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TECHNICAL DECISIONS AND PROBLEMS OF COMPLEX FERTILIZER PRODUCTION BASED ON AMMONIUM NITRATE

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Wide application of ammonium nitrate in agrarian sector, especially in regions with short vegetative cycle (Western Europe, Canada, Russia) and also for winter crops, has determined the scale of its production. In 2002, ammonium nitrate production in the world was 33 million tons, out of which the high density ammonium nitrate (AN HD) was 25 million tons, about 80% of the total and this is used in agriculture. The largest regions, where AN HD are produced are North America (8 million tons), Western and Central Europe (8 million tons), and the FSU-countries (11,5 million tons). Dynamics of ammonium nitrate manufacture by the main producing countries are shown in Fig.1.

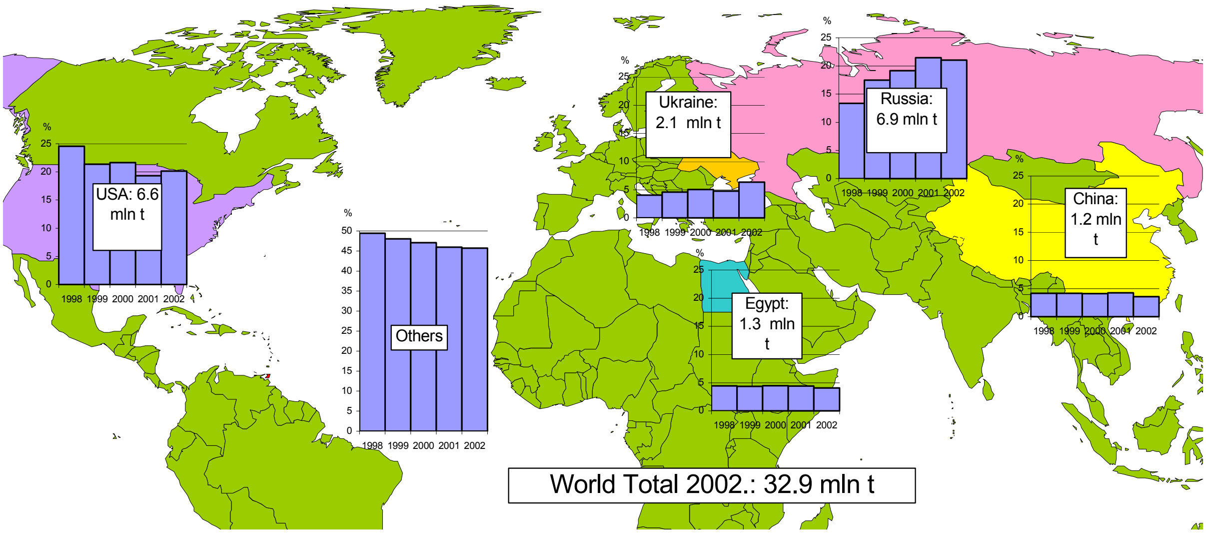

Figure 1. World dynamics of AN production 1998-2002*.*

The explosion of ammonium nitrate in the storage of a chemical enterprise in Toulouse, the reasons of it are not cleared so far and the series of terrorist acts in South-east Asia and Russia with the use of ammonium nitrate put consumers and producers of ammonium nitrate into a complicated position.

A number of countries – China, Philippines, Colombia, and Ireland imposed ban on the application of ammonium nitrate in agriculture.

On one hand, the introduction of extraordinarily strict restrictions in the of production and handling of ammonium nitrate brings to edge the closure of enterprises and leads

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to essential decrease of the use of a really valuable fertilizer and a reduction of nitrogen fertilizer choice. On the other hand, one cannot ignore the risks of uncontrolled situations that may occur at any stage of production, storage and transportation of ammonium nitrate. The risks during transportation and storage can be reduced quite efficiently by means of Directives regulating these procedures. Thus, in many countries restrictions for ammonium nitrate already exist. AN storage standards in some countries are given in Table 1. From 1st May, 2003, a Legislative Act came into force in the UK, which regulates the handling of ammonium nitrate. According to this Act it possible to import the ammonium nitrate only with the availability of detonation test certificate for each lot. The certificate must be issued not later than 60 days before the importation of the product into the country.

Table 1. Restrictions on ammonium nitrate storage in some countries

Country	Restrictions	Storage limit, tons	
		bulk	bagged
Austria	Yes	20-25	20-25
Finland	Yes	1	1
Germany	Yes	0	25-100
Greece	Yes		2.5
Italy	Yes	50	50
Netherlands	Yes	55[1]	55
UK	No	300[2]	300[3]

Notice:
[1] – manufacturers` premises only;
[2] – bulk storage at manufacturers` premises only, preferably 300t in one heap;
[3] – maximal size of stack, no limit to number of stacks, if separated by at least 1 m.

Source: Nitrogen and Methanol, №265

At present, in EC countries strict requirements for chemical and granular ammonium nitrate composition are in force, including the norms for admixtures influencing on oxidative properties of product (Table 2).

Table 2. AN quality requirements for safety handling:

№	Parameter	Unit	Requirement
1	Mass fraction, no more: - Copper - chlorine - combustible substances (in terms of carbon) - heavy metals	%	 10ppm 0.02 0.2 traces
2	pH		>4.5
3	Size distribution: < 1мм < 0.5 мм	%	 5 max. 3 max.
4	Porosity test: oil retention after two thermocycles 25-50^{O}C.	%	4 max.
5	Must pass detonation test		One or more undamaged cylinder

* - according to EC Directive 80/876/EEC, from October 2003 г. EC law relating to fertilizers №2003/2003 (Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilizers)

At present the Russian government is also preparing a number of measures to decrease the hazard when handling the ammonium nitrate.

Today AN producers are confronted with real problems, which can be listed as follows:

To switch fertilizer production on the basis of ammonium nitrate, that preserves agrochemical efficiency but with more resistance to external exposure and less explosion hazard. At the same time, the amount of investments required for upgrading the production facilities, which not the all companies can afford, is limited. The aim is to preserve technical-and-economic figures obtained during the production of ammonium nitrate, namely: working time fund, resource intensity, power consumption, and equipment maintenance intensity. The environmental conditions related to production should not become worse. However, the increase of safety level for production and the product obtained remains the main criterion.

Table 3 shows classification of AN based fertilizers adopted in the world in accordance with their hazardous properties, i.e. high oxidation aptitude, tendency to detonation, self-decomposition upon heating. As appears from this table, two main indices constitute the basis of classification: ammonium nitrate content and also the combustible substances which is suitable from the formal point of view, but this not always reflects a potential danger of the product manufactured on the basis of ammonium nitrate. Thus, in the general classification UN/ADR there is no reference of mixtures (ammonium nitrate with chemically active additives of >90% AN and <0.2% combustible substances).

The following additives with decreasing level of potential danger of AN-containing fertilizers, used:

Carbonate-containing compounds of natural and recycling origin (chalk, calcium carbonate, dolomite);

Potassium-containing substances (potassium chloride, potassium sulphate);

Substances containing similar cation – ammonium: ammonium sulphate, ammonium orthophosphate and polyphosphate;

Other ballast substances (gypsum, phosphogypsum , etc.).

Table 3. Ammonium nitrate classification			
Type/UN Classification/ General Description	**Chemical composition**	**Hazardous Properties**	**Principles of Safety**
Fertiliser Type A **UN/ADR Class 5.1** Ammonium nitrate and ammonium nitrate-based high nitrogen fertilisers. High density, low porosity	**A1** Mixtures of ammonium nitrate with added matter which is inorganic and chemically inert towards ammonium nitrate. > 90% AN and <0,2% of total combustible material > 70% but < 90% AN and < 0,4% of total combustible material **A2** Mixtures of ammonium nitrate with calcium carbonate and/or dolomite with >80% but < 90% and < 0,4% of total combustible material **A3** Mixtures of ammonium nitrate/ammonium sulphate with >45% but < 70% AN and < 0,4 % combustible material **A4** Mixtures containing nitrogen/phosphate or nitrogen/potash with >70% but < 90% AN and < 0,4 % of total combustible material	– Oxidizing – Non-combustible – May decompose – High resistance to detonation	– avoid contamination – avoid sources of fire/heat – avoid sources of explosion – avoid confinement
Fertiliser Type B **UN/ADR Class 9** NPK (nitrogen-phosphorus-potassium compounds) fertilisers	Non-segregating mixtures containing: – nitrogen (nitrate)/phosphate or nitrogen (nitrate)/potash or –complete fertilisers containing nitrogen (nitrate)/phosphate/potash with < 70% AN and < 0,4% of total added combustible material, – or with < 45% of AN with unrestricted combustible material	– decomposes when heated – self-sustaining decomposition (continues even when heat source is removed) – **Note:** If the UN Trough Test shows that a Type B fertilizer does not have a risk of self-sustaining decomposition, the fertiliser is classified as Type C.	– avoid contamination – avoid sources of fire/heat – avoid confinement
Fertiliser Type C **Unclassified** Fertilisers not capable of self-sustained decomposition, e.g., ammonium nitrate mixtures with calcium carbonate, dolomite, ammonium sulphate, or potash (depending on nitrogen content)	– Mixtures of AN with calcium carbonate and/or dolomite containing < 80% AN and < 0,4% total combustible material – Mixtures of ammonium nitrate/ammonium sulphate containing < 45% AN and < 0,4% total combustible material – Fertilisers conforming to the Type B composition and which do not exhibit the property of self-sustaining decomposition	– decomposes when heated – decomposition stops when heat source is removed	– avoid sources of fire/heat – avoid confinement
Industrial Grade Explosive **UN/ADR Class 1.** Low density, high porosity prills - combined with fuel oil	– Ammonium nitrate (AN) with more than 0,2 % combustible materials – AN- fertilisers with sensitivity greater than ammonium nitrate with 0,2 % combustible materials – Explosive preparations of AN	– detonates after rapid decomposition (deflagration to detonation) – detonates due to external shock or heat source	– avoid contamination – avoid sources of explosion – avoid sources of fire/heat – avoid confinement

Table 4: Results of qualitative analysis of efficiency of the use of the above-stated additives for manufacturing AN – based fertilizers.

№	Additive	Balance	
		Advantage	Disadvantage
1	Chalk, dolomite	1.It admits the regulation of chalk; AN ratio within wide range reducing AN content up to 60-75 %. 2.The manufacture of agrochemically valuable fertilizers containing structure former and a deoxidant of soil alongside with the basic nutrient agent. 3.Cheapness and availability of a material (scale manufacture of natural and conversion chalk and also dolomite)	1. It requires an appropriate process equipment and it practically excludes the use of standard equipment for manufacture of AN. 2.Weak influence of carbonate containing additive as a mechanical component on distinctive properties of AN (thermostability, conditions of transition of allotropic modifications) 3.Necessity of the rigid control over the impurity content of carbonate containing component. 4.The low content of the basic nutrient agent limiting economic efficiency of its use.
2	Potassium containing additives (potassium chloride, potassium sulfate)	1.Possibility to manufacture high-grade NK-fertilizers with high total content of nutrient agents (35-55 %) 2.Availability of potassium containing raw materials in the market in view of development of world trade	1.Necessity of an appropriate process equipment for the unit to mix AN melt and powder like K-containing material. Normally, when using KCL the significant corrosion factor is to be taken into account. 2.The presence of a considerable amount of the chlorine being the component, strengthening dangerous properties of AN and the content of which is limited in AN 3.Relanively narrow market niche of NK-fertilizers used for limited number of agricultural crops (tobacco, rice, etc.).
3	Phosphorous containing additives (phosphoric acid, pure phosphoric salts)	1. Possibility of preservation of standard process flow diagram with the construction of additional unit at reasonable cost to receive and to feed of phosphorous containing solution into the system. 2.Formation of appropriate salts with anisotropic crystal lattice with neutralization by ammonia and essential change of distinctive properties of AN. 3.Possibility of the increase of nutrient agents ($N+P_2O_5$) due to the use pure phosphorous containing components and the increase of agrochemical value of fertilizers with the change of concentration N of 29-32 % and P_2O_5 – 12-5 %. 4.Improvement of physical and chemical properties of a product (reduction of hygroscopicity, tendency to compaction and caking)	1. Increase of load on evaporation equipment and, that results in partial loss of production efficiency of the equipment; reduction of period between the washings, growth of shutdowns 2. 2.Increase of corrosive attack on structural material of the equipment.

Thus, on a complex of target criteria of positive influence on properties of ammonium nitrate and commercial value a potential number of fertilizers on the basis of AN can be presented as follows:

NP fertilizers with water-soluble phosphorus> 5.0 % P_2O5

NK-fertilizers with potassium additive of 30-60 %.

Calcium ammonium nitrate (CAN), calcium magnesium ammonium nitrate;

Other mixtures with ammonium nitrate (ammonium sulfate, etc.).

Some Russian manufacturers has begun to manufacture nitrogen–phosphate fertilizers as alternative to traditional ammonium nitrate. A number of manufacturers have conducted tests, and some manufacturers have begun industrial production of nitrogen-phosphate fertilizers at the unit for manufacture of ammonium nitrate.

The most widespread production of ammonium nitrate in Russia is carried out at AS - 72 unit, its basic characteristics and parameters for quality of production are given in Table 5.

Table 5.

№	Parameter	Unit of measurement	Value
1	Production capacity of AS – 72 - design capacity - achieved production capacity	t/day	 1360 1400
2	Granulator type		Acoustic
3	Main actual AN indices		
3.1	Total nitrogen	%	34.5
3.2	Free water (method of drying)	%	0.2
3.3	Mass fraction of granules: - <1 mm - from 1 up to 4 mm - > 4 mm	%	 3 95 2
3.4	Hardness	MPa	1
3.5	Caking		0

The first enterprises which have mastered the industrial production of NP fertilizer on the basis of AN in 2001 as P_2O_5 containing additive used WPA (Fig.2). In the process of operation there were significant difficulties, the most serious of them are as follows:

- A significant corrosive attack of fluorine contained in phosphoric acid, especially on the border of phases liquid - gas, as a result of it some equipment has been replaced with new ones made of steel resistant against influence of this element;
- Problems related to clogging and incrustration of the process equipment, owing to a significant amount of impurities in phosphoric acid: sulfates, cations of metals: iron, aluminium, magnesium, calcium.

As a result of the difficulties, the increased quantity of shutdowns required for washing and repair of the equipment the production capacity of the system has reduced by more than 2 times in comparison with operation on pure ammonium nitrate.

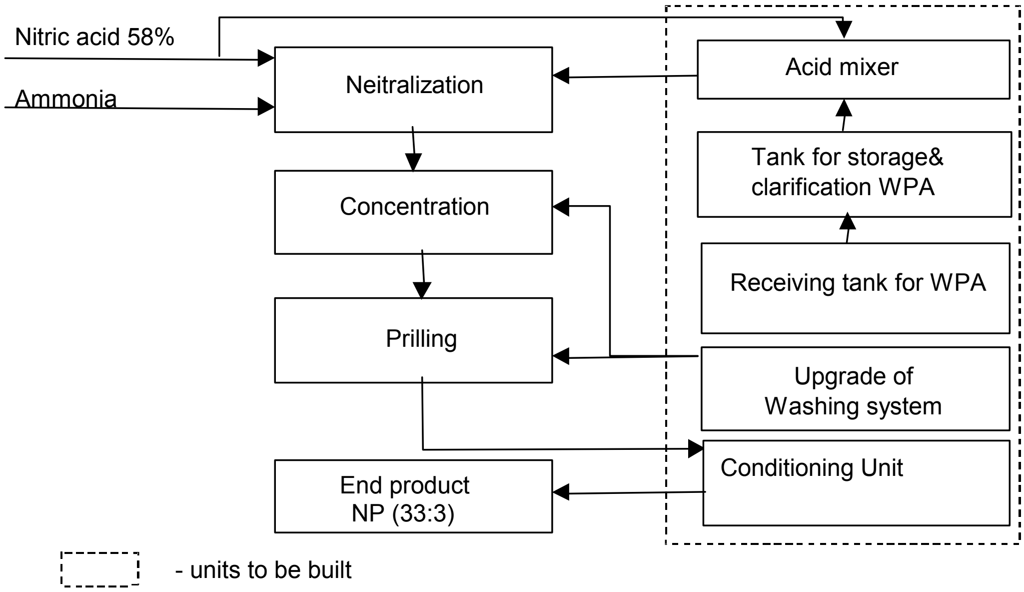

Figure 2. Principle schematic diagram for NP production (33:3) with WPA as additive.

In 2003 the manufacture NP (32:6) fertilizer was started. NP solution produced by phosrock - nitric acid attack from NPK production that has preliminary purification was used as a phosphorous component (Fig.3). In the process of production, this enterprise ran across similar problems as producers who used WPA as phosphorous additive, in particular, considerable difficulties were linked with evaporation equipment. In order to provide a stable process of granulation the acoustic granulators foreseen at the initial design have been replaced with granulators of rotating type. In spite of the entire efforts the enterprise failed to achieve the capacity to provide the efficiency of NP fertilizers production. At present the enterprise continues to carry out the work aimed at perfecting the fertilizer production based on ammonium nitrate with the use of standard unit.

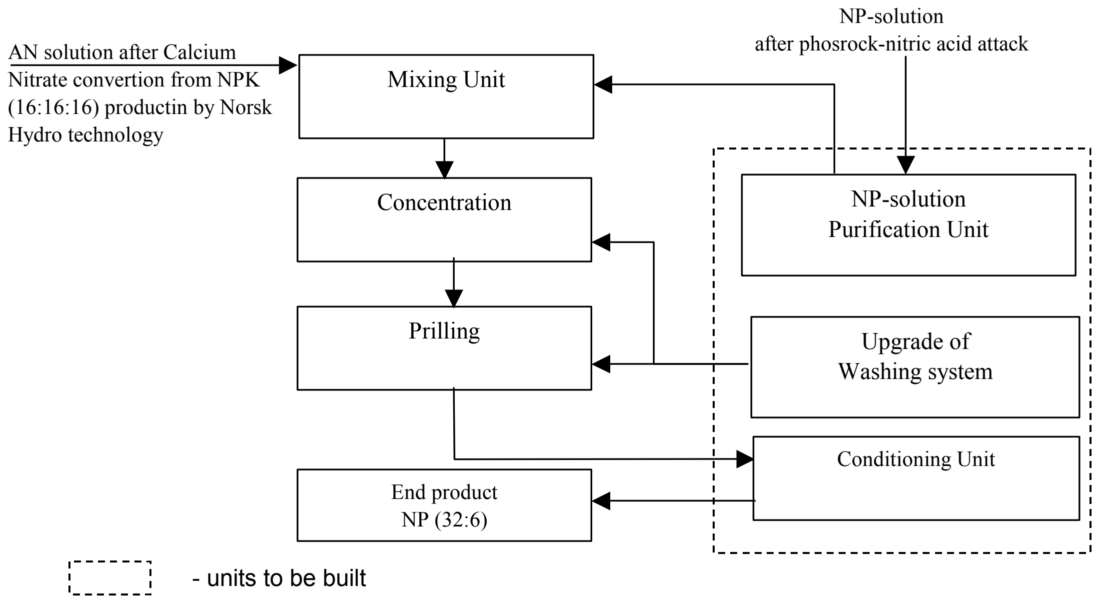

Figure 3. Principle schematic diagram for NP production (32:6)

In the second half of 2003 one of the Russian enterprises commissioned the production of NP fertilizer (27:5). This fertilizer has been obtained on the basis of AN melt, MAP solution and ammonium sulfate. Unlike the above said products obtained at technological system AS-72 (the unit for AN production), this fertilizer is manufactured at the unused NPK production facilities with the use of Drum-Granulator-Dryer apparatuses.

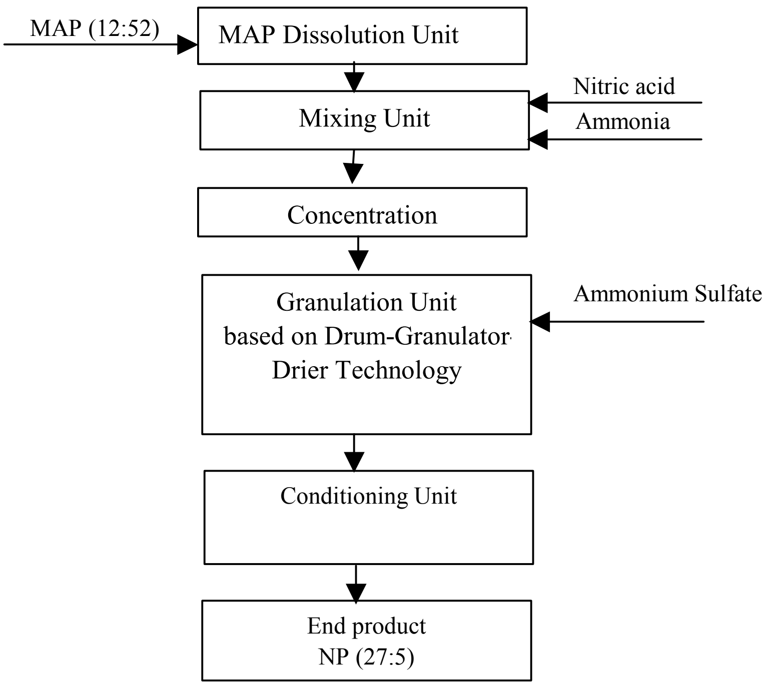

Figure 4. Principle schematic diagram for NP(27:5) production with the use of MAP as P_2O_5 additive

We will discuss in more detail about the operation of AN plant situated in the north-west of Russia which is today the only Russian producer of AN based fertilizers operating steadily at the rates close to the capacity achieved during the production of HD AN. The decision to start the manufacture of less hazardous AN based fertilizer for handling was taken in the beginning of 2002 after the analysis of the situation developed after explosion in France and series of terrorist attacks with usage of ammonium nitrate worldwide, including Russia. Having conducted the research and a series of laboratory tests an option have been selected for the manufacture of NP fertilizers with phosphorous content more than 5 %.

The key moments when preparing the commissioning of industrial NP production on the commercial basis are as follows:

- Determining the type of phosphorous containing additive;
- Determining the physical and chemical properties of intermediate flows and the finished product;
- Determining the inlet for phosphorous containing flow to prevent local supersaturations, the selection of optimum temperature and concentration conditions to operate the process, etc.;
- Selection of additional equipment for the main AN-process and for facilities for receiving, storage and feeding of phosphorous containing additive.

The phosphorous containing additive has been selected owing to the following conditions:

- Maximum content of target component P2O5 and accordingly the minimum content of water;
- Absence of a solid phase and the minimum possible content of corrosion active impurities (fluorides, chlorides) and of the reactive impurities resulting in sediment;
- Low freezing temperatures or metastability at cooling.

Besides, the phosphorous-containing additive should have commercial availability. After thorough selection and test investigations a liquid phosphorus containing additive (LPCA) has been selected as a phosphorous containing additive manufactured in the required industrial amounts at the nearby enterprise. Its main specifications are given in Table 6.

Table 6. Basic physical and chemical specifications of LPCA.

№	Parameter	Unit of measurement	Value
1	Appearance	%	Transparent liquid without mechanical inclusions
2	Total mass P_2O_5	%	37
3	Total mass of water	%	40
4	Freezing point	^0C	-20
5	Density at 20^0 C	g/cm3	1.44
6	Viscosity at 20^0 C	mPa*s	80
7	Total mass of fluorine	ppm	900
8	Total mass of chlorine	ppm	30
9	Total mass of cationic impurities in terms of oxides	%	1.2

Laboratory and trial tests conducted have revealed a technological applicability of LPCA in process.

During trial tests the optimum inlet for P2O5 has been selected and the additional equipment has been chosen (Fig.5).

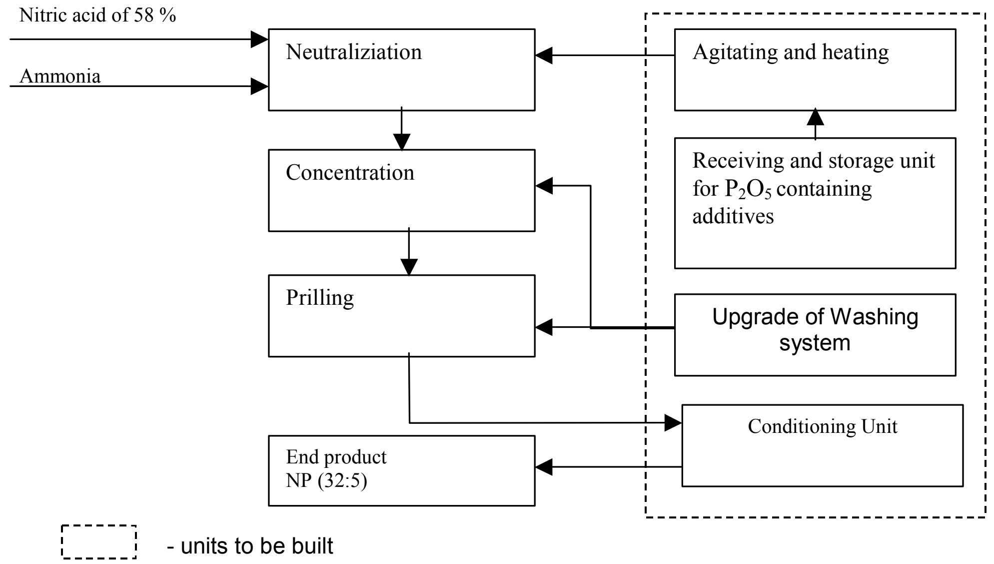

Figure 5. Principle schematic diagram for manufacture of NP-fertilizer with the use of APP as P2O5 additive.

The main task when feeding a phosphorous containing flow was the provision of turbulent mode of agitation of flows to prevent local supersaturations and the formation of residues and deposits inside the equipment and pipelines. The chemistry of the basic processes taking place at mixing of flows are as follows:

NH4+ +H2PO4-→NH4H2PO4 (1)
Mg2++ HPO42-+ 3H2O→MgHPO4*3H2O (2)
Mg2++NH4++PO43-+ H2O→MgNH4PO4*H2O (3)
(Al3+, Fe3+) + NH4++ HPO4-→(Al, Fe) NH4 (HPO4) 2 (4)

Thus, there exist the real danger of clogging the equipment, especially it concerns reactions (2, 3) when switching over from manufacture of standard ammonium nitrate with the use of magnesium additive as volume coating to the manufacture of NP fertilizers.

Therefore, when preparing to switch over to production of NP fertilizer it is necessary to flush thoroughly the equipment and pipelines in order to remove residues of a magnesite. The unit to provide coating is added to the existing equipment, lilamin is preferable as coating agent.

The availability of ammonium dihydroorthophosphate affects crystallization and of modification transitions temperatures, in particularly, the forms I – II, which is important for understanding the kinetic of crystal formation when cooling AN melt (Table 7).

Table 7. Temperatures of crystallization and modification Transition I-II.

Parameter	Unit	AN	NP(32:5)
Temperature at beginning of crystallization	^{0} C	169	160
Temperature at phase transition I-II	^{0} C	125	117

The above data show that NP fertilizer is characterized with overcooling that increases crystallization time about 0.5 sec. Taking into account that the height of prilling tower is limited it may become an important factor. The restrictions in the change of temperature- velocity profile of cooling air in prilling tower and the height of fall there appear certain problems (especially in summer time) in the formation of granule of NP fertilizer. An additional erection of air cooling unit can solve this problem.

The basic parameters of process and comparative specifications of NP & AN are given in Tab.8.

Table 8

No.	Parameter	Unit	Product	
			AN	NP
1	Production capacity achieved	t/day	1400	1100
2	Ratio (volume) between the flow of AN solutions and P_2O_5 containing additive		-	12
3	Flushing life	Days	90	7
4	Conditioner		magnesite	Lilamin
5	Type of conditioning		Volume	Coating
6	Mass fraction of components (typical) Nitrogen (N) including: - ammonium; - nitrate Phosphorous (P_2O_5) water soluble		 34.4 17.2 17.2 	 32.3 17.2 15.1 5.2
7	Mass fraction of free water	%	<0.3	<0.5
8	Granulometry: Size distribution: <1mm <2mm From 2 to 4 mm >4 mm	%	 3 15 80 2	 1 6 90 3
9	Hardness	MPa	>0.8	3.2
10	Density Bulk density Compact packing	Kg/m3	 0.99 1.026	 1.04 1.086

Relative comparative technical and economic analysis of different methods for NP (32:5) manufacture at standard unit AS-72 used for manufacture ammonium nitrate (NP manufactured with LPCA is taken as the basis) are given in Table 9.

Parameter	P_2O_5 containing additive		
	LPCA	NP solution produced by phosrock-nitric acid attack	Phosphoric Acid
Raw materials	0.80	0.84	0.89
Energy	0.06	0.06	0.06
Others	0.03	0.03	0.03
Fixed costs	0.11	0.22	0.13
Total	1.00	1.15	1.11
Capital investments	1.00	0.80	2.50

Table 9.

This table shows that the manufacture of NP (32:5) with LPCA additive has an advantage because of low content of admixtures in phosphorous containing additive. It allows achieving the maximum possible output of production compared to other options with less capital investments, first of all, owing to the use of less expensive structural materials.

Advantages and disadvantages of all above methods for NP manufacture containing about 90% of ammonium nitrate are given in Table 10.

Table 10

P_2O_5 containing additive	Advantages	Disadvantages
Phosphoric acid	Simplicity in equipment and its arrangement, relatively low capex.	High corrosion attack of P_2O_5 containing additive on equipment. Decrease in production capacity of evaporation equipment due to large build-up of scale on its surface. The use of corrosion resistant materials for storage of phosphoric acid Big decrease in production capacity of the system at P_2O_5 increase in fertilizer.
Purified NP solution produced by phosrock –nitric acid attack	The use of own intermediate products for NP manufacturing	Decrease in production capacity of evaporating equipment due to large build-up of scale on its surface.. High capital costs to purify NP solution produced by phosrock – nitric acid attack. High corrosion attack by P_2O_5 containing additive on equipment.
MAP (12:52)	Low capital costs required	The use of facilities destined for other products.
LPCA	Lower capital costs compared to operation on phosphoric acid. Small content of cation impurities that extend the flushing life of equipment compared to operation on WPA and NP solution. Lower level of fluorine without negative impact on structural materials of AN production unit.	Limited choice of LPCA producers. Decrease in production capacity.

Some Russian producers began the manufacture of NK fertilizers and CAN based on ammonium nitrate and in some cases using granulation production capacities destined for other product. However, AN-based granulated products with the use calcium carbonate or potassium chloride as a component under other equal conditions (moisture, size distribution, conditions for granulation) concede to NP fertilizer in respect to aptitude to detonation. Physico-chemical reasons for it are as follows:

1) The lower dispersion of fine crystalline potassium chloride or chemically precipitated calcium carbonate that determine the less number of contacts with crystallites of ammonium nitrate and less hardness of granules accordingly (Table 11).

Table 11. Typical characteristics of potassium chloride and calcium carbonate used for manufacture of fertilizers.

No.	Parameter	Unit	Potassium chloride	Calcium carbonate
1	Size distribution of product: Share of fraction: <0.0045mm <1mm 1-4mm	%	 25 75	 >99
2	Method		Mechanical (crushing)	Chemical (precipitation)

2) Less adhesion affinity of ammonium nitrate to potassium chloride prepared by mechanical method (crushing, grinding) or to calcium carbonate precipitated chemically.

3) Mechanical method of CaCO3 or KCl distribution in AN melt causes non-uniform distribution of components and subsequently it leads to loose contacts in granule, increase of porosity and reduction of granule strength and also to secondary formation of fines.

4) Non-uniform crystallization of ammonium nitrate during the cooling in granulation tower that also promotes the formation of channels, cavities, pits in granule volume and reduces its hardness.

5) Table 12 shows comparative data of detonation test of high density ammonium nitrate and NP fertilizer. The test has been conducted in accordance with Directive 80/876EEC Commission of EC. Prior to detonation the sample was subject to 5 temperature cycles from 25 – 500 C.

6) **Table 12**

№	Parameter	Unit	Product	
			AN	NP (32:5) with LPCA
1	Bulk density	kg/m^3	990	1014
2	Lead cylinder damage: 1 2 3 4 5 6	%	 47 40 31 3 0 0	 45 29 2 0 0 0
3	Undamaged pipe fragment	mm	340	495

Tests conducted have proved a considerable reduction of detonation properties of NP fertilizer compared to ammonium nitrate. The data obtained for NP fertilizer (32:5) are similar to properties of NPK (3 –4 undamaged cylinders depending upon NPK grade) during the test.

The decrease of NP tendency to detonation is determined by a number of factors:

Of the decrease of geometrical dimensions of crystallites providing their more compact package and anisotropy of properties in the granule (Table 13). The latter is a distinctive feature of granulated NP fertilizer obtained in the process of chemical interaction with uniform distribution in mass. The presence of ammonium phosphate interrupts uniformity of AN properties and propagation of detonation wave.

Table 13 Parameters of AN and MAP crystalline lattice

No.	Crystal type	Parameters of crystalline lattice, nm			Specific volume of elementary cell, nm^3
		a	b	c	
1	Ammonium nitrate	0.575	0.575	0.495	0.155
2	Monoammoniumphosphate	0.753	0.753	0.754	0.427

The confirmation of more compact package is higher density of NP fertilizer in comparison with standard AN at comparable granulometric composition and moisture.

Table 14.

No.	Parameter	Unit	Product	
			AN	NP (32:5)
1	Original density	$кg/m^3$	1.725	1.910
2	Size distribution of product <1mm; 1-4mm; >4mm.	%	 3 95 2	 1 96 3
3	Free water percentage	%	<0.3	<0.5
4	Total porosity of product including share of macropores	cm^3/g	0.06 0.04	0.04 0.004

Of the change of a porous structure of granules that is expressed both in general decrease of a porosity and in the decrease in part of macropores in general porosity of granules. It is known that structure of ammonium nitrate pores manufactured at typical large-capacity plants is characterized by bimodal distribution of pores with predominance of macropores (> 60 % of total porosity) at general porosity about 0.06-0.08 cm^3/g. The addition of ammonium orthophosphates defines the decrease of general porosity and the share of macropores up to 10 %, making a granule more homogeneous by structure.

The phosphorous containing additive in the form of ammonium dihydrophosphate and admixtures (Fe, Al) at cooling of NP fertilizer melt in prilling tower behaves like a structure-former (crystallization temperature of $NH_4H_2PO_4$ and accordingly orthophosphates Fe, Al is higher than the temperature of ammonium nitrate). Ammonium dihydrophosphate in the surface layer subjected to cooling air forms a primary crystalline carcass the cavities of which are filled with crystallizing ammonium nitrate. Taking into account the high adhesion of AN melt to crystallites of ammonium dihydrophosphate the more compact structure of granule is formed. Besides, the formation of primary surface film allows to reduce a gradient of temperatures on the cross-section of granule, to reduce effect of compression at crystallization of ammonium nitrate and the formation of cavities in the volume of granule. The availability in the volume of AN granule of crystallization centers in the form of $NH_4H_2PO_4$, $FePO_4$, $AlPO_4$ defines the dislocation mechanism of grain formation with interruption of chain which ensures the growth of phase contacts of crystallites at compact package. As a result of it the formation of numerous inter-crystallite contacts provides mechanically a strong anisotropic structure with distributed on volume and compensated mechanical strains.

The lack of formation of orthorombic Form III and Transition II – III, followed by radical rearrangement of crystal lattice and accordingly, by thermo-mechanical strains in granule volume, caused during further mechanic operations, the appearance of fine fraction with developed external area. The latter presents danger since it can cause a detonation wave.

The replacement of Transition II – III with Transition II – IV stabilizes a granulated product on the basis of ammonium nitrate as far as the aptitude to caking and to detonation is concerned. Subsequent temperature fluctuations in the range of thermo-dynamically stable existence of modification IV do not cause the changes in crystalline lattice and qualitative change in properties of product including the aptitude to detonation. In case of normal ammonium nitrate a lower level of temperature Transition III –IV (32.3^0 C) defines the structural changes of product and its properties under conditions of high temperatures, which may occur during storage and transportation.

Thus, NP among other equal conditions is more stable compared to normal AN.

Summing up the results obtained and comparing the properties of products manufactured on the basis of ammonium nitrate with various phosphorous containing additives we may underline the following points:

- Russian producers search energetically for ways to increase the safety when handling the ammonium nitrate by substituting a portion AN with components that decrease an aptitude to detonation;
- Higher degree of safety in the field of trade is ensured by a number of factors with the changed physico-chemical properties of product, improved granulometric composition and packed that conform to EC Directives;
- Commercial advantages of new products is determined by two nutrient components, preservation of high concentration of N required for countries with moderate climate and short period of vegetation, conservation nitrate base in fertilizers, a phosphorous content entirely in active and water-soluble form, practical absence of unwanted impurities;
- Possibilities to use the existing AN equipment for NP production, reasonable capital costs required to switch over to manufacture of fertilizers with various types of additives;
- Reaching high operation rates for production capacities;

Out of the options that have been discussed in the report, the most preferable as far as economic parameters, capital investments, operating rates of production capacities are concerned, is the manufacture of NP fertilizer with the use of LPCA fertilizers as phosphorous-containing additive.

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