particular attention.

A) Basic features of the wet process manufacture of compound fertilisers containing P2O5

Phosphate rock is the essential raw material for the manufacture of phosphatic fertilisers by wet processes. It consists of apatite as well as other accompanying substances. The molar ratio of CaO/P2O5 in commercial phosphate rocks varies according to origin with the range of 3.4 - 4.1 : 1. Apatites are energy deficient and therefore very stable combinations of

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[*]   See patents DBP No.1060411 and DAS No.1047802.

[**]   See papers by Banthien/Eimers and Brandt/Geiersberger,
ECAFE-Fertiliser Conference, Bombay 1963, Item 7,2, f, iv
of Nov./Dec. 1963.

Table 3

General Scheme of the ODDA PROCESS

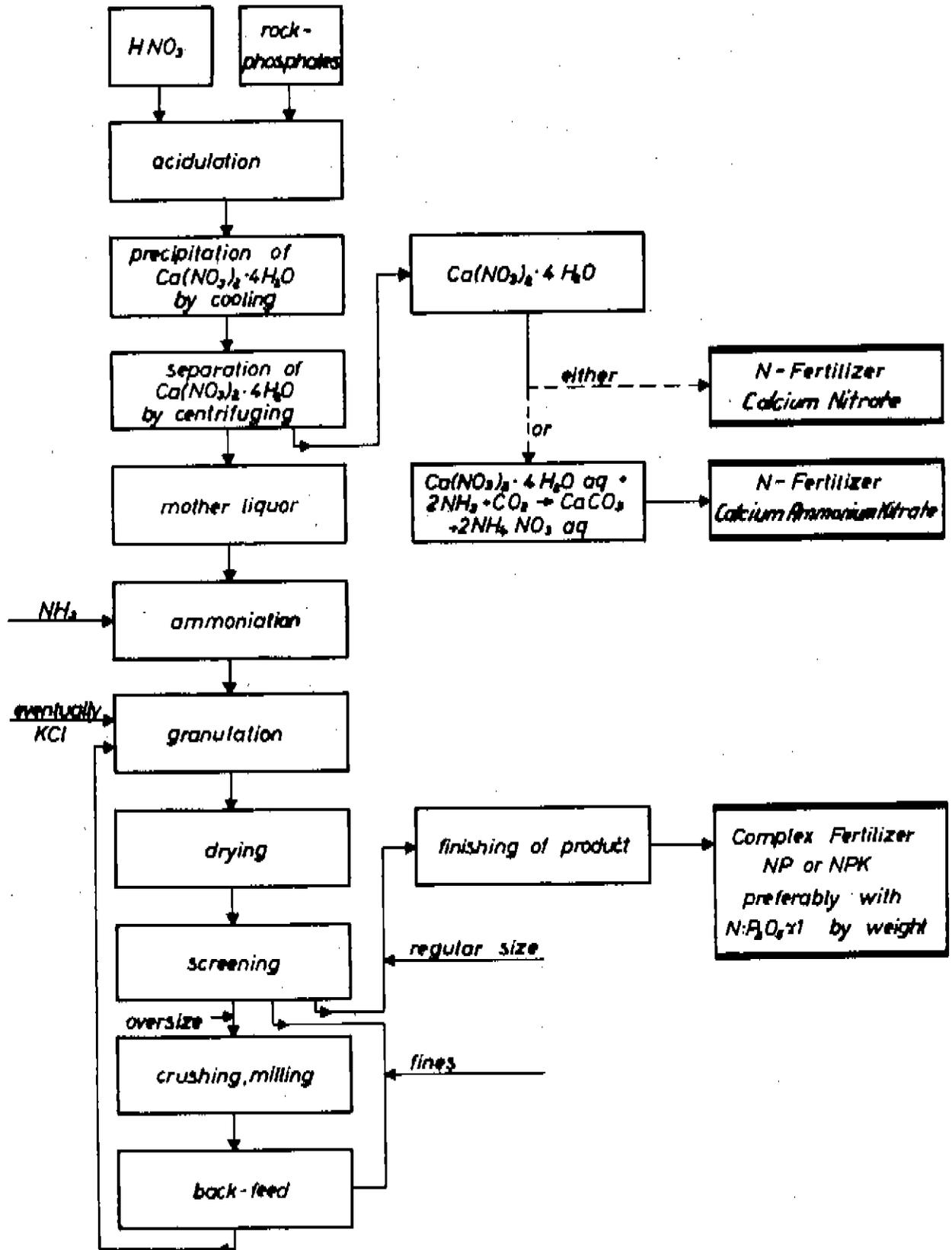### Complex-Fertilizer without consumption of sulfuric acid

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┌─────────┐   ┌─────────────┐
│  HNO₃   │   │    rock-    │
│         │   │ phosphates  │
└────┬────┘   └──────┬──────┘
     │               │
     ▼               ▼
┌──────────────────────────┐
│       acidulation        │
└────────────┬─────────────┘
             │
             ▼
┌──────────────────────────┐        ┌──────────────────────┐
│    precipitation of      │───────▶│   Ca(NO₃)₂·4 H₂O     │
│    Ca(NO₃)₂·4H₂O         │        └──────────┬───────────┘
│      by cooling          │                   │
└────────────┬─────────────┘                   │
             │                                 │
             ▼                            either│  ┌──────────────────┐
┌──────────────────────────┐            ───────┼─▶│   N - Fertilizer  │
│     separation of        │                   │  │  Calcium Nitrate  │
│     Ca(NO₃)₂·4H₂O        │                  or│  └──────────────────┘
│     by centrifuging      │                   ▼
└────────────┬─────────────┘    ┌──────────────────────────┐  ┌──────────────────────────┐
             │                  │ Ca(NO₃)₂·4H₂O aq +        │─▶│   N - Fertilizer         │
             ▼                  │ 2NH₃+CO₂ → CaCO₃          │  │ Calcium Ammonium Nitrate │
┌──────────────────────────┐    │ +2NH₄NO₃ aq              │  └──────────────────────────┘
│      mother liquor        │    └──────────────────────────┘
└────────────┬─────────────┘
             │
 NH₃         ▼
────────▶┌──────────────────────────┐
│         │      ammoniation         │
│         └────────────┬─────────────┘
│                      │
eventually             ▼
 KCl  ─────▶┌──────────────────────────┐
│           │      granulation         │
│           └────────────┬─────────────┘
│                        │
│                        ▼
│           ┌──────────────────────────┐   ┌──────────────────┐   ┌──────────────────────┐
│           │        drying            │   │ finishing of     │──▶│ Complex Fertilizer   │
│           └────────────┬─────────────┘   │ product          │   │ NP or NPK            │
│                        │                 └──────────────────┘   │ preferably with      │
│                        ▼                         ▲              │ N:P₂O₅ ≥ 1  by weight│
│           ┌──────────────────────────┐   regular │ size        └──────────────────────┘
│           │       screening          │◀──────────
│           └────────────┬─────────────┘
│           oversize ─▶   │
│                        ▼
│           ┌──────────────────────────┐      fines
│           │    crushing, milling     │◀──────────
│           └────────────┬─────────────┘
│                        │
│                        ▼
│           ┌──────────────────────────┐
│           │      back - feed         │
│           └────────────┬─────────────┘
└────────────────────────┘
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Table 4

General Scheme of the
KAMPKA-NITRO-PROCESS
Complex-Fertilizer without consumption of sulfuric acid

Flow diagram boxes and labels:

- HNO₃
- rock-phosphate
- Ca(NO₃)₂·4H₂O
- acidulation
- $Ca(NO_3)_2 \cdot 4H_2O$ aq + $2NH_3 + CO_2 \rightarrow CaCO_3 + 2NH_4NO_3$ aq
- precipitation of $Ca(NO_3)_2 \cdot 4H_2O$ by cooling
- filtration
- CaCO₃
- separation of $Ca(NO_3)_2 \cdot 4H_2O$ by centrifuging
- NH₄NO₃ - solution
- NH₄NO₃ - consuming process
- mother liquor
- return part of N-NO₃
- excess part of N-NO₃
- N-fertilizer e.g. Calcium Ammonium Nitrate
- NP-fertilizer e.g. 24-16
- NH₃ → ammoniation
- NK-fertilizer e.g. 20-0-20
- eventually KCl → granulation
- NPK-fertilizer e.g. 15-15-15
- drying
- finishing of product
- Complex Fertilizer NP or NPK preferably with N:P₂O₅ ≈ 1 by weight
- screening
- regular size
- oversize
- crushing, milling
- fines
- back-feed

65/X1

Table 5: Variants of the Odda Process

Small ratio NPK fertiliser / N fertiliser	Large ratio NPK fertiliser / N fertiliser	
Odda Process with full theoretical quantity of HNO3 for compound fertiliser and straight N fertiliser in the reaction.	Kampka Nitro Process without post-reaction. (DAS No. 1047802)	Kampka Nitro Process with post-reaction. (DBP No. 1061411)

Column 1: Odda Process with full theoretical quantity of HNO3

- 1 mol (4CaO/P2O5) → Reaction
- 9.65 mol HNO3 → Reaction

Reaction:
H_3PO_4
1.65 mol HNO_3
4.0 mol $Ca(NO_3)_2 \cdot 4H_2O$

→ Cooling and centrifugation

- Centrifuge mother liquor: H_3PO_4, 1.5 mol $Ca(NO_3)_2 \cdot 4H_2O$, 1.65 mol HNO_3
- Solid material: 2.5 mol $Ca(NO_3)_2 \cdot 4H_2O$ → Ammoniation-carbonation CO_2, $NH_3 + H_2O$

NH3 → Ammoniation
Centrifuge mother liquor → Ammoniation
KCl → Ammoniation

Finished fertiliser slurry:
$NH_4H_2PO_4$
$CaHPO_4$
CaX
NH_4Cl
3.02 mol KNO_3
1.63 mol NH_4NO_3

Calcium ammonium nitrate:
$CaCO_3$
5.0 mol $NH_4NO_3 + aq.$

Column 2: Kampka Nitro Process without post-reaction. (DAS No. 1047802)

- 1 mol (4CaO/P2O5) → Reaction
- 8.2 mol HNO3 → Reaction

Reaction:
H_3PO_4
0.2 mol HNO_3
4.0 mol $Ca(NO_3)_2 \cdot 4H_2O$

→ Cooling and centrifugation

- Centrifuge mother liquor: H_3PO_4, 1.5 mol $Ca(NO_3)_2 \cdot 4H_2O$, 0.2 mol HNO_3
- Solid material: 2.5 mol $Ca(NO_3)_2 \cdot 4H_2O$ → Ammoniation-carbonation CO_2, $NH_3 + H_2O$ → Filtration

NH3 → Ammoniation
NH_4NO_3 soln. 1.4 mol $NH_4NO_3 + aq.$ → Ammoniation
KCl → Ammoniation

Finished fertiliser slurry:
$NH_4H_2PO_4$
$CaHPO_4$
CaX
NH_4Cl
3.02 mol KNO_3
1.63 mol NH_4NO_3

$CaCO_3$

Calcium ammonium nitrate:
$CaCO_3$
3.55 mol $NH_4NO_3 + aq.$

Column 3: Kampka Nitro Process with post-reaction. (DBP No. 1061411)

- 1 mol (4CaO/P2O5) → (4.0 CaO/P2O5) → Reaction
- 7.2 mol HNO3 → Reaction

Reaction:
H_3PO_4
0.4 mol HNO_3
3.4 mol $Ca(NO_3)_2 \cdot 4H_2O$

→ Cooling and centrifugation

- Centrifuge mother liquor: H_3PO_4, 0.9 mol $Ca(NO_3)_2 \cdot 4H_2O$, 0.4 mol HNO_3
- Solid material: 2.5 mol $Ca(NO_3)_2 \cdot 4H_2O$ → Ammoniation-carbonation CO_2, $NH_3 + H_2O$ → Filtration

(4CaO/P2O5) → Post-reaction
Centrifuge mother liquor → Post-reaction

NH3 → Ammoniation
NH_4NO_3 soln. 2.45 mol $NH_4NO_3 + aq.$ → Ammoniation
KCl → Ammoniation

Finished fertiliser slurry:
$NH_4H_2PO_4$
$CaHPO_4$
CaX
NH_4Cl
3.02 mol KNO_3
1.63 mol NH_4NO_3

$CaCO_3$

Calcium ammonium nitrate:
$CaCO_3$
2.55 mol $NH_4NO_3 + aq.$

65/X

Table 2.   Wet Processes for the Manufacture of Compound Fertilisers.

Classification of fertilisers according to plant nutrient content	Process Description	Raw materials		Ca ions				Finished fertilisers								
		Reaction	Ammoniation	fixed in the fertiliser		separated		Nutrient ratio		Ca compounds				Ammonium phosphates	CaO/P2O5 Molar ratio	
				as CaSO4.aq+Cax (mol)	as CaCO3+Cax (mol)	from the fertiliser slurry as Ca(NO3)2.4H2O (mol)	previously during H3PO4 production as CaSO4.aq (mol)	N/P2O5 %(wt.)	N/P2O5/K2O %(wt.)	CaSO4+Cax (mol)	CaCO3+Cax (mol)	CaHPO4 CaO part (mol)	P2O5 part (mol)	P2O5 part	linked to phosphate CaO / total P2O5	total CaO / total P2O5
low-grade	a) Carbon dioxide nitric acid process with phosphate rock	RP HNO3	NH3 CO2	-	2.0	-	-	16.6/14.1	13/11/13	-	2.0	2.0	1.0	-	2.0:1	4.0:1
	b) Sulphuric acid phosphoric acid process with phosphate rock	RP H2SO4 HNO3	NH3	2.7	-	-	-	13.5/13.5	11/11/11	2.7	-	1.3	0.65	0.35	1.3:1	4.0:1
medium-grade	c) Sulphuric acid nitric acid phosphoric acid process with phosphate rock	RP H2SO4 HNO3 H3PO4	NH3	1.7 1.3 0.7	- - -	- - -	1.0 1.4 2.0	15.0/15.0 16.6/16.6 18.3/18.3	12/12/12 13/13/13 14/14/14	1.7 1.3 0.7	- - -	1.3 1.3 1.3	0.65 0.65 0.65	0.35 0.35 0.35	1.3:1 1.3:1 1.3:1	3.0:1 2.6:1 2.0:1
high-grade	d) Nitric acid process with phosphate rock e.g. Odda process e.g. Kampka-Nitro process	RP HNO3	NH3	0.2	-	2.5	-	20.0/20.0	15/15/15	0.2	-	1.3	0.65	0.35	1.3:1	1.5:1
	e) Nitric acid phosphoric acid process with phosphate rock	RP HNO3 H3PO4	NH3	0.2 0.1 0.1	- - -	- - -	2.5 3.2 3.6	20.0/20.0 21.8/21.8 23.5/23.5	15/15/15 16/16/16 17/17/17	0.2 0.1 0.1	- - -	1.3 0.7 0.4	0.65 0.35 0.20	0.35 0.65 0.80	1.3:1 0.7:1 0.4:1	1.5:1 0.8:1 0.5:1
highest-grade	f) Nitric acid phosphoric acid process without phosphate rock	HNO3 H3PO4	NH3	0	-	-	-	~24.7/24.7	~17.5/17.5/17.5	0.1	-	0	0	1.00	0 :1	0.1:1

RP = rock phosphate

N-NO3 balance, and resulting amounts of Ca(NO3)2.4H2O, co-product fertilisers and free, usable CaCO3 per ton of primary fertiliser.

	Odda Process with maximum application of HNO3	Kampka Nitro Process without post-reaction
N-NO3 for reaction mol HNO3/mol P2O5 Kg N-NO3/Kg P2O5	9.65 (≙ 100%) 0.95	8.20 (≙ 85%) 0.81

N-NO3 balance	in the reaction	in the centrifuge mother liquor	in the primary compound fertiliser	Feed-back as NH4NO3	in Ca(NO3)2.4H2O	in the calc. ammon. nitrate as co-product fertiliser	in the reaction	in the centrifuge mother liquor	in the primary compound fertiliser	Feed-back as NH4NO3	in Ca(NO3)2.4H2O	in co-product fertiliser e.g. calc. ammon. nitrate
Kg N-NO3 /t primary fertiliser 13-13-21	122	—	59	—	63	63	105	40	59	19	63	44
Kg N-NO3/t primary fertiliser 15-15-15	142	—	69	—	73	73	121	47	69	22	73	51
Kg N-NO3/t primary fertiliser 20-20-0	189	—	92	—	97	97	162	63	92	29	97	68

Separated Ca(NO3)2.4H2O	Odda Process	Kampka Nitro Process
t Ca(NO3)2.4H2O/prim. fert. 13-13-21	0.53	0.53
t Ca(NO3)2.4H2O/prim. fert. 15-15-15	0.62	0.62
t Ca(NO3)2.4H2O/prim. fert. 20-20-0	0.82	0.82

Co-product fertiliser	calcium ammonium nitrate	NH4NO3 - Proportion for NP, NK or NPK co-product fertiliser	either calcium ammonium nitrate	or NH4NO3 - Proportion for NP, NK or NPK co-product fertiliser
t co-product fert./ prim. fert. 13-13-21	0.59	—	0.41	0.25
t co-product fert./ prim. fert. 15-15-15	0.67	—	0.47	0.29
t co-product fert./ prim. fert. 20-20-0	0.91	—	0.63	0.39

Free usable CaCO3	in the calcium ammonium nitrate co-product fertiliser	either in calc. ammon. nitrate as co-product fertiliser	or in NP, NK or NPK fertilisers as co-product fertilisers
t CaCO3/t primary fertiliser 13-13-21	—	0.04	0.20
t CaCO3/t primary fertiliser 15-15-15	—	0.06	0.24
t CaCO3/t primary fertiliser 20-20-0	—	0.08	0.32

Table 7 : Comparison of production capacities and investment costs for a plant using the $HNO_3 - H_3PO_4$ Process (see Table 2) and for one using the Kampka-Nitro Process..

- It is assumed in the comparison that
  - a) energy supply is available
  - b) workshops are available
  - c) an ammonia synthesis plant, including CO_2 compressors and tanks, is available.

The figures in the table are valid for specific investment conditions. They will vary according to country and circumstances.

Process	$HNO_3 - H_3PO_4$ Process	Kampka-Nitro Process + Calcium ammonium nitrate and $CaCO_3$ section	
Output	200,000 tons/year of 13-13-21 = 615 tons/day	200,000 tons/year of 13-13-21 = 615 tons/day	60,000 tons/year of calcium ammonium nitrate (22% N) + 8,000 tons/year of $CaCO_3$ (dry)
	Capacity	Capacity	Capacity
A) Storage sheds			
Phosphate rock storage	20,000 tons	20,000 tons	–
Potash storage	4,000 tons	4,000 tons	–
Pyrites storage	800 m^3	800 m^3	–
Phosphoric acid storage	800 m^3	–	–
H_2SO_4 storage	1,000 m^3	–	–
HNO_3 storage	500 m^3	500 m^3	250 m^3
Storage shed for NPK fertilisers	65,000 tons	65,000 tons	–
Storage shed for calcium ammonium nitrate	–	–	20,000 tons
$CaCO_3$ silo	–	–	1,000 tons
NPK fertiliser loading shed	200,000 tons/year	200,000 tons/year	–
Calcium ammonium nitrate loading shed	–	–	60,000 tons/year
B) Production plants			
NPK plant	200,000 tons/year	200,000 tons/year	–
Kampka-Nitro section	–	50 tons/day P_2O_5	25 tons/day $CaCO_3$
Calcium ammonium nitrate section	–	–	185 tons/day
HNO_3 plant complete	40 tons/day	40 tons/day	20 tons/day
H_3PO_4 plant complete	50 tons/day	–	–
H_2SO_4 plant complete	120 tons/day	–	–
Phosphate rock grinding plant	30 tons/day	–	–
Investment cost	ca. 38 million DM	Total : ca. 44 million DM	
Plant nutrient production $(N+P_2O_5)$	52,000 tons/year	52,000 tons/year + 13,200 tons/year	
Investment cost per ton of plant nutrient $(N+P_2O_5)$	ca. DM 720/ton/year $(N+P_2O_5)$	ca. DM 680/ton/year $(N+P_2O_5)$ The by-product $CaCO_3$ is not included in this calculation	

calcium ortho-phosphate and fluoride or hydroxide or carbonate, the phosphatic content of which becomes only very slowly available to plants. The art of manufacturing phosphatic fertilisers by wet processes consists in breaking down the apatite contained in the phosphate by means of chemical reaction with acids and in so conducting the manufacturing process that the finished product will have a smaller CaO/P_2O_5 molar ratio than in the apatite. In this way fertilisers are obtained with their phosphatic components in a form which is available to plants (c.f. Table 1).

The following acids are currently used for wet process reaction with phosphate rock, either separately or in mixtures:

$$HNO_3$$

$$H_2SO_4$$

$$H_3PO_4$$

During or after ammoniation, CO_2 is also introduced into the fertiliser slurry in certain processes.

If aq. $CaSO_4$ or $CaCO_3$, which are relatively insoluble compounds formed during the fertiliser production process, are left in the finished product, low-grade fertilisers result. But if the calcium salts formed during the reaction of phosphate rock with, for example, H_2SO_4 or HNO_3 - e.g.

$$aq. \ CaSO_4$$

or

$$aq. \ Ca(NO3)_2$$
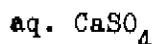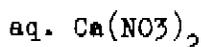
are separated from the reaction slurry, either immediately by filtration or after cooling by centrifugation, one obtains phosphoric acid or a slurry containing phosphoric acid.

Table 2 shows, in order of increasing plant nutrient content, the known processes for compound fertiliser manufacture which meet these possibilities.

For the sake of clear presentation, the following simplifications are incorporated in Table 2:

1. Only Moroccan phosphate, with a CaO/P_2O_5 molar ratio of 4.0, was used as the basis for calculations.

2. The ratios of $N:P_2O_5:K_2O$ in the fertilisers was limited to 1:1:1 (except item a).

3. For all fertilisers up to the 15-15-15, the proportion of water soluble P_2O_5 in the total P_2O_5 content of the fertilisers was put at 35% by weight (except item a).

4. In some cases, the calculated values were rounded.

<u>B) Processes based on the reaction of rock phosphate with nitric acid and the separation of, e.g., $Ca(NO_3)_2.4H_2O$.</u>

Processes of this kind include the Odda-Process and its modifications. One of these modifications is the Kampka-Nitro Process with its two methods of procedure –

with or without the post reaction of phosphate rock

1) <u>The Odda Process (c.f. Table 3).</u>

The Odda Process is designed for the manufacture of concentrated NP or NPK fertilisers <u>without the use of H2SO4</u>. In addition to the compound fertiliser, a straight nitrogen fertiliser (calcium nitrate or calcium ammonium nitrate) is obtained. $Ca(NO_3)_2.4H_2O$ is separated off by centrifugation and by cooling the reaction solution.

2) <u>The Kampka-Nitro Process (c.f. Table 4).</u>

The Kampka-Nitro Process is also designed for the manufacture of high-grade NP or NPK fertilisers <u>without the use of H2SO4</u>. In contrast to the Odda Process, with the introduction of the full amount of HNO3 into the reaction required for both the compound fertiliser and the straight N fertiliser, the Kampka-Nitro Process aims

– with a given quantity of HNO3, to make the ratio

<u>quantity of compound fertiliser</u>
quantity of co-product fertiliser

as large as possible;

– by extending the co-produced fertilisers to NP, NK or NPK formulations, to become free of the restriction represented by a co-product with only nitrogen as its plant nutrient component;

– if possible, to avoid the production of a co-product fertiliser altogether.

To achieve these aims, 3 new steps in the process have been technically worked out and introduced:

– the rock phosphate is treated with just the exact quantity of HNO3 required for the completion of the reaction;

– the $Ca(NO_3)_2.4H_2O$ which is separated by cooling is ammoniated and carbonated with NH3 and CO2 $/(NH_4)_2CO_3/$

and is thus converted to a suspension of $CaCO_3$ in a solution of NH_4NO_3:

- the ammoniation - carbonation process is so conducted that the resulting $CaCO_3$ is filterable and can be separated from the NH_4NO_3 solution by filtration.

a) Chemical and Technical Data.

Tables 5 and 6 show quantitative comparisons between the processes described above in sections B 1) and B 2).

For the sake of clarity, these tables

a) In some cases show only one of the process routes;

b) Relate only to the 15-15-15 fertiliser;

c) Quote figures only in terms of $N-NO_3$.

The Kampka-Nitro Process can be used with advantage for compound fertilisers with an $N:P_2O_5$ ratio (by weight) of 1 to 1.5:1 and a $N-NH_3:N-NO_3$ molar ratio 1:1.

As examples of fertilisers which can be produced by this process, we quote the following, most of which are already manufactured industrially:

$$13-13-21$$
$$15-15-15$$
$$20-20-0$$
$$12-12-20S$$
$$12-12-16$$
$$12-12-24$$
$$24-16-0$$
$$18-12-15$$
$$18-12-12S.$$

In the Kampka-Nitro Process all, or almost all the HNO_3 which is fed into the process attacks the phosphate rock. Practically no nitric acid is fed to the process to combine only with ammonia. After the ammoniation-carbonation of the separated $Ca(NO_3)_2.4H_2O$, practically all of the HNO_3 fed into the Kampka-Nitro Process was used both to react with phosphate rock and to fix ammonia.

If the precipitated $CaCO_3$ is not used in the formation of calcium ammonium nitrate, it can be filtered off from the NH_4NO_3 solution and processed to form a commercial product.

For ammoniation-carbonation, by-product CO_2 from ammonia synthesis or surplus CO_2 from soda production can profitably be used.

Industrial experience has been gained with Kola, Moroccan and Taiba phosphates. The optimum concentration of the nitric acid for the reaction lies within the range of 55 - 61% by weight.

b)   Economic Data

A Kampka-Nitro plant is economically advantageous, compared with the process using wet phosphoric acid, because, in terms of the quantity of N + P2O5 in the fertilisers produced, the investment for a complete Kampka-Nitro plant with a calcium ammonium nitrate section, compared with a plant using the nitric acid-phosphoric acid process, is smaller: DM 680 per metric ton of N + P2O5 in the fertiliser, compared with DM 720 (c.f. Table 7).

The Kampka-Nitro Process makes no use, either directly or indirectly, of sulphuric acid. The anion of the acid used in the reaction passes into the $Ca(NO_3)_2.4H_2O$ and its fertiliser derivatives $CaSO_4$ on the other hand, is not used.

Again, in terms of the plant nutrient content of the finished product, the Kampka-Nitro Process has an economic advantage over the normal Odda-Process with the introduction of the full amount of HNO_3 for both the compound fertiliser and the straight nitrogen fertiliser,

- since there is less or no production of the co-product fertiliser;

- since the co-product fertilisers are not limited to straight N fertilisers, and thus the Kampka-Nitro Process is independent of the straight N fertiliser market;

- since the capacity of the HNO_3 plant and the cooling section of the Kampka-Nitro Plant can be smaller;

- since, with 1 ton of $N-NO_3$ in the form of HNO_3, up to 1.4 times more available P2O5 can be produced.

By using the post reaction, which, for the same amount of HNO_3 used, consists in the treatment of an additional amount of rock phosphate with the centrifuge mother liquor, the ratio

tonnage of compound fertiliser
tonnage of co-product fertiliser

can be still further increased.

The Kampka-Nitro Process may also be used advantageously in combination with an available wet process phosphoric acid plant. In this way, NP or NPK fertilisers falling outside the range offered by the Kampka-Nitro Process alone, can be manufactured. These fertilisers can take up the co-produced ammonium nitrate to

such an extent that no straight N fertilisers need to be marketed.

c) Equipment Data.

The design of equipment for the Kampka-Nitro Plant incorporates new developments. The cooling of the reaction slurry takes place in several stages. If these stages are accurately managed, a coarse, crystalline calcium nitrate-tetrahydrate is produced. As a result the mother liquor can be easily separated from the salt by centrifugation. A comparative reduction in the required number of centrifuges can be achieved. With this process, the quantity of phosphoric acid remaining in the calcium nitrate-tetrahydrate can be reduced. A further reduction of the phosphoric acid content can, if desired, be effected in a special purification stage.

Cooling is fully automated. The control system regulates the course of the individual cooling stages and the intervals for cleaning the cooling surfaces.

For the ammoniation - carbonation of the calcium nitrate, a special apparatus has been developed in which the calcium carbonate can be precipitated in easily filterable form. The ammonium nitrate solution obtained after the filtration of the calcium carbonate can, amongst other things, be used in well known ways in compound fertiliser slurries, or processed into N, NP, NK or NPK fertilisers. Only two men per shift are required for cooling, purification of the calcium nitrate, ammoniation - carbonation and ammonium nitrate concentration. Energy consumption and maintenance requirements are of the same order of magnitude as with complete compound fertiliser processes using nitric, sulphuric and phosphoric acids, or merely nitric and phosphoric acids in the reaction stage.

A large scale plant, with a capacity of 250,000 tons per year of compound fertilisers, has been operating successfully since the end of 1963.

Table 1

P205 content and CaO/P205 molar ratios of orthophosphates involved
in wet processes for fertiliser production.

Material	P205 content (% by weight)	Molar ratio CaO/P205
Moroccan phosphate	~33.5	~3.9 : 1
Pebble phosphate	~34.0	~3.7 : 1
Togo phosphate	~36.5	~3.6 : 1
Taiba phosphate	~37.0	~3.5 : 1
Kola phosphate	~38.5	~3.4 : 1
Fluor-apatite	42.22	3.3 : 1
Tricalcium phosphate (formal)	45.76	3.0 : 1
Dicalcium monohydrogen phosphate	52.16	2.0 : 1
Monocalcium dihydrogen phosphate	60.65	1.0 : 1
Orthophosphoric acid, anhydrous	72.43	0.0 : 1
Industrial phosphoric acids	e.g. 28	0.1 : 1
	54	0.0 : 1
Ammonium phosphates	53.74 or 61.71	0.0 : 1
Potassium phosphates	40.75 or 52.16	0.0 : 1

The table shows schematically the trend of P205 contents (in % by weight)
and CaO/P205 molar ratios. Thus, it does not include all types of commercial
phosphate rocks.

The P205 contents (in % by weight) and the CaO/P205 molar ratio of the
phosphate rocks quoted are approximate values for moist material. The analyses
of commercial materials show slight variations from these formal values.

DISCUSSION

Dr. H. NEES (Chemische Fabrik Kalk, Germany) : As an introduction
to our paper, I should like to show a few slides.

The Kampka-Nitro Process is, as you know, a modified form of the
Odda Process. The first two slides show the formal difference between
the Odda Process and the Kampka-Nitro Process.

Slide 1: Odda Process

The Odda Process gives a complex fertiliser and, in addition,
a straight nitrogen fertiliser.

Slide 2: Kampka-Nitro Process

The special feature of the Kampka-Nitro Process consists in the
production of a filterable calcium carbonate during the ammoniation-
carbonation of the $Ca(NO_3)_2.4H_2O$. Thus, apart from calcium carbonate,
one obtains a solution of ammonium nitrate which can be partly fed
back to the fertiliser slurry and partly used to produce another
fertiliser as a co-product. This co-product does not need to be a
straight nitrogen fertiliser. One can produce NPK, NP and NK
compounds. Thus the Kampka-Nitro Process does not restrict pro-
duction to a straight N fertiliser in addition to the primary complex
fertiliser.

Slide 3:

The slide shows the reaction of Kola phosphate as a function of
the quantity of acid used. You can see that after two hours with
$6.6-6.8$ mol $Ca(NO_3)_2$ per mol P_2O_5 from Kola phosphate the reaction
is already complete.

Slide 4:

This slide shows how the amount of calcium nitrate to be separated
is a function of acid concentration and temperature.

Slide 5:

This slide shows the existing cooling stream in our factory at
Köln/Kalk for the separation of $Ca(NO_3)_2.4H_2O$. This cooling stream
is automated and fully continuous.

Slide 6:

This is an example of the particle size distribution of
$Ca(NO_3)_2.4H_2O$ separated from a slurry produced with Kola phosphate
and from one produced with Moroccan phosphate.

Slide 7:

This shows the $CaCO_3$ filter. The $CaCO_3$ is easily filterable and
contains about 10% water.

Slide 8:

.This illustrates the particle size distribution of the $CaCO_3$, this time shown only for material produced from Kola phosphate. Particle size and particle size distribution can be widely varied by changing the process conditions.

Slide 9:

This shows the control panel. The room is very long and not very broad, so that it is difficult to photograph.

Dr. H. STICH (Oesterreichische Stickstoffwerke, Austria) : With their paper on the Kampka-Nitro Process, Dr. Brandt and Dr. Nees have demonstrated a means of alleviating, and perhaps even of solving, the problem of the by-products arising as gypsum in phosphoric acid manufacture or calcium nitrate (or calcium ammonium nitrate) in the Odda Process. Furthermore, in the light of rising sulphur prices the paper is also extremely interesting.

To examine critically the advantages put forward for this process, it must be considered essentially from two aspects: in comparison with the complex fertiliser process involving reaction with nitric and phosphoric acids; and in comparison with the Odda Process, of which the Kampka-Nitro Process is a further development.

I should therefore like to recall once again the essential differences :

1. No phosphoric acid requirement and therefore no sulphuric acid requirement.

2. Lower nitric acid requirement than with the Odda Process, and with the after-reaction a further decrease in the nitric acid requirement.

3. Less co-product fertiliser, but with production of $CaCO_3$ which, contrary to the gypsum from phosphoric acid production, can be commercially profitable.

My questions relating to these individual points are as follows:

With regard to the absence of any requirement for phosphoric and sulphuric acids, do you not have to take into account some restriction of the possibilities for varying the fertiliser formulations? I am thinking mainly of formulations in which the $N:P_2O_5$ ratio is smaller than 1, or formulations with a low total plant nutrient content (although the latter are perhaps only of theoretical interest)?

With regard to the smaller nitric acid consumption than in the Odda Process, has this any influence on the proportion of citrate soluble P_2O_5? And is there not a danger that some mono-calcium phosphate will be precipitated and then separated off with the calcium nitrate?

And if you use the after-reaction, in which case the consumption of nitric acid can be still further reduced, does not the $CaO:P_2O_5$ ratio in the finished fertiliser increase again, since the proportion of CaO in the after-reacted phosphate rock is not separated out as calcium nitrate? As a result, the obtainable plant food content might have to be less.

With regard to the after-reaction, one might also ask whether the same reaction efficiency is achieved with this as with the main reaction, i.e. whether a larger proportion of insoluble P_2O_5 results from the after-reaction, or whether this can be counter-balanced by, for example, a longer retention time.

With regard to the smaller production of co-product fertiliser and the production of calcium carbonate, I should like to ask whether, in the separation of $CaCO_3$ from the ammonium nitrate solution, the solution must be diluted to achieve better filtration of the $CaCO_3$, as this would incur higher evaporation costs. Moreover, is this calcium carbonate generally of commercial use, or does this perhaps depend on the local situation of your factory? Under certain circumstances, gypsum produced in phosphoric acid manufacture can also be profitably used, e.g. in ammonium sulphate production or in the building materials industry. Unfortunately, these possibilities are only limited.

The reduction in the amount of co-product fertiliser which occurs - calcium nitrate or calcium ammonium nitrate - is certainly of great importance, particularly when such straight fertiliser plants are not already available. However, the further processing of the calcium nitrate into compound fertilisers necessitates a phosphoric acid plant and, thus, a sulphuric acid requirement; and hence the advantage of economy in capital costs would possibly be eliminated.

Lastly, could you give comparative figures relating the energy consumption in the Kampka-Nitro Process with that in the nitric-phosphoric acid process or the classical Odda Process?

Dr. NEES: First with regard to the influence of the smaller quantity of nitric acid on the extent of the reaction, the reaction must proceed exactly in the same way as if more nitric acid were being used. The possibility of conducting the reaction in this way has been proved in practice over a long period of experimentation in a pilot plant and for the last two years in an industrial plant. The reaction must go to completion.

With regard to the effect of the smaller quantity of sulphuric acid on the co-precipitation of mono-calcium phosphate during cooling, there must be no co-precipitated mono-calcium phosphate, because if this occurs, the process is finished, and one would be practically unable to carry it through. In our cooling stream, no mono-calcium phosphate is co-precipitated. We produce fertilisers with 35% of their P_2O_5 in water soluble form: 13-13-21, 20-20-0, 15-15-15, the classical fertilisers for the Odda Process.

You asked whether the Odda Process, compared to processes using phosphoric acid, restricts the plant food content and the $N:P_2O_5$ ratio. The Odda and Kampka-Nitro Processes do, indeed, restrict the $N:P_2O_5$ ratio. The best ratio is about 1:1. They also restrict the plant food content, and as you can see from table 2, the classical fertilisers for both processes are a 20-20-0 and those fertilisers which can be manufactured from a 20-20-0 slurry: 13-13-21 and 15-15-15. Lower grade fertilisers can also be produced, e.g. a 14-14-14. A 24-16-0 fertiliser can also be manufactured with the Kampka-Nitro Process if all the ammonium nitrate which is formed during ammoniation-carbonation is fed back in to the primary complex fertiliser.

The after-reaction is to be understood as follows: if one uses just the theoretical amount of nitric acid required to complete the attack of the phosphate rock - and this was one of the conditions of the Kampka-Nitro Process - one can encounter certain small difficulties which one naturally seeks to prevent. We therefore use a small excess of acid in the reaction. However, this surplus nitric acid, in relation to the theoretical quantity required, reduces the possibility of feeding back calcium nitrate into the primary fertiliser. Thus the after-reaction is simply designed to make subsequent use of this excess nitric acid, previously introduced into the system for technical reasons, in a further reaction with phosphate rock, so that the theoretical ratio of HNO_3/phosphate rock can be maintained as far as possible. The primary acidulation of phosphate rock also plays some part in determining the extent of the after-reaction. The distribution of phosphate rock between the main reaction and the after-reaction is established quite experimentally from experience. The overall reaction efficiency in the slurry is not decreased by the after-reaction. The process must be so conducted that reaction efficiencies are completely identical, irrespective of whether the after-reaction is used or not. This depends on local conditions and on the type of phosphate rock used.

As to the dilution of the calcium nitrate solution, when one melts $Ca(NO_3)2.4H_2O$ one obtains a calcium nitrate solution of about 65%. A certain amount of water is still with the tetrahydrate, so that the concentration of such a solution is roughly 60%. Some dilution must be made in order to obtain a suitable quality of calcium carbonate. But so far the economic advantages of the process have compensated for this excess water.

Next, with regard to your question as to the commercial use of the calcium carbonate, the material we obtain is very pure - at least 99% $CaCO_3$. The amount of impurities it contains is very small - some F and some N of course, but the N can be eliminated. Thus one can make a filler from this $CaCO_3$. Wherever chalks of any kind are required, it can be used according to the local situation, according to the country or the products in this country which are used; and one can also use it as agricultural lime. It can be converted with ammonium nitrate solution into calcium ammonium nitrate. What one does with it depends on local circumstances.

You mentioned the question of sulphuric acid consumption in

relation to the co-product fertiliser. If one manufactures an NP
or NPK fertiliser as the co-product of the process, one obviously
uses either sulphuric acid and/or phosphoric acid, and this
phosphoric acid requires sulphuric acid. One is thus not free
from the need for sulphuric acid. In Kalk we have an integrated
works: we have phosphoric acid available, and it is possible for
us, using the pure Kampka-Nitro Process, and making other fertilisers
as well, to make whatever formulations are required by the market.
When considering where the Kampka-Nitro Process can be used, one
must consider whether one is in a highly industrialised area such
as Europe or whether one is in a developing country, and according
to circumstances one must take into account the various possibilities.
To use a Kampka-Nitro plant in conjunction with a phosphoric acid
plant is very favourable, since it permits the production of these
compound co-products. In this way, part of one's phosphoric acid
production can be used for the manufacture of high analysis ferti-
lisers with the Kampka-Nitro Process, whilst the remainder can be
used in a phosphoric acid process. But one does not need to operate
in this way. In a developing country, for example, where there is
no available sulphuric acid, one must produce a straight nitrogen
fertiliser in conjunction with the primary complex fertiliser.

As far as your question on energy consumption is concerned,
we have often tried to establish production costs (excluding raw
materials costs) for complex fertilisers, using sulphuric and
phosphoric acids on the one hand, and on the other operating
according to the Odda Process or the Kampka-Nitro Process. In
order to obtain an accurate picture, one should not consider a
part of these costs in isolation: one must view them overall,
starting with ammonia synthesis, or with the production of sulphuric,
phosphoric or nitric acids, and taking into account the plants
required for the production of secondary fertilisers. As you can
imagine, only some of the statistics used in these studies were
definite. We try to use definite values as far as possible, in
order not to deceive ourselves. But part of the figures were also
estimated. Thus, according to the number of observations, slight
discrepancies crept in, but in general we established that the
production costs of the Odda Process and the Kampka-Nitro Process,
in relation to the cost - or a part of the cost - of sulphuric acid,
were more favourable than those using the phosphoric acid process.
Overall energy consumption and maintenance costs were roughly the same.

Now that the industrial Kampka-Nitro plant has been in operation
for two years, we are currently engaged in an analysis of energy
consumption and maintenance costs in the various sections of the
plant, in order to obtain genuine figures. Production costs depend
on so many factors, and whether the Kampka-Nitro Process is suitable
or not must always be studied individually from case to case. The
cost of phosphate rock, the types of fertiliser to be produced, acid
costs, ammonia costs, the concentration of the acids used, and, in
the case of the Kampka-Nitro Process, the carbonic acid required -
all these factors play a part. Naturally, it is advantageous to use
the Kampka-Nitro Process where carbonic acid is available from, for

example, a soda works or an ammonia synthesis plant. But, in any case, one can only decide on the suitability of a process for a particular locality when one installs the process in the locality, in the local conditions, and then makes one's calculations.

I should also like to remark on certain fundamental developments, the end of which is not yet in sight or can only be partially seen. The price of ammonia - nitrogen in ammonia and nitric acid - has been continually decreasing. It has already reached very low levels. Whether it can fall any further, I do not know. Conversely, the price of sulphur has been rising for some time. How this will develop we do not know, but one can only observe that the trend of sulphur prices is still rising. And this observation is also relevant to the circumstantial consideration of which process is most suitable.

Mr. D. J. COATES (Chemical Construction (G.B.) Ltd., U.K.): This process clearly has the advantages mentioned by the two previous speakers, i.e. the significance of the rising price of sulphur and the fact that one no longer has to dispose of the calcium ammonium nitrate mixtures. Have there been any further developments in the further removal of the calcium nitrate tetrahydrate by further cooling, or by any other techniques, in order to reduce the calcium content of the fertiliser, to increase its nutrient concentration and to lower the citrate soluble P_2O_5 content ? Secondly, what type of filter do you use for the separation of the calcium carbonate ? What is the ammonium nitrate content of the calcium carbonate, and what is the actual concentration of the filtrate, including the wash water used to obtain that ammonium nitrate content ?

Dr. NEES: As far as we are concerned, we guarantee that we can get an NPK fertiliser, e.g. a 15-15-15, with about 35% of its P_2O_5 content in water-soluble form. We do not dare to guarantee more, although we know we can obtain more.

The $CaCO_3$ contains roughly 0.1% N as ammonium nitrate, but by heating it to 250°C the nitrogen content can be completely eliminated.

We used a normal rotating filter for separating the $CaCO_3$.

Mr. M. DELAPORTE (Ets. P. Linet, France) : On page 2 you say : "For all fertilisers up to the 15-15-15, the proportion of water-soluble P_2O_5 in the total P_2O_5 content of the fertilisers was put at 35% by weight". What percentage of P_2O_5 is soluble in ammonium citrate?

At what concentration is the calcium ammonium nitrate normally obtained at the tail of the process? Can this calcium ammonium nitrate be concentrated still further without any particular difficulties and without undue cost, in order to obtain a commercial grade?

On page 4, you say: "If the precipitated $CaCO_3$ is not used in the formation of calcium ammonium nitrate it can be filtered off from the NH_4NO_3 solution and processed to form a commercial product". Can you

indicate the degree of purity of the precipitated calcium carbonate obtained? What in your opinion are the possible markets for this material, apart from its use as a soil amendment?

Dr. NEES: The ammonium citrate solubility of the complex fertiliser is 98-99%. In Germany, we have the FN method - a determination in neutral ammonium citrate solution. Petermann solubility is roughly 98%. This is the same with all other complex fertilisers with this kind of plant nutrient concentration.

We concentrate the ammonium nitrate solution to 85%. At this strength, part of the solution is fed back into fertiliser production, and the remainder can be used in the production of calcium ammonium nitrate - as far as we are concerned, we do not manufacture calcium ammonium nitrate - e.g. by the Kaldenbach process. And in the opinion of Mr. Giles, who spoke to me yesterday, this calcium ammonium nitrate can perhaps also be made by the spherodizer process.

As I have already said, the $CaCO_3$ is at least 99% pure but contains some water, some ammonium carbonate, some calcium ammonium nitrate, some fluorine and sundry other small impurities. And so it can be used, for example, as a source of pure Ca, for there are relatively few natural sources of pure Ca. The other uses for $CaCO_3$ have already been mentioned.