International Fertilizer Industry Association

IFA Technical Conference

The Hague, The Netherlands
6-8 October 1992

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SPECIALIZED LIQUID COMPLEX FERTILIZERS IN LITHUANIA

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ABSTRACT

The main standard fertilizers: urea, ammonia, liquid ammonia, ammonium nitrate, superphosphate, ammonium phosphate, are produced in large scale at two Lithuanian chemical plants - Kedainiai and Jonava.

The new research objective of the last years was seeking technology for the production of specialized liquid fertilizers and these were developed at Jonava "Azotas" state enterprise-nitrogen factory.

According with results obtained, many grades of specialized liquid fertilizers were developed at Jonava "Azotas" state enterprise-nitrogen factory.

Liquid fertilizers process is based on flow type technological scheme. It involves the production of potassium nitrate, ammonium nitrate and ammonium phosphate solutions as well as the preparation of chelated microelements and mixing all components. The compounds mentioned above are produced simultaneously.

1. INTRODUCTION

Specialized complex fertilizers destined for greenhouse plants, flowers, horticulture are usually produced by dissolving and mixing salts in water.

This paper describes the NPK process using only liquid ammonium phosphate, ammonia and potassium nitrate solutions. Corresponding laboratory investigation was carried out to ensure an extraction of the compounds mentioned from by-products and intermediates of large scale nitrogen and phosphoric fertilizers production.

Crystallization temperature and solid phase of:

KNO_3 - $(NH_4)_2HPO_4$ - NH_4NO_3- H_2O and KNO_3 - $(NH_4)_2HPO_4$ - $CO(NH_2)_2$ - H_2O

systems were determined by visual -polythermic method. Chemical composition of the solutions with salting out temperature at 0°C was defined.

Production involves processes to obtain potassium nitrate, ammonium nitrate and ammonium phosphate solutions by the neutralization of potassium carbonate with nitric acid as well as ammonia water solution by nitric acid and phosphoric acid simultaneously. By mixing all the components, 10-7-5, 7-7-5, 5-7-7 and 5-3-7 NPK liquid grades are produced.

Magnesium-nitrogen liquid composition was investigated:

$Mg(NO_3)_2$ - $Ca(NO_3)_2$ - NH_4NO_3-H_20 salting out temperature was determined.

Liquid magnesium-nitrogen fertilizers technology consists of:

1) magnesite decomposition by nitric acid,
2) ammoniazation of acid magnesium nitrate solution,
3) liquid fertilizers standardization and packing.

2. LABORATORY SCALE EXPERIMENTS ON COMPOSITION OF LIQUID NPK

These experiments were carried on using visual-polythermic method to determine crystallization temperature of:

$$KNO_3 - CO(NH_2)_2 - (NH_4)_2HPO_4 - H_2O \qquad (1)$$

$$KNO_3 - NH_4NO_3 - (NH_4)_2HPO_4 - H_2O \qquad (2)$$

systems. The results are summarized below:

2.1. Polythermic crystallization data of 9 different initial compositions of (1) and 8 compositions of (2) systems were obtained. The graphic view is presented in Figure 1.

2.2. Compositions of liquid and solid phase in critical points of each curve were determined. These results are given in Table 1.

Table I - Chemical composition of critical points of systems (I and II)

N° of System	Section	Composition of liquid phase (w)				Crystallization temperature, °C	Composition of solid phase
		KNO_3	$CO(NH_2)_2$ or NH_4NO_3	$(NH_4)_2HPO_4$	H_2O		
I	I	8,76	30,00	8,76	32,48	- 6,0	$KNO_3 \downarrow CO(NH_2)_2$
	II	7,36	26,50	11,04	55,10	- 12,0	$KNO_3 \downarrow CO(NH_2)_2$
	III	9,86	34,30	6,57	45,07	- 0,2	"
	IV	12,03	38,50	9,23	40,24	16,6	"
	V	7,80	4,61	18,44	69,15	- 9,8	ice $\downarrow KNO_3$
	V	18,00	4,10	16,40	61,50	21,0	$KNO_3 \downarrow CO(NH_2)_2$
	VI	8,00	9,20	13,00	69,00	- 12,6	ice $\downarrow KNO_3$
	VI	13,00	8,70	13,05	65,25	3,5	$KNO_3 \downarrow CO(NH_2)_2$
	VII	7,70	4,61	23,07	64,62	- 10,8	ice $\downarrow KNO_3$
	VII	13,90	4,30	21,32	60,27	11,2	$KNO_3 \downarrow CO(NH_2)_2$
	VIII	8,70	4,56	13,69	73,05	- 8,5	ice $\downarrow KNO_3$
	VIII	17,40	4,13	12,39	66,08	14,6	$KNO_3 \downarrow CO(NH_2)_2$
	IX	6,50	4,67	28,05	60,77	- 12,9	ice $\downarrow KNO_3$
	X	15,00	4,25	25,50	55,25	23,4	$KNO_3 \downarrow CO(NH_2)_2$
2	I	8,9	28,8	8,9	53,4	- 4,8	$KNO_3 \downarrow NH_4NO_3$
	II	7,7	62,30	11,6	57,7	- 8,3	"
	III	11,9	20,8	7,9	59,4	2,2	"
	IV	16,0	20,0	12,0	52,0	24,4	"
	V	6,8	4,7	13,6	69,9	- 10,5	ice $\downarrow KNO_3$
	V	15,0	4,3	17,0	63,7	14,0	$KNO_3 \downarrow NH_4NO_3$
	VI	6,4	9,4	14,0	70,2	- 12,7	ice $\downarrow KNO_3$
	VI	13,5	8,7	13,0	64,8	8,4	$KNO_3 \downarrow NH_4NO_3$
	VII	5,0	4,7	23,8	66,5	- 10,5	ice $\downarrow KNO_3$
	VIII	15,0	4,3	21,3	59,4	20,6	$KNO_3 \downarrow NH_4NO_3$
	IX	7,7	4,6	13,9	73,8	- 10,0	ice $\downarrow KNO_3$
	X	17,5	4,1	12,4	66,0	18,5	$KNO_3 \downarrow NH_4NO_3$

2.3. Composition of solutions in crystallization point at 0°C, obtained from polythermic investigations by extrapolation, is presented in Table 2. It was suggested to be used as liquid complex fertilizers. The manufacturing of 10-7-5, 7-7-5, 5-7-7 and 5-3-7 grade were chosen according to agrochemical requirements.

Table 2 - Composition of solution with crystallization temperature 0°C

N° solution	Composition of solution (w)				Composition of nutrients (w)				Ratio of $N:P_2O_5:K_2O$
	$KNO_3(NH_4)_2$	HPO_4	$CO(NH_4)_2$	NH_4NO_3	H_2O	N	P_2O_5	K_2O	
1	8,4	8,4	33,0	-	50,2	18,3	4,5	3,9	4:1:0,9
2	8,7	10,1	32,6	-	50,6	18,3	5,4	3,1	3,4:1:0,6
3	10,1	6,7	32,8	-	50,4	18,2	3,6	4,7	5:1:1,3
4	9,9	6,6	34,2	-	49,3	18,7	3,5	4,5	5,3:1:1,3
5	11,2	17,8	4,4	-	66,6	7,4	9,6	5,0	0,8:1:0,5
6	12,0	13,2	8,8	-	66,6	8,5	7,2	5,4	1,2:1:0,7
7	10,6	22,3	4,5	-	62,6	8,3	12,0	4,8	0,7:1:0,4
8	11,8	13,2	4,4	-	70,6	6,5	7,0	5,6	0,9:1:0,8
9	8,7	8,7	-	30,3	52,3	13,7	4,7	4,1	2,9:1:0,9
10	7,4	11,2	-	25,7	55,7	12,4	3,5	6,0	3,5:1,1,7
11	10,3	17,9	-	4,5	67,3	6,8	9,7	4,8	0,7:1:0,5
12	10,6	13,4	-	8,9	67,1	7,4	7,2	4,9	1:1:0,7
13	8,3	22,9	-	4,6	64,2	7,2	12,3	3,9	0,6:1:0,3
14	11,2	13,3	-	4,4	71,1	6,0	7,2	5,2	0,6:1:0,3

3. CHEMISTRY AND FLOW SHEET OF LIQUID NPK PROCESS

Liquid complex fertilizers process is represented by equations as follows:

$$2NH_4OH + H_3PO_4 \text{ -----> } (NH_4)_2HPO_4 + 2H_2O$$

$$NH_4OH + HNO3 \text{ -----> } NH_4NO_3 + H_2O$$

$$K_2CO_3 + 2HNO_3 \text{ -----> } 2KNO_3 + CO_2 + H_2O$$

Referring to the liquid NPK process (Figure 2), ammonia water solution as by-product from tank (4) is reacted simultaneously with nitric acid from tank (1) in reactor (3) as well as with phosphoric acid from tank (5) in reactor (6). Potassium carbonate is reacted with nitric acid in reactor (2). The products obtained are diluted by water in appropriate reactors at 60-80°C. Ammonia nitrate, ammonia phosphate and potassium nitrate solutions are mixed in reactor (8), which is supplied with chelated microelements. These are prepared in reactor (7). The final product is pumped by (9) to standardization (10) and packing (11).

Physical and chemical properties of liquid NPK are presented in Table 3.

Table 3 - Physical and chemical properties of liquid complex fertilizers

Grade of liquid complex fertilizers	Temperature (°C)	Viscosity (sst)	Electro-conductivity (sm)
5-7-5	20	2,50	4,8
	40	1,91	4,2
	60	1,72	3,8
5-7-7	20	1,63	5,0
	40	1,35	4,5
	60	1,26	4,1
10-7-5	20	1,84	5,5
	40	1,73	4,9
	60	1,54	4,1
5-3-7	20	2,10	5,1
	40	1,96	4,6
	60	1,85	4,1

Liquid NPK contains six microelements: Cu, Zn, B, Mn, Co, Mo usually in chelated form free of chlorine, heavy metals and other toxic substances. Agrochemical research illustrates that liquid NPK obtained decreases nitrate amount in vegetables and fruits as well as increases amount of sugar and lemon acid. The equipment desired was used from the other plant necessary for restructuring. The capacity of plant complex is 10 000 tons per year.

4. LABORATORY SCALE INVESTIGATION OF LIQUID MAGNESIUM-NITROGEN FERTILIZER

These experiments were carried out on by visual-polythermic method too in order to determine crystallization temperature of $Mg(NO_3)_2$ - $Ca(NO_3)_2$ - NH_4NO_3 - H_2O system. The results are as follows:

4.1. Polythermic crystallization data of 5 different initial compositions are presented in Figure 3. Each curve consists of two parts corresponding to crystallization of $Mg(NO_3)_2.6H_2O$ and NH_4NO_3.

4.2. Composition of solutions corresponding to crystallization temperature at O°C obtained by extrapolation is presented in Table 4.

Table 4 - Composition of magnesium-nitrogen solutions

Composition of solutions %		Nutrient concentration %					Solid phase
$Mg(NO_3)_2$	$Ca(NO_3)_2$	NH_4NO_3	H_2O	MgO	CaO	N	
33,20	3,00	11,50	52,20	8,97	1,06	10,83	$MgO(NO_3)_2 \cdot 6H_2O$
28,63	2,67	23,66	45,04	7,78	0,91	14,15	NH_4NO_3
28,67	1,91	23,66	45,80	7,78	0,65	14,01	NH_4NO_3
32,50	1,67	16,67	49,16	8,83	0,57	12,26	$MgO(NO_3)_2 \cdot 6H_2O$
30,47	1,56	21,88	46,09	8,28	0,53	13,68	NH_4NO_3
31,82	2,07	17,36	48,75	8,65	0,70	12,26	$MgO(NO_3)_2 \cdot 6H_2O$
29,39	1,91	23,66	45,04	7,98	0,66	14,16	NH_4NO_3

It shows the possibility of production of 14-7 and 10-9 N:MgO grade liquid magnesium-nitrogen fertilizers.

5. CHEMISTRY AND FLOW SHEET OF THE LIQUID MAGNESIUM-NITROGEN FERTILIZERS

The chemistry of the liquid magnesium-nitrogen fertilizers technology is presented by following chemical equations:

$$MgO + 2HNO_3 \text{ -----> } Mg(NO_3)_2 + H_2O$$

$$CaO + 2HNO_3 \text{ -----> } Ca(NO_3)_2 + H_2O$$

$$R_2O_3 + 6HNO_3 \text{ -----> } 2R(NO_3)_2 + 3H_2O$$

The magnesium-nitrogen liquid fertilizers process is described below by reference to Figure 4.

Magnesite (storage 2) is flowed by pneumotransport to reactor (4) fed by nitric acid (5) and condensate from set. The mixing continues about 30 min. at 85°C. Magnesium nitrate solution is pumped (11) to settler (6) and depositives are sent to (12). A clear solution is pumped for neutralisation (7) with ammonia water solution while pH value 4,5 is reached. Liquid magnesium-nitrogen fertilizer manufactured is sent to storage tank (9) and into cartank or bottles.

This process is mastered in pilot plant scale.

CONCLUSIONS

1. The chemical compositions of specialized liquid complex and magnesium-nitrogen fertilizers are chosen as result of visual-polythermic investigations of multicomponent systems.

2. Flow sheet of liquid complex fertilizers is proposed and pilot plant process is mastered.

3. Chemical and physical properties of liquid fertilizers are determined.

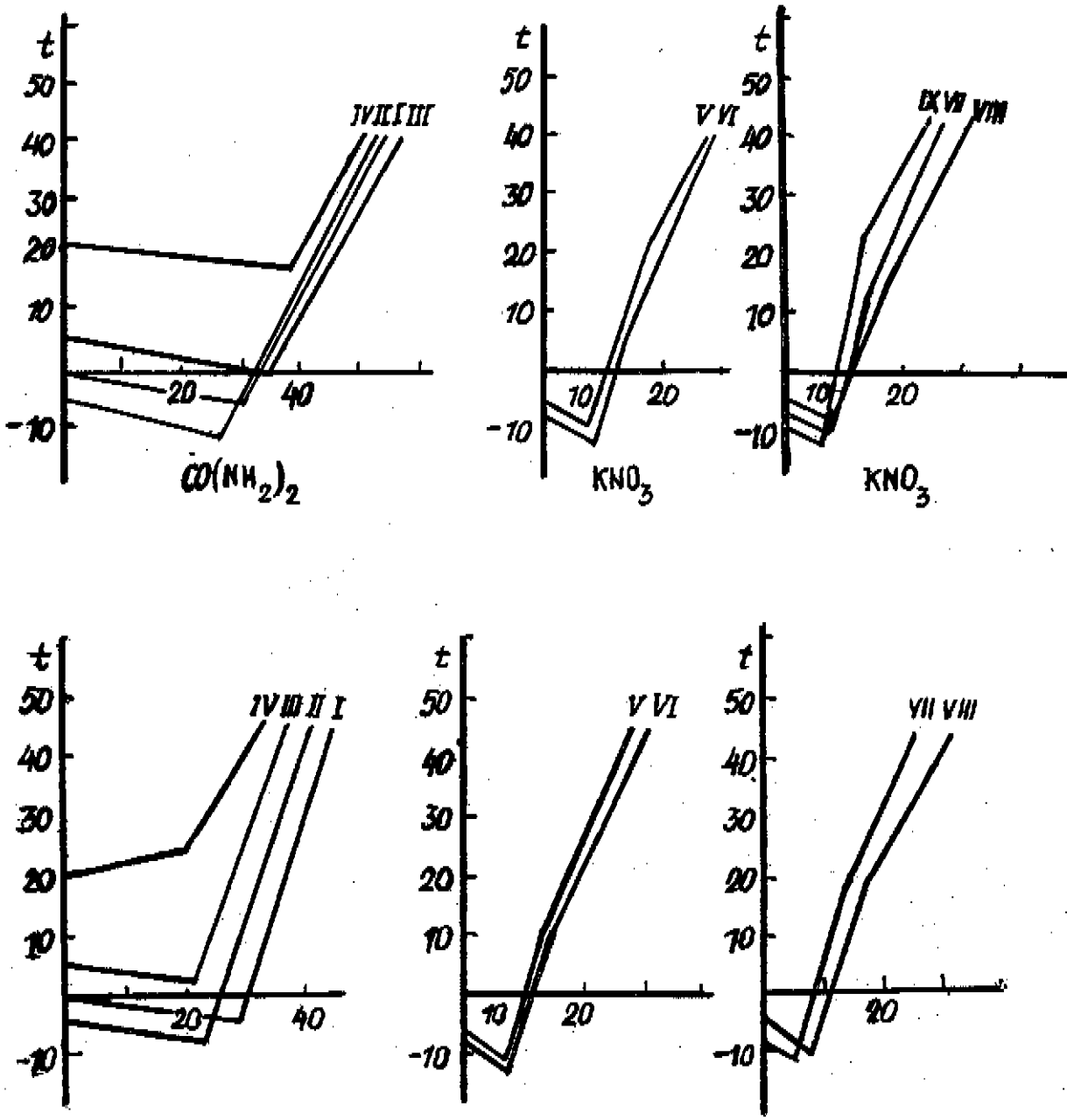

FIGURE 1 *Polythermic curves of systems 1(a) and 2(b)*

t - temperature (°C)

Section (%, w): a) I – [12.5 KNO_3 + 12.5 $(NH_4)_2HPO_4$ + 75 H_2O] → $CO(NH_2)_2$, II – [10 KNO_3 + 15 $(NH_4)_2HPO_4$ + 75 H_2O] → $CO(NH_2)_2$, III – [15 KNO_3 + 10 $(NH_4)_2HPO_4$ + + 75 H_2O] → $CO(NH_2)_2$, IV – [20 KNO_3 + 15 $(NH_4)_2HPO_4$ + 65 H_2O] → $CO(NH_2)_2$, V – [20 $(NH_4)_2HPO_4$ + 5 $CO(NH_2)_2$ + 75 H_2O] → KNO_3, VI – [15 $(NH_4)_2HPO_4$ + 5 $CO(NH_2)_2$ + + 80 H_2O] → KNO_3.

b) I – [12.5 KNO_3 + 12.5 $(NH_4)_2HPO_4$ + 75 H_2O] → NH_4NO_3, II – [10 KNO_3 + 15 $(NH_4)_2HPO_4$ + + 75 H_2O] → NH_4NO_3, III – [15 KNO_3 + 10 $(NH_4)_2HPO_4$ + 75 H_2O] → NH_4NO_3, IV – [20 KNO_3 + 10 $(NH_4)_2HPO_4$ + 75 H_2O] → NH_4NO_3, V – [20 $(NH_4)_2HPO_4$ + 5 NH_4NO_3 + + 75 H_2O] → KNO_3, VI – [15 $(NH_4)_2HPO_4$ + 10 NH_4NO_3 + 75 H_2O] → KNO_3, VII – [25 $(NH_4)_2HPO_4$ + 5 NH_4NO_3 + 70 H_2O] → KNO_3, VIII – [15 $(NH_4)_2HPO_4$ + + NH_4NO_3 + 80 H_2O] → KNO_3.

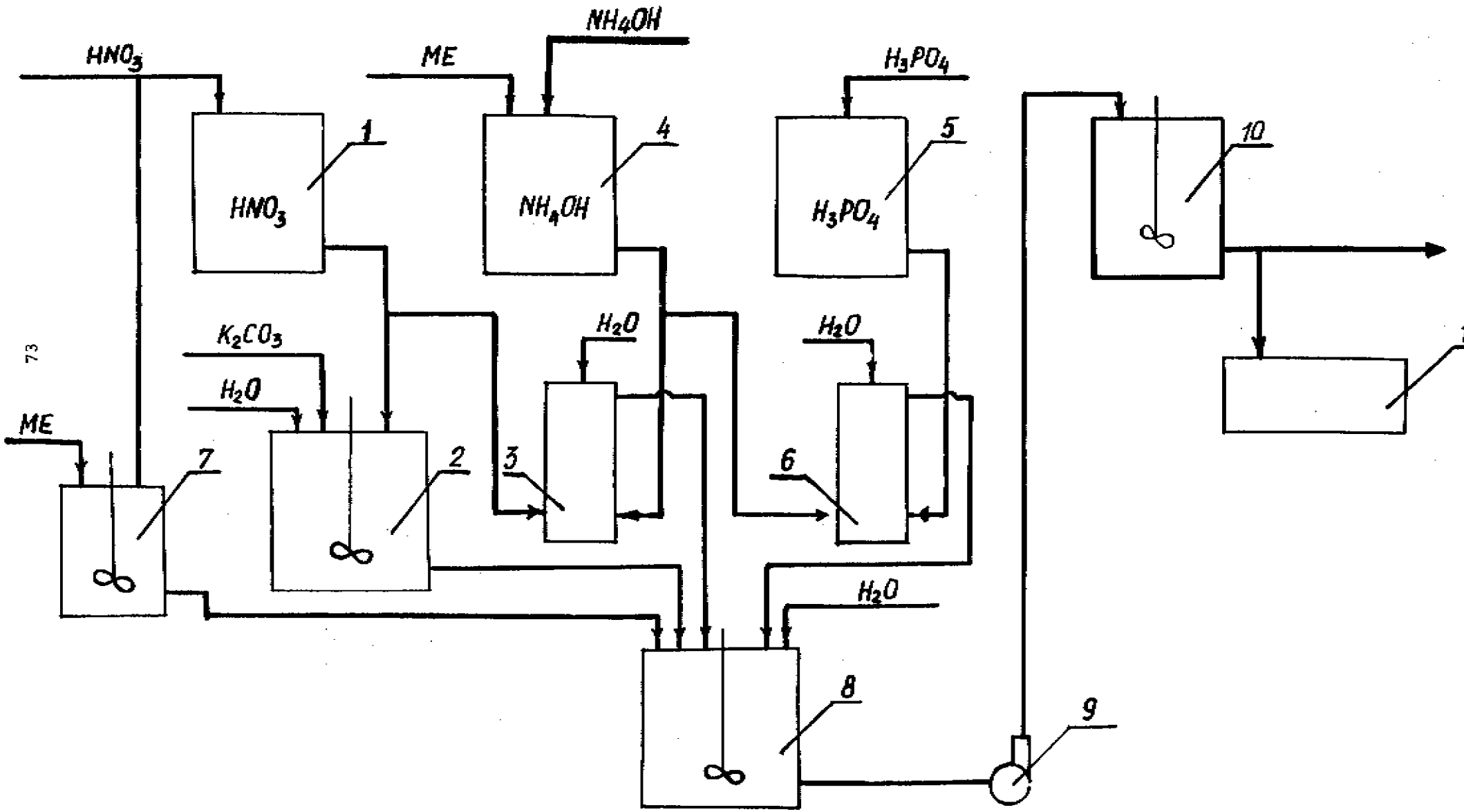

FIGURE 2 - FLOW SHEET OF LIQUID COMPLEX FERTILIZERS PRODUCTION

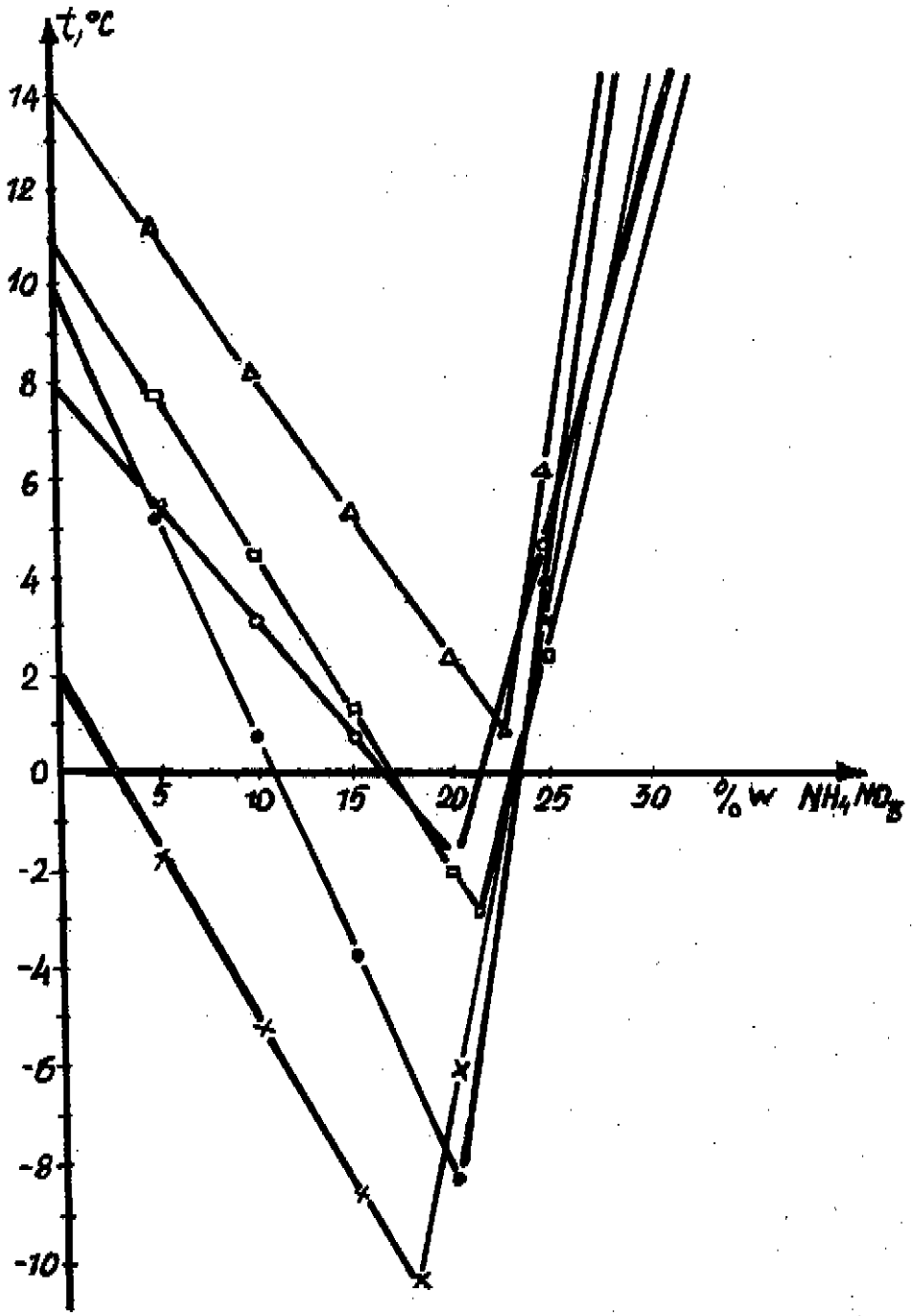

FIGURE 3 *Polythermic curves of system* $Mg(NO_3)_2 - Ca(NO_3)_2 - NH_4NO_3 - H_2O$

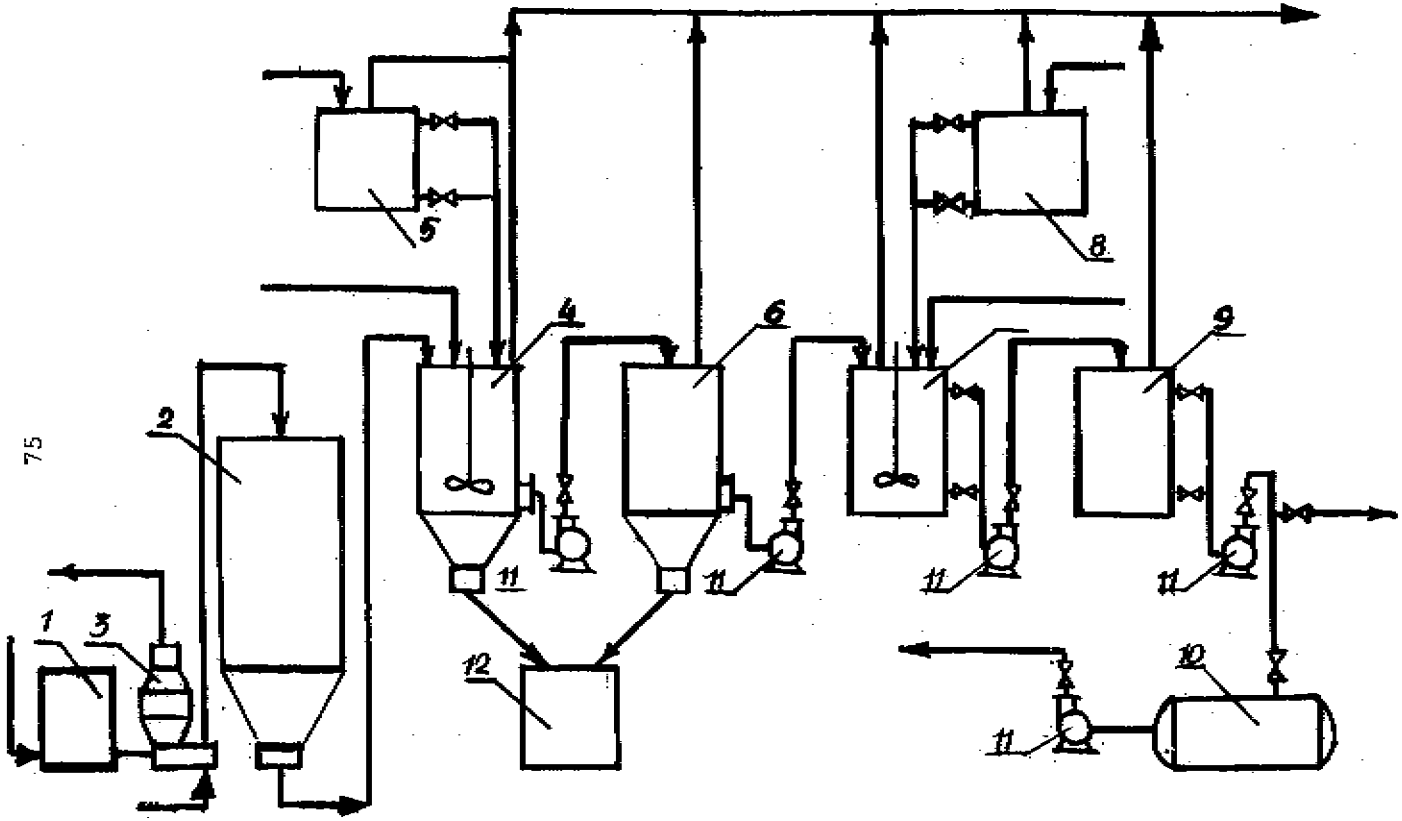

FIGURE 4 - FLOW SHEET OF LIQUID MAGNESIUM - NITROGEN FERTILIZERS