Manufacture of Low-Chloride Multicomponent Fertilizers Based on Conversion in Aqueous Solution

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The interaction of potassium chloride with ammonium dihydrogen phosphate and ammonium sulfate in aqueous solution was investigated. The influence of process variables such as substrates ratio and salt content in the initial mixture on solid-phase composition and on yield of reaction was determined.

INTRODUCTION

Potassium phosphates possess advantageous physico-chemical properties, which make them very attractive as fertilizer constituents. They comprise more nutrient ingredients than multicomponent fertilizers made, for example, from superphosphate and potassium chloride, and therefore the costs of their transport and application are relatively low.

Compared to potassium chloride, potassium phosphates are ideal for use with chloride-sensitive crops such as tobacco, tomatoes, potatoes, some vegetables, and fruit bushes (*Phosphorus and Potassium*, 1973, 1977). The salt index for these compounds is lower than for most conventional fertilizers, which is advantageous for plant growth. The salt index (Rader, 1943), formerly the osmotic index number, is a quantitative indication of the tendency of fertilizer materials to inhibit seed germination or, in extreme cases, to "burn" or damage plants, obtained by comparing their effect on the osmotic pressure of the soil solution with that of sodium nitrate (expressed as 100).

Previously the use of potassium phosphates as fertilizers was discouraged by the high cost of their manufacture. Caustic potash and potassium carbonate are too expensive for use as raw materials in the production of fertilizers for conventional soil application.

A method for manufacturing potassium phosphates, which attracted the most attention, was the acidulation of potassium chloride, the cheapest source of potassium, at high temperature with phosphoric (*Chemical Engineering*, 1963; *Phosphorus and Potassium*, 1964, 1972) or sulfuric acid (*Phosphorus and Potassium*, 1971, 1973, 1977, 1979) accompanied by evolution of hydrogen chloride gas. In the first case a poorly soluble potassium polyphosphate—$(KPO_3)_n$—was the final product. The second process involved the formation of $KHSO_4$ as an intermediate for the decomposition of phosphate rock with a mixture of this salt and sulfuric acid. A solvent can be employed for separation of KH_2PO_4 as a final product. A large number of operations, the necessity of recovery and utilization of HCl waste, material handling, and serious corrosion problems tend to occur during these complex processes.

The most obvious and economical method of producing potassium phosphates, eliminating simultaneously the corrosion problem (as a result of high corrosive power of reaction medium), would be a procedure in which the chloride introduced as KCl can be removed from the reaction mixture by crystallization of a low-chloride solid product. This process would proceed in aqueous solution without energy consumption. On this basis 60 years ago,
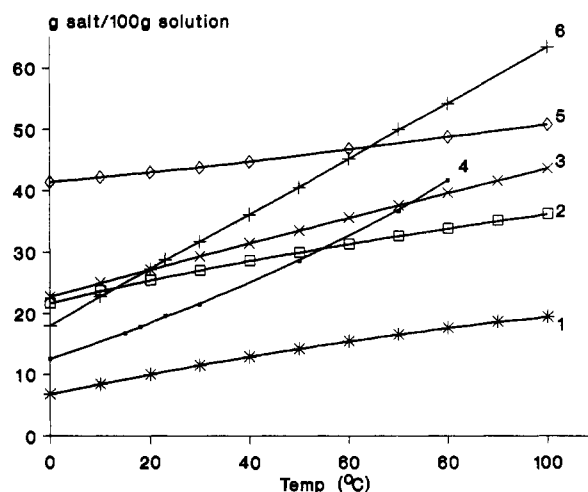

Figure 1. Solubility of salts participating in conversion reaction of potassium chloride: (1) K_2SO_4; (2) KCl; (3) NH_4Cl; (4) KH_2PO_4; (5) $(NH_4)_2SO_4$; (6) $NH_4H_2PO_4$.

a method was developed for obtaining low-chloride fertilizer, containing KH_2PO_4, by conversion of KCl with $NH_4H_2PO_4$ (Askenasy and Nessler, 1930). A similar procedure was reported by Orlandi (1931) for the manufacture of NH_4KHPO_4 by reaction of ammonia water with a mixture of phosphoric acid (45–48% P_2O_5) and a potassium salt (KCl, KNO_3, or K_2SO_4). Askenasy and Nessler (1930), however, determined that under similar conditions in an excess of ammonia $(NH_4)_3PO_4\cdot3H_2O$ was the only solid product and K_2HPO_4 could be obtained after ammonia was removed.

On the basis of this information we have proposed a concept for manufacturing a low-chloride multicomponent fertilizer by conversion of KCl with ammonium dihydrogen phosphate and ammonium sulfate. According to this assumption the main components of the final product would be two poorly soluble potassium salts, namely potassium dihydrogen phosphate and potassium sulfate, chlorides being removed with the liquid phase.

EXPERIMENTAL PROCEDURES

The experimental conditions were selected to make use of the results as a basis for a new manufacturing process. The initial mixtures were prepared from reagent grade chemicals at a constant salt content of 50 wt %. The samples were shaken at 20 °C for 24 h. Then the liquid phase was separated under vacuum from the solid phase and their quantity compositions were determined for a material balance.

Flame photometry was used to measure the potassium content, and a molybdeno–vanado–colorimetric method was employed
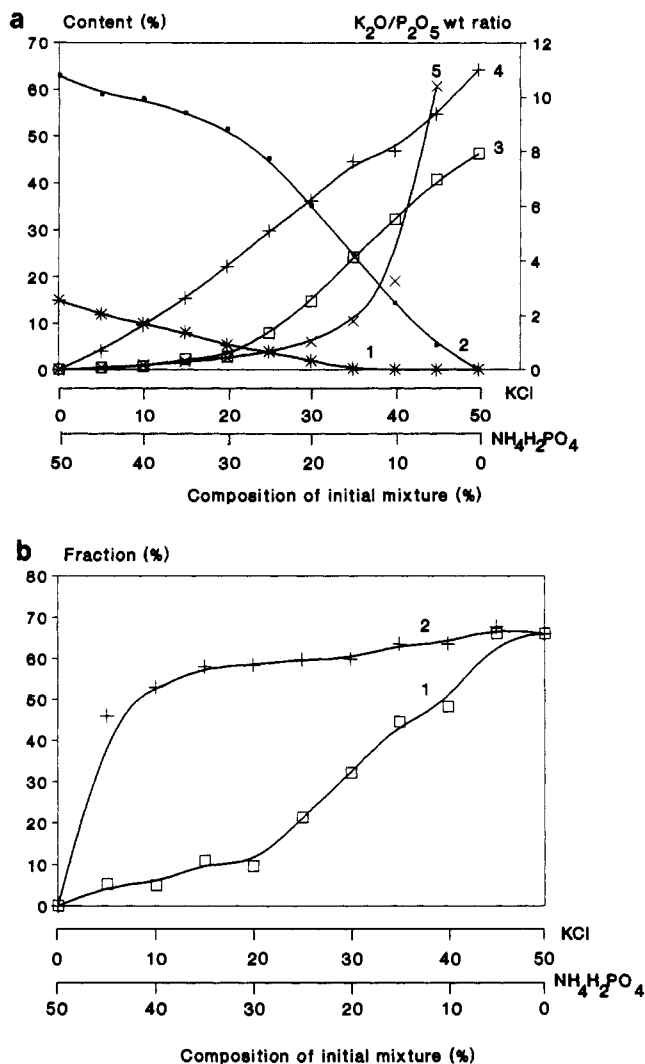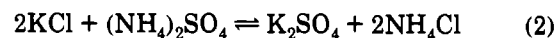
a

b

Figure 2. Influence of initial mixture composition on the conversion course for the system $KCl-NH_4H_2PO_4-H_2O$. (a) Solid-phase composition: (1) NH_3; (2) P_2O_5; (3) Cl^-; (4) K_2O; (5) K_2O/P_2O_5. (b) K_2O and Cl^- fraction in solid phase: (1) Cl^-; (2) K_2O.

for phosphate determination. NH_4^+ and Cl^- contents were measured with a suitable ion-selective electrode, and sulfate

concentration was determined gravimetrically. X-ray diffraction analysis was used for identification of solid-phase composition.

RESULTS AND DISCUSSION

According to this concept the conversion process of potassium chloride is based on the following reactions:

$$KCl + NH_4H_2PO_4 \rightleftharpoons KH_2PO_4 + NH_4Cl \qquad (1)$$

$$2KCl + (NH_4)_2SO_4 \rightleftharpoons K_2SO_4 + 2NH_4Cl \qquad (2)$$

Two less soluble salts, namely potassium sulfate and potassium dihydrogen phosphate, would be precipitated as a solid phase from selected concentration conditions of the initial components. The chloride ion would remain in the mother solution.

It is evident from the solubility diagram of all six salts from the above reactions (Figure 1) (Menzel and Gäbler, 1929; Chomjakow et al., 1933; Askenasy and Nessler, 1930; Apfel, 1911; Poradnik fizykochemiczny, 1974) that at 20 °C the least soluble of all of these salts are potassium sulfate and potassium dihydrogen phosphate. Under the above conditions, ammonium sulfate is the most soluble compound, whereas ammonium dihydrogen phosphate and ammonium as well as potassium chloride take the middle position. Di- and triammonium phosphates are not considered in the above system. The precipitation of these conversion products (K_2HPO_4 and K_3PO_4), independent of the solubility of these compounds, would have to occur at much higher pH.

The relation between the initial mixture composition and the component contents of the liquid and solid phase as well as the yield of reaction was determined for three systems:

$$KCl-NH_4H_2PO_4-H_2O \qquad (a)$$

$$KCl-(NH_4)_2SO_4-H_2O \qquad (b)$$

$$KCl-NH_4H_2PO_4-(NH_4)_2SO_4-H_2O \qquad (c)$$
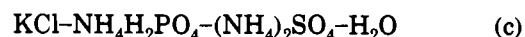
Operating conditions were as follows: temperature, 20 °C; total salt content in reaction mixture, 50 wt %; on the

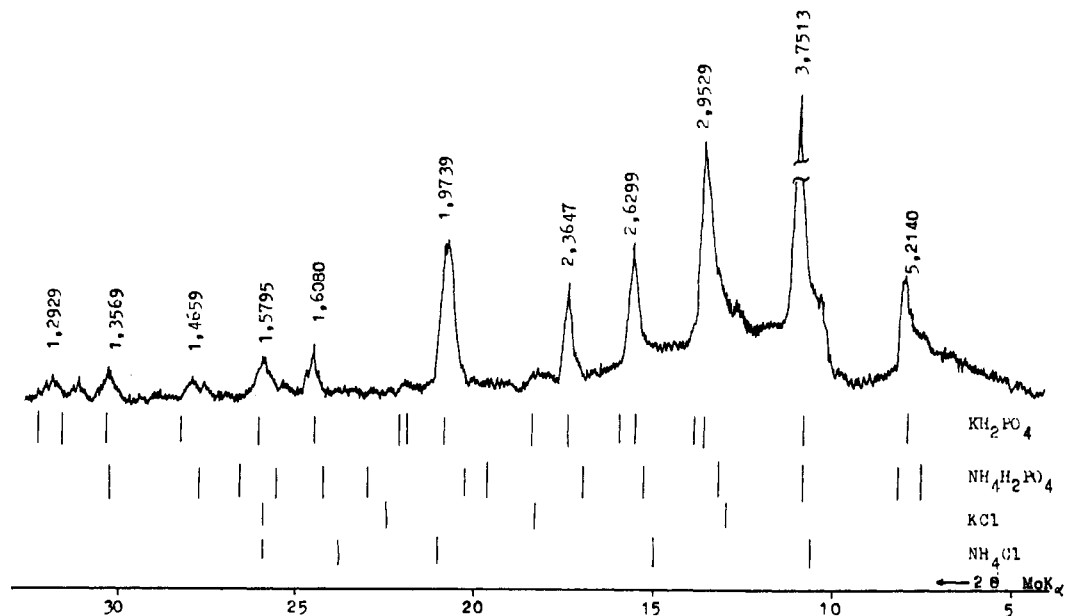**Figure 3.** Diffraction analysis of solid phase for the system $KCl-NH_4H_2PO_4-H_2O$ (20 wt % KCl in initial mixture).

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Table I. Conversion of KCl for the System KCl-NH₄H₂PO₄-H₂O

		content, %								
initial mixture		liquid phase				solid phase				
NH₄H₂PO₄	KCl	P₂O₅	K₂O	NH₃	Cl⁻	P₂O₅	K₂O	NH₃	Cl⁻	K₂O/P₂O₅ wt ratio
	50		16.71		12.31		64.20		46.12	
5	45	1.19	14.83	0.91	11.79	5.26	54.66	0.01	40.61	10.39
10	40	2.30	13.17	1.52	16.96	14.37	46.73	0.01	32.25	3.25
15	35	2.54	11.77	2.71	13.85	24.81	44.53	0.15	24.11	1.79
20	30	2.69	10.26	3.52	13.65	35.22	36.11	1.91	14.75	1.02
25	25	3.42	10.09	3.61	14.62	45.06	29.83	3.83	7.84	0.66
30	20	4.26	7.96	4.24	13.50	51.40	22.19	5.28	2.83	0.43
35	15	6.10	6.47	3.90	10.79	54.89	15.35	7.96	2.25	0.28
40	10	7.74	4.39	3.93	6.51	57.91	9.69	9.88	0.65	0.17
45	5	12.78	2.47	3.31	3.35	58.94	4.01	11.89	0.35	0.07
50		16.83		4.03		62.89		15.02		

Table II. Conversion of KCl for the System KCl-(NH₄)₂SO₄-H₂O

		content, %							
initial mixture		liquid phase				solid phase			
(NH₄)₂SO₄	KCl	K₂O	SO₃	NH₃	Cl⁻	K₂O	SO₃	NH₃	Cl⁻
50	0		23.08	9.81			60.61	25.76	
40	10	1.95	15.12	8.47	5.74	25.89	52.20	13.50	1.42
30	20	3.53	5.12	6.79	12.29	40.60	46.08	5.73	1.72
20	30	8.74	0.80	5.15	16.64	49.38	42.00	2.46	5.19
10	40	11.31	0.32	3.01	14.56	61.32	17.44	0.84	32.60
0	50	16.71			12.31	64.20			46.12

Table III. Conversion of KCl for the System KCl-NH₄H₂PO₄-(NH₄)₂SO₄-H₂O

|										
		composition, wt %								
initial mixture		liquid phase				solid phase				
content KCl, %	(NH₄)₂SO₄/NH₄H₂PO₄ wt ratio	P₂O₅	K₂O	NH₃	Cl⁻	P₂O₅	K₂O	NH₃	Cl⁻	K₂O/P₂O₅ wt ratio
10	7.00	3.83	2.39	9.75	6.50	0.87	27.51	10.60	1.25	31.62
10	3.00	4.58	2.20	8.62	5.56	14.14	24.45	9.12	0.68	1.73
10	1.67	6.26	3.00	8.87	5.95	29.14	20.75	9.27	0.40	0.71
10	1.00	6.55	3.90	6.85	5.83	42.32	16.36	9.96	0.35	0.39
10	0.60	6.56	4.28	6.20	5.31	44.50	12.44	9.44	0.31	0.28
10	0.33	7.38	5.17	5.66	6.14	51.92	9.51	11.36	0.25	0.18
10	0.14	8.21	5.50	4.48	7.00	56.53	9.96	8.56	0.50	0.18
15	6.00	4.08	3.14	9.50	0.81	0.61	37.99	6.19	1.33	62.28
15	1.33	4.85	3.88	5.20	8.90	25.24	27.10	7.05	0.70	1.07
15	1.00	5.22	5.03	6.38	9.01	32.71	24.68	10.88	0.51	0.75
15	0.75	5.33	4.79	6.21	8.89	34.93	21.65	8.98	0.64	0.62
15	0.40	6.55	5.81	5.90	9.01	45.07	18.93	6.81	0.60	0.42
15	0.17	6.60	7.25	5.35	9.27	53.52	15.13	6.51	0.85	0.28
20	5.00	4.22	4.12	8.36	11.78	0.46	43.66	3.38	1.24	94.91
20	2.00	4.14	5.01	7.16	12.38	14.40	36.97	6.04	0.88	2.57
20	1.00	4.13	5.53	5.95	12.21	27.17	30.63	9.56	1.06	1.13
20	0.50	5.58	7.03	4.31	9.42	36.08	28.55	4.55	0.88	0.79
20	0.20	4.94	8.79	5.65	12.43	49.08	23.82	3.63	1.05	0.48

basis of a preliminary test a retention time of 24 h was employed; the independent variable was the composition of initial mixture, for example, the weight ratio of KCl to NH₄H₂PO₄ and to (NH₄)₂SO₄ or the weight ratio of KCl to (NH₄)₂SO₄/NH₄H₂PO₄. The results are given in Tables I–III.

By the interaction of potassium chloride with ammonium dihydrogen phosphate (reaction 1) at a suitable ratio of salts in primary mixture (Figure 2a), it was possible to achieve a relatively high degree of chloride separation. The yield of conversion as the fraction of K₂O and Cl⁻ in the solid phase is shown in Figure 2b. At an initial concentration of 20 wt % KCl and 30 wt % NH₄H₂PO₄, the product with a weight ratio K₂O/P₂O₅ of 0.43 contains about 3% Cl⁻. For this case X-ray diffraction analysis showed a high amount of KH₂PO₄ and a small quantity of KCl and NH₄H₂PO₄ in the final solid product (Figure 3). The composition of this product (the separation yield)

for the above conditions is as follows: solid phase, P₂O₅ 51.4% (85.9%), K₂O 22.19% (58.5%), NH₃ 5.28% (38.6%), Cl⁻ 2.83% (9.6%); liquid phase, P₂O₅ 4.26%, K₂O 7.96%, NH₃ 4.24%, Cl⁻ 13.5%.

A relatively pure product in respect to chloride content (1.7% Cl⁻) can be obtained with a high yield of potassium (the fraction of K₂O equal to 78%) by conversion of KCl with ammonium sulfate (reaction 2) by a suitable ratio of substrates [20 wt % KCl and 30 wt % (NH₄)₂SO₄] (Figure 4). In this case potassium sulfate was the main component of the solid phase (Figure 5).

Likewise, the influence of the conversion parameter such as the initial salt ratio was determined for the system

$$KCl-NH_4H_2PO_4-(NH_4)_2SO_4-H_2O \qquad (c)$$
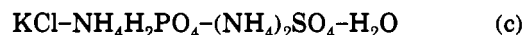
The final solid phase contained the products from both conversion processes (reactions 1 and 2). The chloride content in the precipitate was maintained at a low level
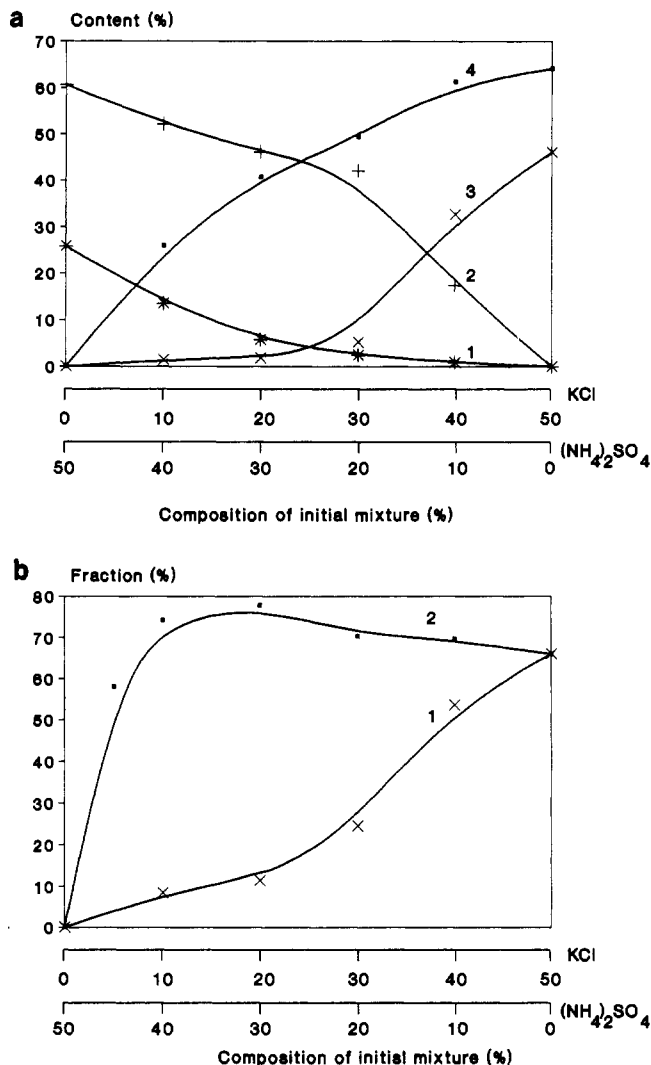
a

b

Figure 4. Influence of initial mixture composition on the conversion course for the system KCl-(NH₄)₂SO₄-H₂O. (a) Solid-phase composition: (1) NH_3; (2) SO_3; (3) Cl⁻; (4) K_2O. (b) K_2O and Cl⁻ fraction in solid: (1) Cl⁻; (2) K_2O.

at 20 wt % KCl or less in the primary mixture independently of the $(NH_4)_2SO_4/NH_4H_2PO_4$ weight ratio. This represents less than a stoichiometric quantity of KCl for both ammonium salts [$NH_4H_2PO_4$ and $(NH_4)_2SO_4$]. The chloride level in the precipitate rose rapidly above this content (Figure 6a).

The next diagram (Figure 6b) presents the influence of the initial mixture composition on the weight ratio K_2O/P_2O_5 in the solid phase. This ratio is a very important value for the selection of fertilizers or their mixtures suitable for a given plant and its vegetation period. For KH_2PO_4 this ratio is equal to 0.66; however, the desirable value for farmers is higher than 1. Increasing the K_2O/P_2O_5 ratio in the final product was achieved according to the proposed concept by the precipitation of potassium sulfate simultaneously with potassium dihydrogen phosphate (see eq 3).

The yield of KCl conversion with both ammonium salts as K_2O and Cl⁻ fractions in the solid phase is illustrated in Figure 6c. The results obtained were satisfactory. For the weight ratio of $(NH_4)_2SO_4/NH_4H_2PO_4$ above 2, the fraction of K_2O in the separated precipitate is contained in the range 60–70% and above with the simultaneous low fraction of chloride (in the range 2–5%).

The influence of the initial salt level on solid-phase composition was also determined (Figure 7a) for conversion of potassium chloride with the mixture of ammonium dihydrogen phosphate and ammonium sulfate. The salt content in successive tests was changed from 35 to 60 wt %. The quantity of KCl in the initial mixture [22 wt % KCl, 12.5 wt % $NH_4H_2PO_4$, 12.5 wt % $(NH_4)_2SO_4$)] was stoichiometric to the sum of both ammonium salts. It was found that the chloride level in the solid phase rose rapidly and simultaneously with the increase of salt content above 45 wt %.

The value of the second very important parameter, namely the K_2O/P_2O_5 ratio for the solid phase, was diminished with the increase of initial salt content from 35 to 45%. However, with the further rise of this value the ratio remained constant. The influence of salt content on the fraction of the main components (K_2O, P_2O_5) in the precipitated solid was also evident; it increases proportionally with the increase of the initial salt content (Figure 7b).

CONCLUSIONS

The data obtained show that the conversion of KCl with ammonium dihydrogen phosphate and ammonium sulfate in aqueous solution or suspension is effective in separating the chloride ion from the solid reaction product. An economical procedure for the manufacture of low-chloride potassium salts, namely KH_2PO_4 and K_2SO_4, which have favorable properties as fertilizers, can be based on this
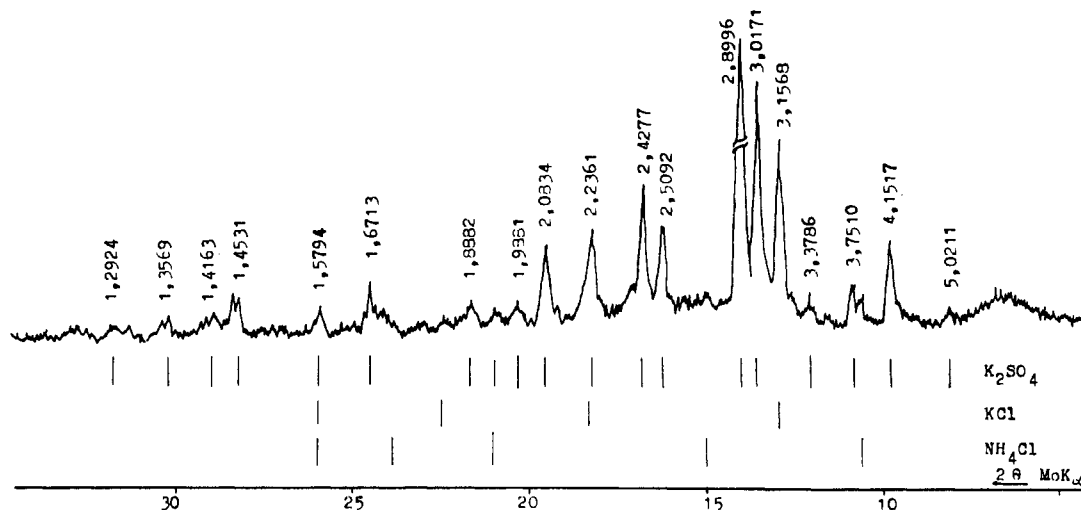

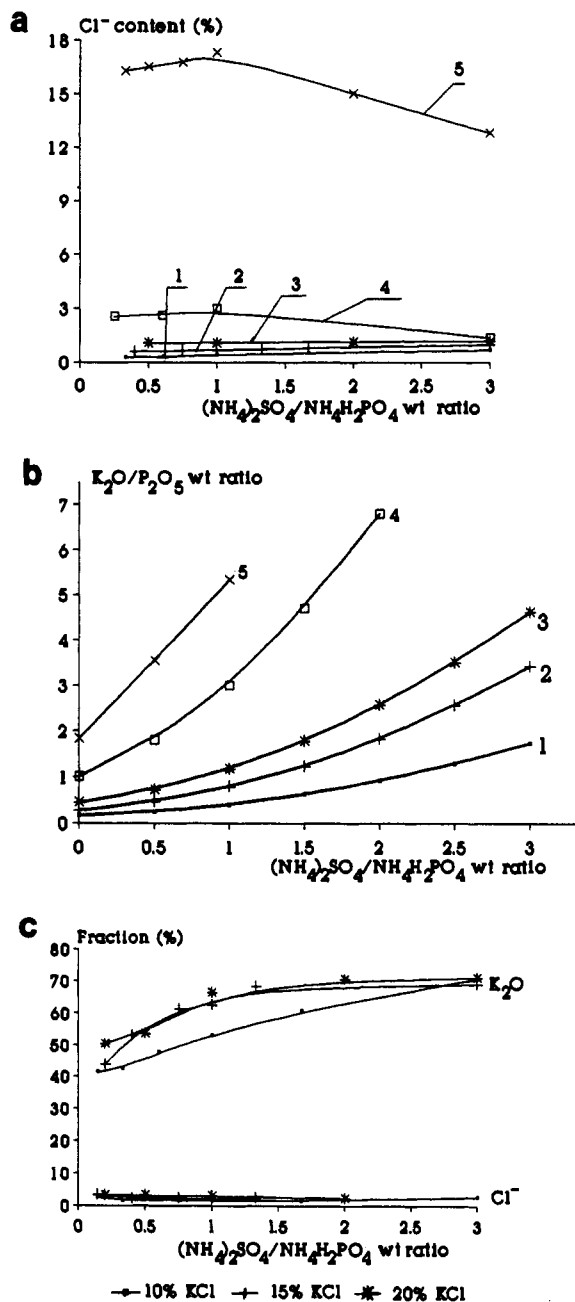**Figure 5.** Diffraction analysis of solid phase for the system KCl-(NH₄)₂SO₄-H₂O (20 wt % KCl content in initial mixture).

Figure 6. Influence of initial mixture composition on the conversion course for the system $KCl-NH_4H_2PO_4-(NH_4)_2SO_4-H_2O$. (a) Chloride concentration in solid phase: (1) 10 wt % KCl; (2) 15 wt % KCl; (3) 20 wt % KCl; (4) 30 wt % KCl; (5) 35 wt % KCl. (b) K_2O/P_2O_5 weight ratio in solid phase: (1) 10 wt % KCl; (2) 15 wt % KCl; (3) 20 wt % KCl; (4) 30 wt % KCl; (5) 35 wt % KCl. (c) K_2O and Cl^- fraction in solid phase.

Figure 7. Influence of salt content in initial mixture on the conversion course for the system $KCl-NH_4H_2PO_4-(NH_4)_2SO_4-H_2O$. (a) Chloride content and K_2O/P_2O_5 weight ratio in solid phase: (1) K_2O/P_2O_5; (2) Cl^-. (b) K_2O and P_2O_5 fraction in solid phase: (1) K_2O; (2) P_2O_5.

principle. Changing the potassium sulfate content can also be used for K_2O/P_2O_5 control in the final product.

The high-chloride liquid phase from the conversion stage contains also all other components of the separated precipitate. We have developed (Glabisz et al., 1990) a simple method for reusing this byproduct in a process of manufacturing another multicomponent fertilizer. The liquid phase is mixed with powdered superphosphate in a ratio equal to 1:3. In consequence, the water introduced with the mother liquid to the system is fixed in a phase change of anhydrite—a component of superphosphate—to dihydrate of calcium sulfate. The chloride content in the final solid product does not exceed 4 wt %.

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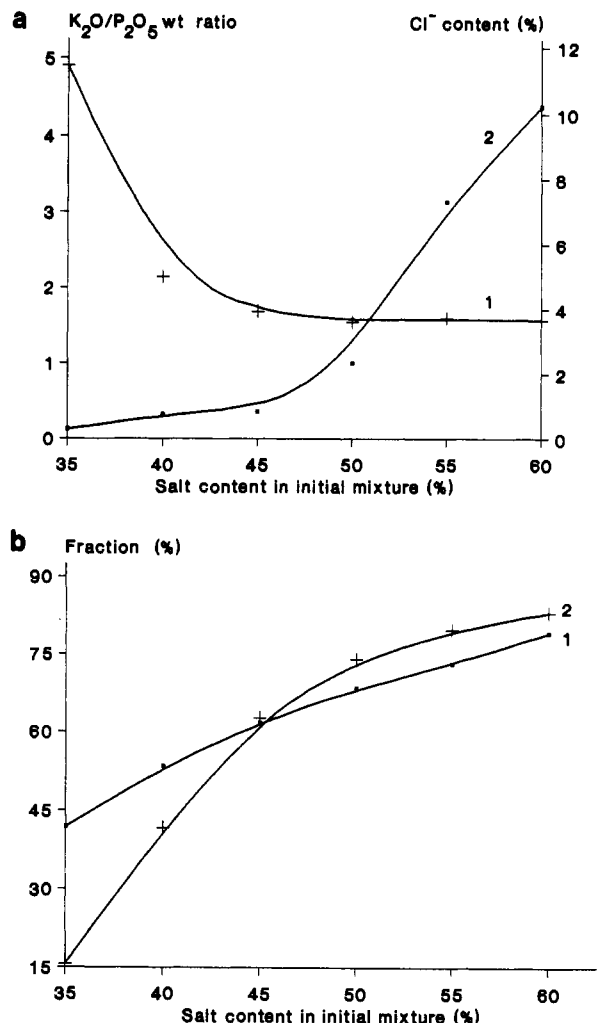Apfel, O. Dissertation, Darmstadt, T. H., 1911; p 12.

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