International Fertilizer Industry Association

IFA Technical Conference

New Orleans, Louisiana, USA
1-4 October 2000

PRESSURE-TYPE NITROGEN SOLUTION PRODUCTION USING UAN FACILITIES*

A. Laurinaitis, A. Ancuta, A. Senuta, A. Šostakas
SC “Achema”, Lithuania

RESUME

Des engrais liquides d’azote sous la pression sont bien convenables à utiliser au lieu de l’ammoniaque, largement utilisé jadis dans l’agriculture de l’ancienne l’Union soviétique. L’autre application s’appuie sur la production NPK en utilisant le procédé de granulation à vapeur. Toutes les deux encouragent la production de ces engrais pour nécessités nouvelles du marché régional de Lituanie. Pour cet but rééquipement d’UNA sur place de SA ,,Achema,, est achevé.

L’article présenté examine des aspects technologiques et les résultats de cet rééquipement d’UNA en procédé périodique ainsi q’en continuel pour la production de quantités limitées d’engrais liquides d’azote sous la pression jusque 0,69 kg/cm^2 abs.

Egalement les propriétés physiques de diverses sortes du produit et les paramètres du procédé sont examinés. Ainsi la présentation fournie de donnés expérimentaux nécessaires à combler la description du système quaternaire l’eau – ammoniac – nitrate d’ammonium – urée sous l’aspect de pression de la phase gazeux dans le vaste intervalle de sortes du produit. Les donnés obtenus conviennent à déterminer la relation juste d’urée/nitrate d’ammonium et l’ammoniac libre pour produire des engrais d’azote ayant la pression de la phase gazeuse au-dessous de 0,69 kg/cm^2 abs. Ces engrais peuvent être utiliser directement dans l’agriculture ainsi que pour la production des engrais solides. De plus, cet article présente des données thermochimiques sur l’ammonification et la chaleur spécifique de certaines sortes du produit.

SUMMARY

Pressure-type nitrogen solutions not exceeding 0.69 kg/cm^2 abs. have auspicious conditions to be applied in Baltic States instead of ammonia water as one widely used in FSU agriculture. Another application is based on their usability for NPK production through steam granulation and/or fusion blending. It is a reason to endeavour of low-pressure ammonia solution grades implantation into regional market under new conditions. UAN facilities are used for above-mentioned purpose on the site of SC “Achema” (Lithuania).

This paper presents technical aspects of UAN facilities conversion into pressure-type nitrogen solution’s batch installation with limited capacity. Further development into flow process and its control are described.

Physical-chemical properties of grades to be produced as well as process parameters are considered too. Given paper represents also a case study aimed to fulfill the data lack on the quaternary system water-ammonia-ammonium nitrate-urea and to predict vapor pressure

*Production des solutions d’azote à pression limitée en utilisant l’équipement de la production des engrais liquides d’urée - nitrate d’ammonium (UNA) over the whole range of pressure-type nitrogen solutions. The data obtained enable to check a composition in proper proportions of urea/ammonium nitrate and free ammonia suitable to produce low-pressure (below 0.69 kg/cm^2 abs.) nitrogen solutions for use in ammonization - granulation plants as well as for direct application. Thermo chemical data concerning ammonization and heat capacity for several solutions are presented too.

1. INTRODUCTION

As during the oncoming years bigger consideration will be given to the domestic market, SC “Achema” is going to expand further its activity on the terrain of Baltic States in respond to fertilizer market changes. Mostly traditional and widely used fertilization corresponds to one by ammonia water, today being almost entirely abolished in the agriculture of Lithuania. The main requirements for reviving of liquid fertilizer utilization at the region under consideration are linked with the nitrogen content and ammonia partial pressure.

Higher nitrogen content in liquid and less ammonia in gaseous phase stimulates the usage of nutrient in form of nitrate and ammonia nitrogen. Thus is the reason for partial replacement of UAN by limited pressure nitrogen solutions based on the system of water - ammonia – ammonium nitrate, because of the relatively high content of amide nitrogen in diverse grades of UAN. Fertilizer processing through fusion blending is another reason for the production of pressure – type nitrogen solution in Lithuania. This one stipulates the content of the solution in terms of the concentration of amide nitrogen and total pressure requested below 0.69 kg/cm^2 abs.

The enterprise “Liquid fertilizers”, established by SC “Achema” in August, 1994, produces divers grades of liquid NPK as well as large quantity of UAN solution. The latter enables to use UAN facilities for limited production of stipulated pressure–type solution, containing mainly nitrate and ammonium nitrogen. “Achema’s” designers projected in collaboration with staff of enterprise “LF” the pilot plant for production of requested grades of pressure–type nitrogen solution. The project was preceded with scientific investigation, performed by “Achema’s” lab. and Kaunas university of technology, in order to fulfill the data lack on the quaternary system water – ammonia – ammonium nitrate – urea, to predict vapor pressure over the whole range of pressure–type nitrogen solutions and supply project–group with thermo-chemical data indispensable for designing. Below essential results are submitted saving usual numbering code for the grades of such solution: the first number in N_t(A-AN-U) is the percentage of total N in tenths of percent; the number in parentheses are the percentages of free ammonia, ammonium nitrogen and urea respectively.

2. CASE STUDY

Tables 1, 2 present the composition and main physic-chemical properties of samples investigated. As it follows from these data crystallization temperature highly depends on ammonia concentration. Consequently, seasonal production of appropriate grades is desirable.

Table 1
Composition (%) and physic-chemical properties of pressure-type liquid fertilizers produced by ammonization of ammonium nitrate (AN) solution

Item No*	Grades	AN	Free NH_3	H_2O	Total N	Gaseous phase pressure, p_{20}, kg/cm^2	Boiling point at 760 mmHg, ^oC	pH	Density d_t, g/cm^3	Crystallization temp., ^oC
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
$1_{0,09}$	243(3-63-0)	61,6	3,3	35,1	24,3	0,10	80	10,0	$1,232_{18,7}$	+11,9
$2_{0,21}$	282(8-62-0)	62,2	7,8	30,0	28,2	0,19	67	10,4	$1,204_{18,2}$	+10,9
$3_{0,35}$	325(13-62-0)	62,0	13,2	24,8	32,5	0,33	50	10,8	$1,164_{18,5}$	+5,5
$4_{0,46}$	361(17-63-0)	63,1	17,1	19,8	36,1	0,59	34	11,1	$1,128_{18,8}$	-4,8
$5_{0,63}$	410(22-65-0)	64,7	22,4	12,9	41,0	0,87	24	11,3	$1,102_{18,6}$	-15,7
$6_{0,43}$	349(15-65-0)	65,4	14,7	19,9	34,9	0,43	43	10,8	$1,150_{18,7}$	+3,7
$7_{0,27}$	307(9-67-0)	67,3	8,7	24,0	30,7	0,22	63	10,3	$1,224_{18,7}$	+21,1
$8_{0,41}$	346(13-69-0)	68,6	12,9	18,5	34,6	0,38	47	10,7	$1,189_{18,6}$	+15,1
$9_{0,55}$	381(17-68-0)	68,3	17,3	14,4	38,1	0,62	33	11,1	$1,159_{18,5}$	+6,2

*Index of Item No represents relation $NH_3/(NH_3+H_2O)$ or degree of ammonization

Table 2

Composition (%) and physic-chemical properties of pressure-type liquid fertilizers produced by ammonization of ammonium nitrate (AN) – urea (U) solution

Item No*	Grades	Free NH_3	AN	U	H_2O	Total N	Gaseous phase pressure, p_{20}, kg/cm^2	Boiling point at 760 mmHg, ^oC	pH	Density d_t, g/cm^3	Crystal-lization temp., ^oC
1	**2**	**5**	**3**	**4**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
$1_{0,47}$	408(27-6-35)	27,4	6,5	34,9	31,2	40,8	>1,20	12	13,4	$0,986_{3,5}$	+6,4
$2_{0,43}$	391(25-6-36)	25,0	5,6	36,1	33,3	39,1	>1,20	11	12,9	$1,005_{8,2}$	+6,3
$3_{0,47}$	405(22-18-36)	21,9	18,4	35,0	24,7	40,5	1,13	17	12,4	$1,045_{9,1}$	+3,9
$4_{0,39}$	389(18-26-32)	18,1	26,1	32,5	23,3	38,9	0,80	27	11,6	$1,105_{9,4}$	+3,7
$5_{0,46}$	395(14-36-33)	13,8	36,5	33,5	16,2	39,5	0,59	35	11,3	$1,164_{11,5}$	+9,1
$6_{0,49}$	389(13-49-24)	13,4	48,7	23,7	14,2	38,9	0,50	40	11,0	$1,184_{10,5}$	+0,6

1	2	5	3	4	6	7	8	9	10	11	12
$7_{0,58}$	398(11-59-22)	10,6	59,3	22,5	7,6	39,8	0,41	47	10,8	$1,237_{8,4}$	+1,3
$8_{0,49}$	378(12-60-14)	12,4	60,2	14,2	13,2	37,8	0,45	43	10,9	$1,210_{7,5}$	+2,9
$9_{0,46}$	370(14-60-9)	14,4	59,9	9,2	16,5	37,0	0,49	41	10,9	$1,190_{7,5}$	+2,8
$10_{0,45}$	360(16-61-3)	15,9	61,5	3,1	19,5	36,0	0,55	37	11,1	$1,159_{6,8}$	+2,1
$1_{0,42}$	387(25-7-35)	24,8	6,7	34,9	33,6	38,7	1,0,1	21	12,6	$0,985_{18,7}$	-2,0
$2_{0,40}$	379(21-11-36)	21,2	11,1	36,1	31,6	37,9	0,94	24	12,3	$1,008_{18,7}$	-1,7
$3_{0,32}$	352(14-21-35)	14,3	21,1	35,0	29,6	35,2	0,61	35	11,5	$1,103_{21,5}$	+2,9
$4_{0,37}$	371(13-34-32)	12,7	33,6	32,5	21,2	37,1	0,48	42	11,1	$1,146_{18,6}$	-1,8
$5_{0,42}$	386(10-43-33)	9,7	43,4	33,5	13,4	38,6	0,37	47	10,3	$1,199_{18,7}$	+5,7
$6_{0,30}$	345(9-46-24)	9,0	46,2	23,7	21,1	34,5	0,34	>50	10,3	$1,213_{18,7}$	-2,0
$7_{0,29}$	341(9-47-22)	9,0	46,8	22,5	21,7	34,1	0,29	>50	10,5	$1,249_{18,5}$	+0,8
$8_{0,35}$	348(9-59-14)	9,5	58,6	14,2	17,7	34,8	0,33	>50	10,6	$1,217_{18,6}$	+2,4
$9_{0,32}$	333(10-59-9)	10,3	58,9	9,2	21,6	33,3	0,36	47	10,6	$1,196_{18,5}$	+1,3
$10_{0,39}$	343(14-62-3)	13,6	62,0	3,1	21,3	34,3	0,39	45	10,8	$1,167_{18,7}$	+0,1
$1_{0,33}$	337(21-3-33)	21,0	3,1	33,5	42,4	33,7	0,54	37	12,2	$1,025_{18,5}$	+5,3
$2_{0,29}$	323(16-10-34)	16,1	10,0	33,9	40,0	32,3	0,50	40	12,0	$1,043_{18,5}$	+2,0
$3_{0,29}$	338(13-20-35)	13,4	19,7	34,7	32,2	33,8	0,43	43	11,5	$1,099_{18,4}$	+1,7
$4_{0,30}$	354(9-34-34)	9,4	33,9	34,4	22,3	35,4	0,30	55	11,0	$1,180_{18,7}$	+0,7
$5_{0,30}$	363(7-44-34)	6,8	43,6	33,6	16,0	36,3	0,24	62	10,7	$1,228_{18,3}$	+2,1
$6_{0,28}$	363(5-52-31)	4,8	52,1	30,7	12,4	36,3	0,18	71	10,4	$1,291_{18,7}$	+4,7
$7_{0,29}$	343(7-55-19)	7,3	55,5	19,4	17,8	34,3	0,22	63	10,6	$1,240_{18,1}$	+2,5
$8_{0,30}$	338(8-60-14)	8,0	60,0	13,6	18,4	33,8	0,25	61	10,6	$1,215_{18,6}$	+2,6
$9_{0,31}$	322(11-59-6)	10,9	59,1	5,6	24,4	32,2	0,28	55	10,7	$1,178_{18,2}$	+1,6

1	2	5	3	4	6	7	8	9	10	11	12
$1_{0,17}$	249(11-3-32)	11,3	3,0	31,8	53,9	24,9	0,28	56	11,7	$1,060_{17,5}$	-0,7
$2_{0,16}$	258(10-8-33)	9,8	7,7	32,7	49,8	25,8	0,27	57	11,4	$1,079_{16,9}$	-0,3
$3_{0,17}$	293(8-19-35)	8,0	19,0	34,9	38,1	29,3	0,23	62	11,0	$1,136_{17,5}$	-0,8
$4_{0,18}$	320(6-31-35)	5,9	31,1	35,3	27,7	32,0	0,20	67	10,6	$1,211_{17,3}$	+2,2
$5_{0,17}$	333(4-40-34)	4,3	40,2	34,1	21,4	33,3	0,14	78	10,4	$1,311_{16,6}$	+2,6
$6_{0,13}$	335(3-46-33)	2,7	45,8	33,1	18,4	33,5	0,11	87	10,2	$1,257_{16,8}$	-4,7
$7_{0,18}$	329(4-56-22)	4,1	56,0	21,6	18,3	32,9	0,16	74	10,4	$1,259_{18,7}$	+3,1
$8_{0,16}$	298(5-51-16)	5,2	51,5	16,3	27,0	29,8	0,16	74	10,5	$1,244_{18,1}$	+5,5
$9_{0,18}$	273(7-52-6)	7,4	52,1	6,5	34,0	27,3	0,17	69	10,5	$1,199_{18,2}$	+1,1

*Index of Item No represents relation $NH_3/(NH_3+H_2O)$ or degree of ammonization

Crystallization temperature of grades presented in tab. 2 is close up to 0°C (with rare exceptions). It enables to compile Gibbs triangle plane projection of quaternary system water-ammonia-ammonium nitrate- urea where the composition corresponds to crystallization at 0°C depending on degree of ammonization (fig. 1).

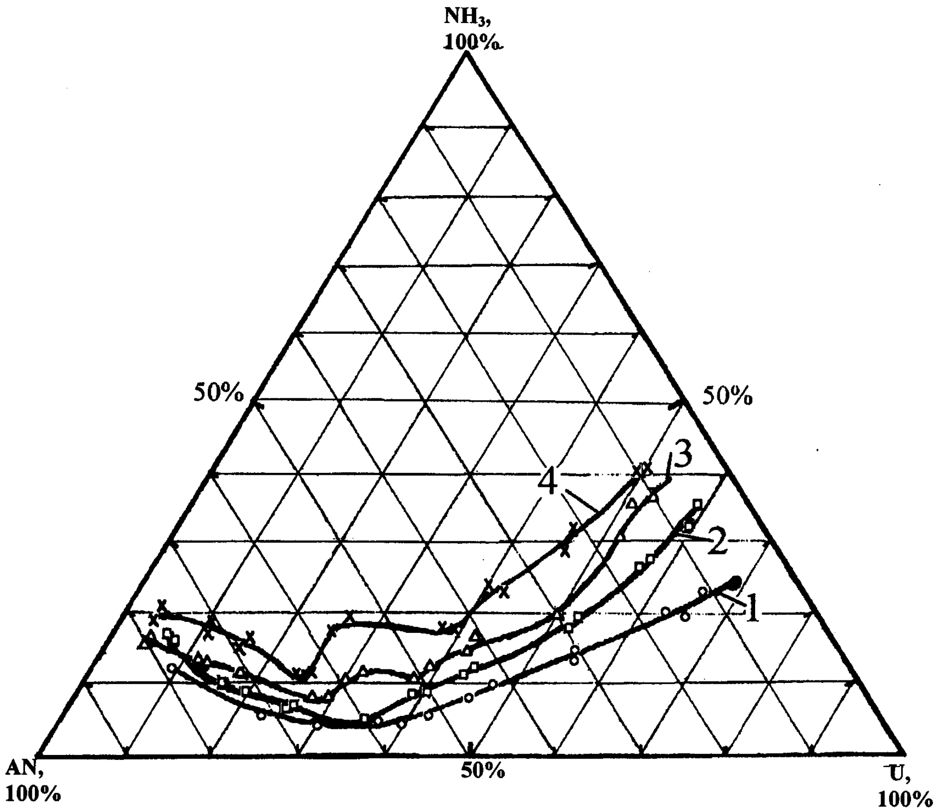

Figure 1 Quaternary system H_2O-NH_3-AN-U plane projection, crystallizable at 0°C depending on degree of ammonization [$NH_3/(NH_3+H_2O)$]: 1-0,2; 2-0,3; 3-0,4; 4-0,5

It is necessary to estimate relation of NH_3:AN:U in ternary system adequate to one in quaternary system H_2O-NH_3-AN-U in order to calculate the composition of pressure-type fertilizers crystallizable at the temperature about 0^oC.
The sequel of detailed measurements of the pressure dependence on the temperature is presented by charts (fig. 2) that enable to define the composition and temperature of liquid fertilizers that vapor pressure equals to 0,69 kg/cm^2.

Ammonization and heat capacities for several solutions are presented in tables 3, 4.

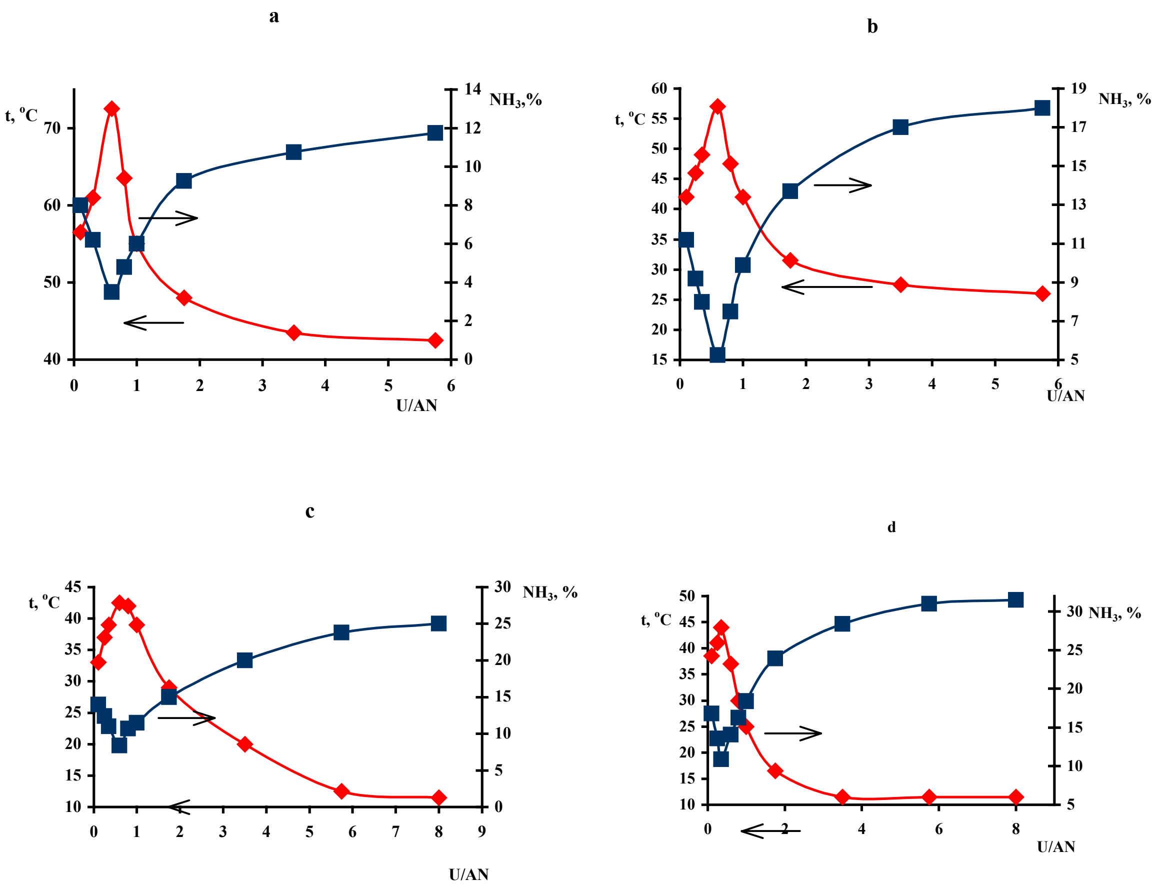

Figure 2. Charts for composition and temperature determination of liquid fertilizers that vapor pressure equals to 0,69 kg/cm^2 depending on degree of ammonization [$NH_3/(NH_3+H_2O)$]: a-0,2; b-0,3; c-0,4; d-0,5

Table 3
Heat of ammonization (L)

Composition from table 1									
Item No	$1_{0,09}$	$2_{0,21}$	$3_{0,35}$	$4_{0,46}$	$5_{0,63}$	$6_{0,43}$	$7_{0,27}$	$8_{0,41}$	90,55
L, kJ	33,2	31,5	30,6	27,6	25,9	29,1	30,5	29,5	27,4

Composition from table 2						
Item No	$1_{0,47}$	$2_{0,40}$	$4_{0,37}$	$6_{0,49}$	$8_{0,49}$	$9_{0,46}$
L, kJ	25,7	23,9	27,8	27,7	28,34	27,61
U:AN	5,37	3,01	0,99	0,49	0,24	0,15
Item No	$2_{0,29}$	$4_{0,30}$	$5_{0,30}$	$5_{0,42}$	$7_{0,29}$	$10_{0,39}$
L, kJ	27,4	29,5	29,7	28,4	30,0	29,8
U:AN	3,40	1,01	0,77	0,76	0,35	0,07

Table 4
Heat capacity of some grades from table 1

Item No	Temperature, K			
	293	298	303	308
	C_p, J/(g·deg)			
$1_{0,09}$	2,191	2,698	2,974	3,281
$2_{0,21}$	2,246	2,847	3,552	4,035
$3_{0,35}$	2,317	3,294	4,646	5,396

3. PROCESS DESCRIPTION

Fig. 3 presents the principal flow sheet of pressure-type nitrogen solutions the various grades production with limited gaseous phase pressure (up to 0,69 kg/cm^2).

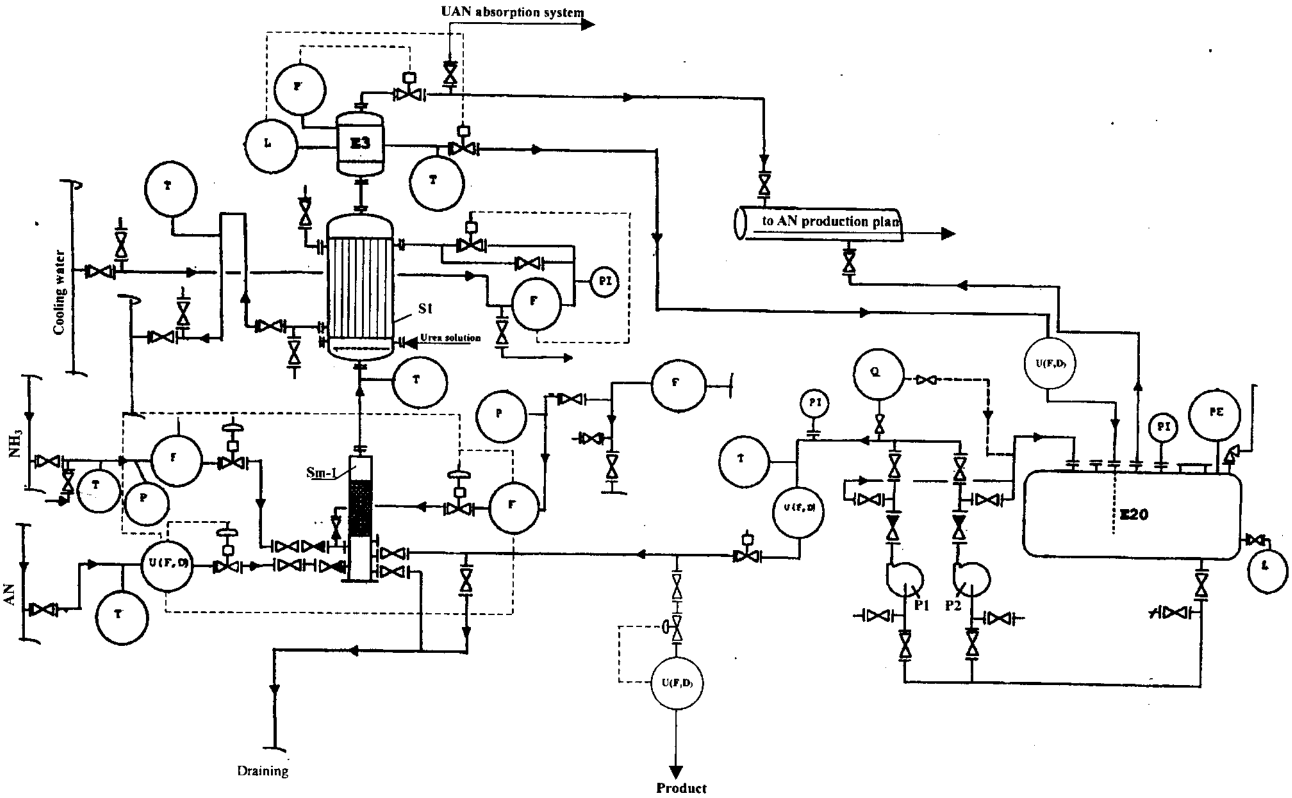

Figure 3. Flow sheet for production of pressure-type nitrogen solution
F-flow; L-level; P-pressure; T-temperature; Q-pH;

Main equipment for 10000 t/yr liquid fertilizers production is specified in table 5.

Table 5
Description of main equipment

Item No position	Name	Material	Description
Sm1	Mixer	Stainless steel 1218H10T	D=200 mm H=2400 mm P=0,2 Mpa t<150 ^oC
S1	Absorber/cooler	Item	D=400 mm H=7130 mm F=60 m^2 P=0,2/0,6 Mpa
E2	Gas separator	Item	D=400 mm H=2000 mm t>30 ^oC
E20	Buffer/storage tank	OX22H6T	D=3500 mm L=11000 mm V=100 m^3 t>30 ^oC
P1 P2	Centrifugal pumps	Stainless steel	W=25 m^3/h; N=7 kW W=6,3 m^3/h; N=3 kW

The reason to use UAN facilities and problems faced
There are two main reasons to coincide the unit under consideration with that of UAN production: 1) supply of concentrated (90 % NH_4NO_3) AN solution directly from UAN unit as well as utilities and 2) employment of existing equipment which includes automatic regulation, using computer-drived Fisher-Rosemount system RS-3 version. Practically all soft wear and hard wear are lent and/or coincided from that of UAN. Main points of measurement and automatic regulation are shown on fig.3. They are employed to switch the unit being in operation from batch process to that continuous.

Corrosion
AN based solutions distinguish there in corrosion activity. Only Ni, Cr stainless steel with its characteristic corrosion resistance is suitable for the handlings of such solution without, anticorrosive additives. Urea, as fertilizers component in permissible quantity, checked-out using chart of fig.2, diminishes considerably corrosive properties of solution obtained.

The location of the unit and mass transfer problems
As UAN equipment being used on the site of enterprise “Liquid fertilizers”, the vertical configuration of the unit was decided with special refit of absorption and cooling mass/heat exchanger (S1). Perforated plate in the bottom of S1 ensured uniformity of heterogeneous gas/liquid system providing sufficient absorption and cooling. Besides characteristic UAN mixer (Sm1), gas separator (E3) was added.

4. CONCLUSION

Investment cost saving unit of 10000 t/yr Capacity for pressure-type nitrogen solution production using UAN facilities is elaborated and commissioned. Gas phase pressure not exceeds 0,69 kg/cm^2.