Potassium, Sodium, and Calcium Polyphosphates with Controlled Solubility

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The process of low-temperature condensation of a KH_2PO_4 and $NH_4H_2PO_4$ mixture, as the product of conversion of potassium chloride with ammonium dihydrogen phosphate, was investigated. At the same time, the ammonium ion was replaced with sodium ion (as Na_2CO_3) or calcium ion (as $CaCO_3$ or CaO). The effects of process temperature (300–450 °C) and the initial mixture composition on the structure and on the qualitative constitution of produced polyphosphates were determined as were their water solubilities and the fraction of ortho, pyro, tripoly, and higher condensed phosphates. The most favorable conditions to obtain all water-soluble potassium–sodium polyphosphates or potassium–calcium condensed phosphates with controlled solubility were determined. The possibility of application of such products as complexing agents of nutrient microelements or as controlled-release fertilizers was considered.

INTRODUCTION

One important ecological problem associated with fertilization is the carrying away of nutrients from the soil, which can cause an undesirable phenomenon of eutrophication of natural waters. This is a result of changes of soil parameters related to the deterioration of sorption complex, affected mainly by acid rain. This phenomenon, in the case of potassium–phosphate fertilizers, can be limited by using a controlled-release composition, i.e. one containing potassium and phosphate in a form which can be assimilated over longer periods (Araten, 1970; U.S. Pat., 1979; Nielsson, 1987; Peng et al., 1979; *Phosphorus Potassium*, 1972; Volfkovic and Cerepanova, 1973; Zawartka, 1984). Potassium polyphosphate, the so-called Kurrol's salt, is an example of that kind of fertilizer.

Microelements such as B, Cu, Zn, Fe, Mn, Mo, and Co raise the nutrient effect of fertilizer macroelements, and they take part in assimilation processes as activators of enzymes. The most obvious is their use as fertilizer additives in the form of simple salts. However, with that procedure, there is a danger of transition of a given microelement in an unavailable form (above all in the presence of orthophosphates). The trace elements are protected from undesirable secondary reactions by converting them to stable, water-soluble chelates. Ethylenediaminetetraacetic acid and similar compounds are applied as complexing reagents (Mortvedt, 1985; Ger. Pat., 1986; PRL Pat., 1985; U.S. Pat., 1985). The application of polyphosphates, which could be at the same time the carriers of fertilizer macroelements, has also been suggested (Fleming, 1969; Glabisz and Grzmil, 1991; Grzmil and Trojanowski, 1992).

It was stated that the main stable crystalline phase in the condensation of KH_2PO_4 was Kurrol's salt $(KPO_3)_n$. Potassium di- and triphosphates were intermediate products. The forming of ring trimetaphosphate was controversial (Gimblett, 1963; Van Wazer, 1961). Kurrol's salt is practically insoluble in water. It was found that the introduction of some additives, such as CaO, MgO, Al_2O_3, ZnO, SiO_2, NaCl, and B_2O_3, in the reaction mixture causes an increase in water solubility of the modified phosphates connected with deformation of the crystalline structure of $(KPO_3)_n$ and appearance of an amorphous phase (Lavrov et al., 1975; Portnova et al., 1973; Volfkovic and Cerepanova, 1970). An essential statement is that the condensation of KH_2PO_4 in the presence of trace elements (Zn, Cu, Mn, Mo, Co) results in formation of chain compounds with a prevalence of tri and pyrophosphates (Glabisz and Grzmil, 1991).

The subject of the investigation was the low-temperature condensation of solid product obtained by conversion of potassium chloride with ammonium dihydrogen phosphate (RP Pat., 1990; Glabisz et al., 1992, 1993). In the separated final solid product mainly KH_2PO_4 was present in a mixture with unreacted $NH_4H_2PO_4$. Because of the decomposition of this salt and ammonia desorption during the dehydration process, it was assumed that the NH_4^+-ion in the reaction mixture would be substituted with sodium ion (introduced as Na_2CO_3) or calcium ion (introduced as $CaCO_3$ or CaO).

EXPERIMENTAL PROCEDURES

The condensation of potassium, sodium, and calcium dihydrogen phosphates was carried out under low-temperature conditions (300–450 °C). The ammonium ion in the reaction mixture was substituted with sodium ion (introduced as Na_2CO_3) or calcium ion (introduced as CaO or $CaCO_3$) with a stoichiometric mole ratio of $NH_4H_2PO_4/MeCO_3$ (or MeO) equal to 1:0.5. The initial substances for polycondensation are given below.

system	mole ratio	
KH_2PO_4		(1)
NaH_2PO_4		(2)
$Ca(H_2PO_4)_2 \cdot H_2O$		(3)
$NH_4H_2PO_4-Na_2CO_3$	1:0.5	(4)
$NH_4H_2PO_4-CaCO_3$	1:0.5	(5)
$NH_4H_2PO_4-CaO$	1:0.5	(6)
$KH_2PO_4-NaH_2PO_4$	1:1, 1:0.5	(7)
$KH_2PO_4-Ca(H_2PO_4)_2 \cdot H_2O$	1:0.5, 1:0.25	(8)
$KH_2PO_4-NH_4H_2PO_4-Na_2CO_3$	1:1:0.5, 1:0.5:0.25	(9)
$KH_2PO_4-NH_4H_2PO_4-CaCO_3$	1:1:0.5, 1:0.5:0.25	(10)
$KH_2PO_4-NH_4H_2PO_4-CaO$	1:1:0.5, 1:0.5:0.25	(11)

To obtain better reaction conditions, some water was introduced into the substrates mixture. The ratio of liquid to solid phase was equal to 0.1. The heating time of the reaction

Table 1. Condensation of Dihydrogen Phosphates

| system | temp (°C) | content (%) and **fraction (%)** | | | | | | content of individual forms of P$_2$O$_5$ (%) and **fraction (%)** | | | |
| | | P$_2$O$_5$ | | | K or Ca | | | | | | |
		total	5 N HCl soluble	water soluble	total	5 N HCl soluble	water soluble	ortho	pyro	tripoly	higher condensed phosphates
KH$_2$PO$_4$											
1	300	56.74[a]	56.74	29.32	30.84[a]	30.84	17.48	9.26	11.45	6.96	1.65
			100.00	**51.67**		**100.00**	**56.68**	**31.57**	**39.06**	**23.74**	**5.63**
2	350	62.55[a]	62.55	3.40	32.89[a]	32.89					
			100.00	**5.44**		**100.00**					
3	400	61.60[a]	61.60	2.37	32.60[a]	32.60					
			100.00	**3.85**		**100.00**					
4	450	61.84[a]	61.84	1.81	32.16[a]	32.16					
			100.00	**2.93**		**100.00**					
Ca(H$_2$PO$_4$)$_2$·H$_2$O											
1	300	64.35[b]	64.35	44.82	16.65[b]	16.65	11.67	7.91	33.55	2.61	0.75
			100.00	**69.65**		**100.00**	**70.09**	**17.66**	**74.86**	**5.81**	**1.67**
2	350	65.81[b]	20.86	7.80	17.03[b]	6.58	1.24				
			42.64	**11.85**		**38.64**	**7.28**				
3	400	68.10[b]	21.15	4.97	17.62[b]	4.10	0.24				
			31.06	**7.30**		**23.27**	**1.36**				
4	450	68.76[b]	15.24	3.40	17.79[b]	2.88	0.20				
			22.16	**4.94**		**16.19**	**1.12**				

[a] Soluble in 5 N HCl. [b] Soluble in 5 N HCl after fusion with Na$_2$CO$_3$.

Table 2. Condensation of Dihydrogen Phosphates

| system | temp (°C) | content (%) and **fraction (%)** | | | | | | | | content of individual forms of P$_2$O$_5$ (%) and **fraction (%)** | | | |
| | | P$_2$O$_5$ | | | | K | | Na | | | | | higher condensed phosphates |
		total	water soluble	NH$_3$	CO$_2$	total	water soluble	total	water soluble	ortho	pyro	tripoly	
KH$_2$PO$_4$−0.5NaH$_2$PO$_4$													
1	300	59.02	58.70			22.30	21.97	6.23	6.20	8.50	18.88	28.80	2.83
			99.46				**98.52**		**99.52**	**14.41**	**32.00**	**48.80**	**4.79**
2	350	62.50	60.00			23.04	21.00	6.60	6.00	4.88	9.27	39.04	7.80
			96.00				**91.15**		**90.91**	**8.13**	**15.45**	**65.06**	**13.00**
3	400	63.44	49.15			23.17	15.18	6.66	5.54	4.19	6.50	25.48	12.98
			77.47				**65.52**		**83.18**	**8.52**	**13.22**	**51.84**	**26.41**
4	450	65.00	48.49			23.65	13.37	6.89	4.95	2.44	5.39	16.66	24.50
			74.60				**54.57**		**71.84**	**5.03**	**11.12**	**34.36**	**50.53**
KH$_2$PO$_4$−0.5NH$_4$H$_2$PO$_4$− 0.25Na$_2$CO$_3$													
1	300	61.08	60.14	0.20	0.00	22.16	19.86	6.58	6.06	8.20	20.33	29.93	1.59
			98.46				**89.62**		**92.10**	**13.66**	**33.86**	**49.84**	**2.65**
2	350	62.06	57.70	0.07	0.05	23.03	16.31	6.59	5.82	4.92	12.36	35.56	4.92
			92.97				**70.82**		**88.32**	**8.52**	**21.38**	**61.57**	**8.52**
3	400	64.01	51.55	0.10	0.06	23.12	14.69	6.01	5.74	3.39	5.83	19.95	22.28
			80.83				**63.54**		**86.34**	**6.58**	**11.34**	**38.77**	**43.30**
4	450	65.76	51.80	0.07	0.37	23.23	13.81	6.80	5.71	1.78	6.12	12.24	31.59
			78.72				**59.45**		**83.97**	**3.44**	**11.83**	**23.65**	**61.68**

mass to the assumed temperature was equal to 0.5 h and the polycondensation time at constant temperature to 1.0 h. The process was carried out in a vertical pipe furnace with automatic control system. For carrying away the waste gases, such as ammonia, carbon dioxide, and water vapor, some air was passed through the reactor.

The analytical control included the determination of total (5 N HCl soluble—directly or after melting with Na$_2$CO$_3$) and water-soluble P$_2$O$_5$ content of the products as well as the separation of the individual forms of P$_2$O$_5$, which include ortho, pyro, tripoly, and higher condensed phosphates (H. Mateňko, Institute of Organic Chemistry, Gliwice, unpublished results, 1975). For quantitative determination of the phosphates a colorimetric vanadium—molybdenum method was employed (Marczenko, 1979). The ammonium content was determined with ion selecting ammonium electrode (Orion Research, 1979). Gasometric analysis was used for determination of carbon dioxide content (Struszyński, 1954) and flame photometric technique for estimation of sodium, calcium, and potassium content (Połuektov, 1969). Diffraction analysis was used for the qualitative identification of crystalline condensation products.

RESULTS AND DISCUSSION

In the studies on condensation of potassium, sodium, and calcium dihydrogen phosphates the effect of process temperature and composition of the initial mixture were determined in relation to (a) the water solubility of the final compositions in relation to total P$_2$O$_5$ content, (b) the fraction of ortho, pyro, tripoly, and higher condensed forms of P$_2$O$_5$ in the products in relation to water-soluble P$_2$O$_5$ content, and (c) their structure and qualitative composition.

In the first stage the effect of temperature on the condensation degree of single potassium, sodium, and calcium dihydrogen phosphate was determined (systems 1−3). The obtained results have confirmed the earlier data (Corbridge and Tromans, 1958; Gimblett, 1963; McIntosh and Jablonski, 1956). Then the dehydration course of dihydrogen phosphates with the parallel decomposition of NH$_4$H$_2$PO$_4$ and the desorption of
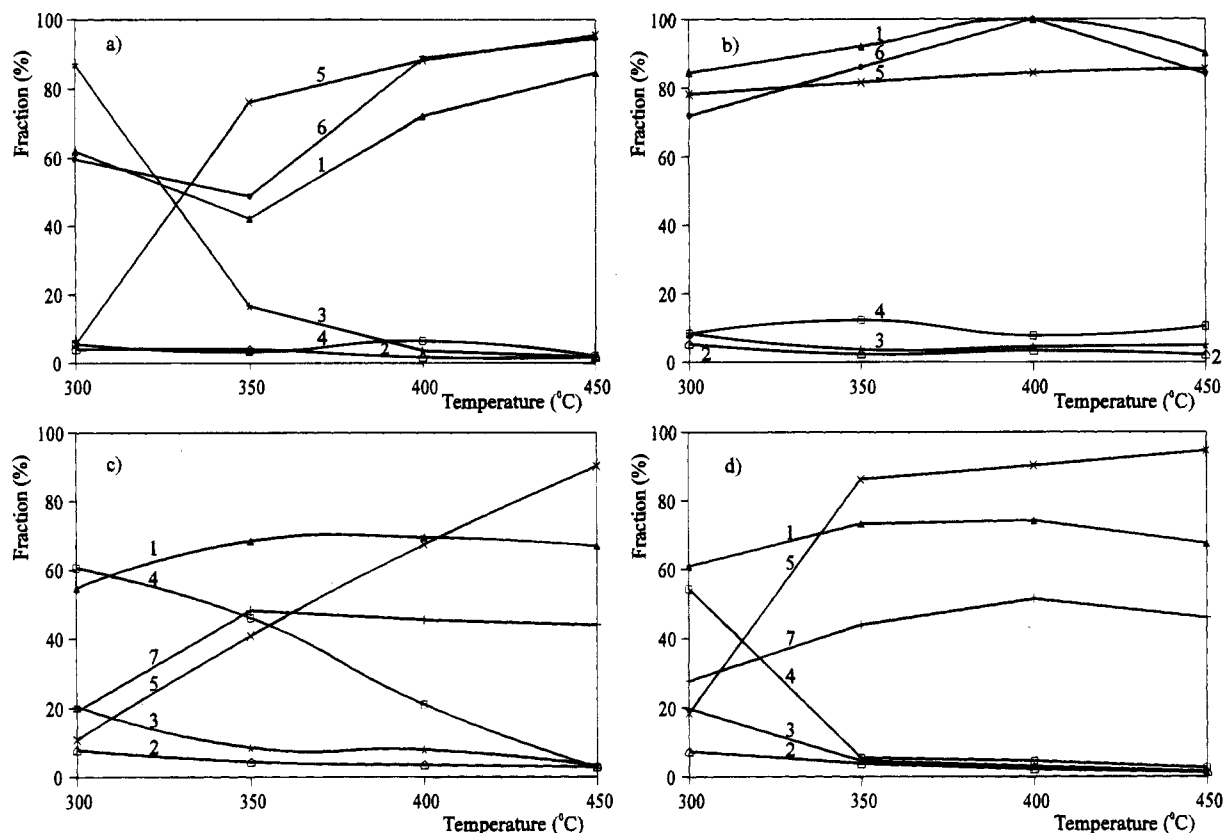
Figure 1. Influence of temperature on the fraction of individual water-soluble condensation products of systems (a) NaH_2PO_4, (b) $NH_4H_2PO_4-0.5Na_2CO_3$, (c) $NH_4H_2PO_4-0.5CaCO_3$, and (d) $NH_4H_2PO_4-0.5CaO$. 1, Water-soluble P_2O_5; 2, ortho, 3, pyro, 4, tripoly, 5, higher condensed phosphates; 6, water-soluble Na^+; 7, water-soluble Ca^{2+}.

Table 3. Condensation of Dihydrogen Phosphates

system	temp (°C)	P₂O₅ total	P₂O₅ water soluble	NH₃	CO₂	K total	K water soluble	Ca total	Ca water soluble	ortho	pyro	tripoly	higher condensed phosphates
$KH_2PO_4-0.25Ca(H_2PO_4)_2\cdot$ H_2O													
1	300	60.15	57.89			22.40	20.83	6.35	5.32	9.27	24.88	21.95	1.76
			96.18				**92.99**		**83.78**	**16.02**	**43.01**	**37.94**	**3.04**
2	350	59.79	45.56			23.10	18.13	6.36	2.49	4.63	9.99	14.07	16.88
			76.20				**78.48**		**39.15**	**10.16**	**21.93**	**30.88**	**37.06**
3	400	63.03	42.26			23.75	17.76	6.50	2.71	2.88	4.82	7.69	27.87
			67.05				**74.78**		**41.69**	**6.81**	**11.41**	**18.20**	**65.95**
4	450	62.90	37.07			24.26	16.56	6.58	2.62	0.98	1.95	5.10	28.44
			58.93				**68.26**		**39.82**	**2.64**	**5.26**	**13.76**	**76.72**
$KH_2PO_4-0.5NH_4H_2PO_4-$ $0.25CaCO_3$													
1	300	58.67	46.23	1.60	0.036	22.18	17.62	5.54	2.39	8.95	17.91	17.00	2.38
			78.80				**79.44**		**43.14**	**19.36**	**38.74**	**36.77**	**5.15**
2	350	57.06	45.74	1.68	0.041	22.04	18.20	5.71	2.60	9.20	14.91	9.20	11.50
			80.16				**82.57**		**45.53**	**20.11**	**32.60**	**20.11**	**25.14**
3	400	61.22	44.73	1.48	0.102	22.63	18.09	5.62	2.43	13.13	11.67	8.26	11.67
			73.06				**79.94**		**43.24**	**29.35**	**26.09**	**18.47**	**26.09**
4	450	60.51	42.74	0.97	0.102	21.27	16.90	5.41	2.24	15.40	8.95	9.94	8.45
			70.63				**79.45**		**41.40**	**36.03**	**20.94**	**23.26**	**19.77**
$KH_2PO_4-0.5NH_4H_2PO_4-$ $0.25CaO$													
1	300	58.67	57.76	1.38		20.96	17.82	5.73	4.18	6.48	23.94	24.94	2.39
			98.45				**85.02**		**72.95**	**11.22**	**41.45**	**43.18**	**4.14**
2	350	62.07	42.96	0.76		22.88	17.68	6.33	2.09	2.78	6.99	12.13	20.05
			69.21				**77.27**		**33.02**	**6.47**	**16.27**	**28.24**	**46.67**
3	400	62.50	38.29	0.13		23.47	17.10	6.40	1.80	0.96	1.58	2.38	33.37
			61.26				**72.86**		**28.13**	**2.51**	**4.13**	**6.22**	**87.15**
4	450	61.52	32.72	0.11		23.43	16.58	5.90	0.97	2.80	1.86	1.40	26.65
			53.19				**70.76**		**16.44**	**8.56**	**5.68**	**4.28**	**81.45**

ammonia from the reaction mixture was investigated (systems 4–6).

The products from dehydration of KH_2PO_4, within the temperature range 350–450 °C were insoluble in water

Table 4. Main Reaction Products for Particular Systems

no.	system	temp (°C) 300	350	400	450
1	KH_2PO_4	KH_2PO_4 $K_3H_2P_3O_{10} \cdot H_2O$ $(KPO_3)_n$		$(KPO_3)_n$	
2	NaH_2PO_4	$Na_2H_2P_2O_7$		$(NaPO_3)_3$ $(NaPO_3)_nII$	
3	$NH_4H_2PO_4-0.5Na_2CO_3$	$(NaPO_3)_nII^a$		$(NaPO_3)_3$ $(NaPO_3)_nII$	
4	$Ca(H_2PO_4)_2 \cdot H_2O$	$CaH_2P_2O_7$ $Ca_3H_2(P_2O_7)_2 \cdot H_2O^a$ $\delta Ca(PO_3)_2^a$		$\gamma Ca(PO_3)_2$ $Ca_4H_2(P_3O_{10})_2$ $\beta Ca(PO_3)_2$	
5	$NH_4H_2PO_4-0.5CaCO_3$	$(NH_4)_3H_2P_3O_{10} \cdot H_2O$ $CaH_2P_2O_7$		$NH_4CaP_3O_9 \cdot H_2O$ $NH_4CaP_3O_9$ $(NH_4PO_3)_4$	
6	$NH_4H_2PO_4-0.5CaO$	$(NH_4)_3H_2P_3O_{10}^a$ $Ca_3H_2(P_2O_7)_2 \cdot H_2O^a$		$NH_4CaP_3O_9 \cdot H_2O$ $NH_4CaP_3O_9$ $(NH_4PO_3)_4$	
7	$KH_2PO_4-NaH_2PO_4$	amorphous		$KNa_2(PO_3)_3^a$ $Na_3K(PO_3)_4^a$	
8	$KH_2PO_4-0.5NaH_2PO_4$		amorphous	$KNa_2(PO_3)_3$ $Na_3K(PO_3)_4$ $(KPO_3)_n$	
9	$KH_2PO_4-NH_4H_2PO_4-0.5Na_2CO_3$		amorphous	$KNa_2(PO_3)_3^a$ $Na_3K(PO_3)_4^a$	
10	$KH_2PO_4-0.5NH_4H_2PO_4-0.25Na_2CO_3$	amorphous	$(KPO_3)_n{}^a$	$KNa_2(PO_3)_3$ $Na_3K(PO_3)_4$ $(KPO_3)_n$	
11	$KH_2PO_4-0.5(0.25)Ca(H_2PO_4)_2 \cdot H_2O$	amorphous		$KCa(PO_3)_3$ $(KPO_3)_n$ $\delta Ca(PO_3)_2$	
12	$KH_2PO_4-NH_4H_2PO_4-0.5CaCO_3$		$(NH_4, K)H_2PO_4, KH_2PO_4$ $K_2CaP_2O_7, Ca_2KPO_3O_{10}$		
13	$KH_2PO_4-0.5NH_4H_2PO_4-0.25CaCO_3$		$KH_2PO_4, K_2CaP_2O_7$ $Ca_2KP_3O_{10}, (KPO_3)_n$		
14	$KH_2PO_4-NH_4H_2PO_4-0.5CaO$		amorphous	$KCa(PO_3)_3$ $(KPO_3)_n$ $\delta Ca(PO_3)_2$	
15	$KH_2PO_4-0.5NH_4H_2PO_4-0.25CaO$	$K_2CaP_2O_7$		$(KPO_3)_n$ $KCa(PO_3)_3$ $\delta Ca(PO_3)_2^a$	

^{a} Small amount of component.

(Table 1). The fraction of soluble P_2O_5 was equal to 50% only in the product obtained at 300 °C, which contained considerable amounts of ortho along with pyro and tripoly phosphates. This result was confirmed with X-ray analysis (Table 4). In the composition produced at 300 °C KH_2PO_4, $K_3H_2P_3O_{10} \cdot H_2O$, and $(KPO_3)_n$ (Kurrol's salt) were identified. This last compound was the only crystalline phase in potassium polyphosphates obtained at higher condensation temperatures (>300 °C).

The water solubility of condensation products of NaH_2PO_4 changed from 62% to 85% for temperatures 300, 400, and 450 °C (Figure 1a). At 350 °C this value was far less and was equal to 42%. The main condensation product obtained at 300 °C was pyrophosphate (the fraction being about 92%). As the temperature increased, its content rapidly decreased parallel to the rise of the higher condensed phosphates fraction. In final products (Table 4) there were identified besides $Na_2H_2P_2O_7$ (at 300 °C) two forms of sodium polyphosphates: one insoluble with the chain structure $(NaPO_3)_n$-II and the other one soluble $(NaPO_3)_nI$, i.e. ring trimetaphosphate $(NaPO_3)_3$ (in the range 350–450 °C).

In the case of dehydration of $NH_4H_2PO_4$ with parallel replacement of the NH_4^+ ion with Na^+ (introduced as Na_2CO_3) the reaction degree of substrates was high. In the products of condensation the content of ammonia varied from 2% (at 300 °C) to 0.2% (at higher temperature >300 °C), the amount of carbonate was in-

significant—about 0.4% CO_2. The water solubility of the products changed in the range 300–450 °C from 85% to 100% (Figure 1b). The fraction of higher condensed phosphate (with a small amount of tripolyphosphate) was considerable, unlike the condensation product of single NaH_2PO_4.

It was found from X-ray analysis (Table 4) that the dehydration products obtained at 300 °C were amorphous and those above that temperature were crystalline. Sodium ring trimetaphosphate $(NaPO_3)_3$ was identified as the main component together with insoluble $(NaPO_3)_nII$.

By the condensation of $Ca(H_2PO_4)_2 \cdot H_2O$ it was found that only the product obtained at 300 °C was quite water-soluble (about 70%). Pyrophosphate occurs as the main constituent (about 75% P_2O_5). By the higher reaction temperature the products were insoluble not only in water but also in 5 N HCl (Table 1). The results of X-ray analysis indicated that $CaH_2P_2O_7$ occurred mainly together with small amounts of $Ca_3H_2(P_2O_7)_2 \cdot H_2O$ and $\delta Ca(PO_3)_2$ as a crystalline phase in the product obtained at 300 °C. At higher temperatures $\gamma Ca(PO_3)_2$ was identified as a main component together with $Ca_4H_2(P_3O_{10})_2$ and $\beta Ca(PO_3)_2$ (Table 4).

An essential change of the properties of condensation products of $Ca(H_2PO_4)_2$ was observed in the presence of NH_4^+ ion in the reaction mixture. By the dehydration of ammonium dihydrogen phosphate in the presence of $CaCO_3$ the replacement degree of NH_4^+ ion with Ca^{2+}

ion was not so high as in the case of Na_2CO_3. The rest of ammonia in the condensation products (from 300 °C) was equal to 3–5% NH_3, and the decomposition degree of CO_3^{2-} was equal to about 90% (residue of CO_2 equal to 2%). The condensation products were about 55–70% water-soluble and completely soluble in 5 N HCl, unlike solid phases resulting from dehydration of single Ca-$(H_2PO_4)_2$. Tripoly and pyro phosphates (by 300 °C) and higher condensed phosphates in the range from 350 to 450 °C were the main water-soluble forms (Figure 1c). X-ray analysis showed mainly the presence of NH_4-$CaP_3O_9 \cdot H_2O$, $NH_4CaP_3O_9$, and $(NH_4PO_3)_4$ with a small fraction of $CaHPO_4$, $(NH_4)_4H_2P_4O_{13}$, $Ca_3H_2(P_2O_7)_2 \cdot H_2O$, and $\gamma Ca(PO_3)_2$ in the compositions obtained at temperatures in the range from 350 to 450 °C. Crystalline $(NH_4)_3H_2P_3O_{10} \cdot H_2O$ and $CaH_2P_2O_7$ and trace amounts of previously mentioned compounds were present in the condensation product formed at 300 °C (Table 4).

Likewise, by the use of CaO to replace ammonia from the reaction mixture the water solubility of condensation products was equal to 60–75% and the fractions of the individual forms of P_2O_5 were similar (Figure 1d). The data obtained from the qualitative identification of final phases were identical, too. In the composition produced at 300 °C the amount of the crystalline phase was small and only trace amounts of $(NH_4)_3H_2P_3O_{10}$ and Ca_3H_2-$(P_2O_7)_2 \cdot H_2O$ were identified (Table 4).

The aim of the second stage of our studies was determining the effect of Na^+ or Ca^{2+} ion additions on the condensation course of KH_2PO_4 (systems 7–11). It was found that the dehydration products of the mixture of KH_2PO_4 and NaH_2PO_4 (mole ratios equal to 1:1 and 1:0.5) were all water-soluble within the whole investigated temperature range in the first case and dependent upon reaction temperature 100–75% in the second, unlike the compositions produced from single components (Figure 2a; Table 2). The content of ortho, pyro, and tripoly phosphates decreased gradually with the rise of temperature to the advantage of higher condensed forms. Their fraction of water-soluble P_2O_5 decreased from 70% to 50%. The products obtained for the first ratio of substrates were amorphous with a small amount of crystalline phase as $KNa_2(PO_3)_3$ and $Na_3K(PO_3)_4$ at temperatures of 400–450 °C and for the other only ratio within the lower temperature range (300 and 350 °C). The products obtained at 400 and 450 °C were crystalline, and the following compounds were identified: $KNa_2(PO_3)_3$, $Na_3K(PO_3)_4$, and $(KPO_3)_n$ (Table 4).

By the replacement of ammonia by means of Na^+ ion in the mixture of KH_2PO_4 with $NH_4H_2PO_4$ and Na_2CO_3 with two different mole ratios of substrates (1:1:0.5 and 1:0.5:0.25) a high water solubility of the resulting composition was found regardless of temperature for the first case (Figure 2b; Table 2), while with twice as little fraction of additives the solubility was gradually decreasing (from 100% at 300 °C to 80% at 450 °C). The degree of reaction of sodium carbonate with ammonium dihydrogen phosphate was very high (about 0.2% NH_3 and 0.4% CO_2). The fraction of individual water-soluble poly and higher condensed phosphates changed with temperature. An increase of the higher condensed forms of P_2O_5 content was observed in products with a decrease of the lower polymerized ones. X-ray diffraction analysis showed (Table 4), to a large extent, an amorphous structure of the solid phase obtained over the whole temperature range for first ratio of substrates and for the other only within the lower temperature
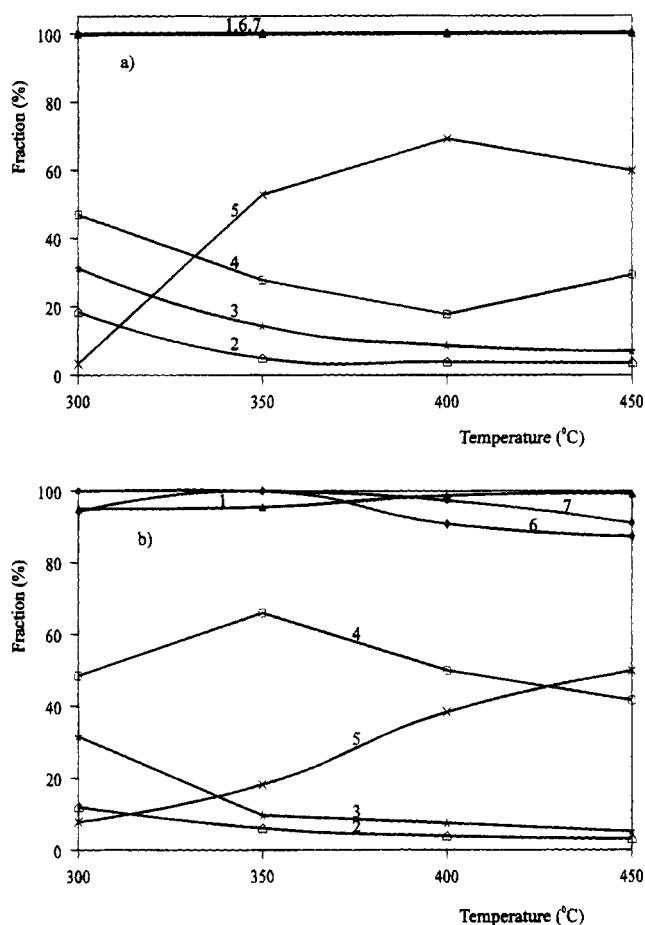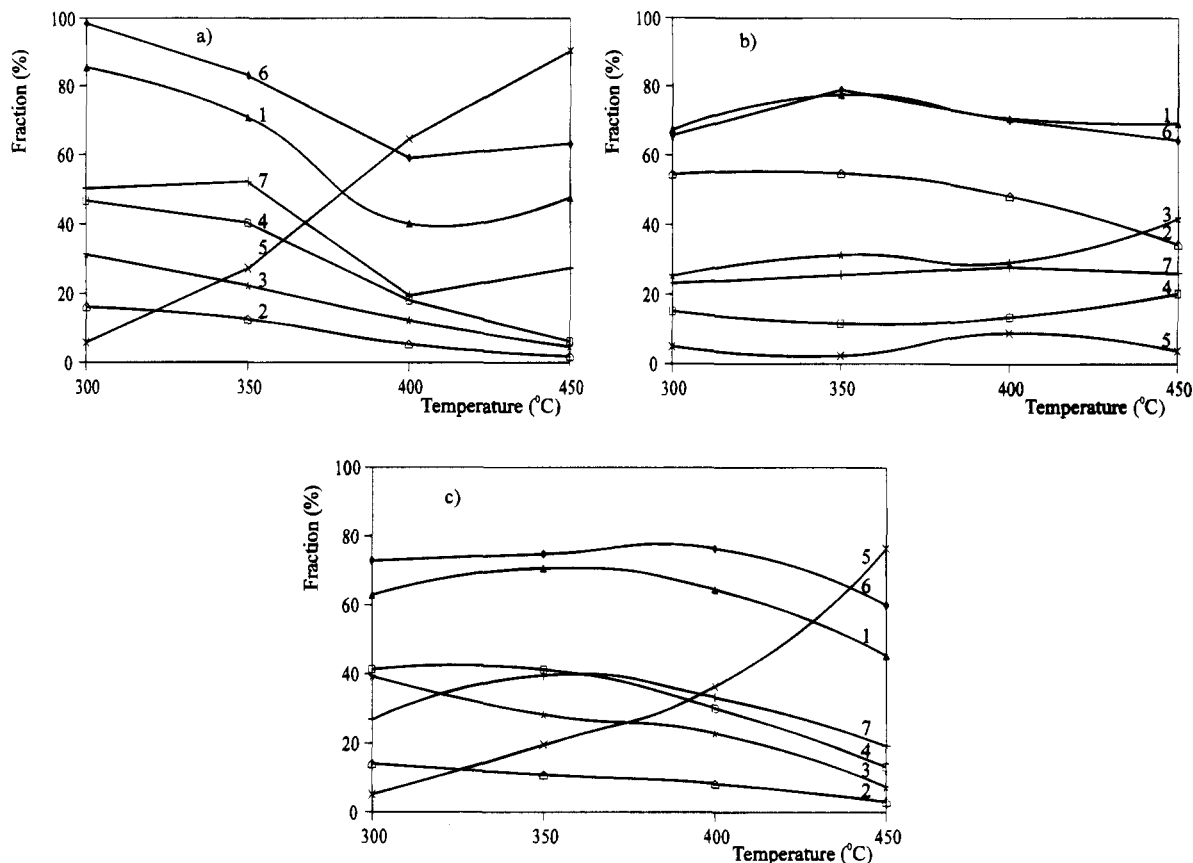

Figure 2. Influence of temperature on the fraction of individual water-soluble condensation products in the systems (a) KH_2PO_4–NaH_2PO_4 and (b) KH_2PO_4–$NH_4H_2PO_4$–$0.5Na_2CO_3$. 1, Water-soluble P_2O_5; 2, ortho, 3, pyro, 4, tripoly, 5, higher condensed phosphates; 6, water-soluble K^+; 7, water-soluble Na^+.

range (300–350 °C). Whereas the products obtained at 400 and 450 °C were crystalline and $KNa_2(PO_3)_3$, Na_3K-$(PO_3)_4$, and $(KPO_3)_n$ phases were identified. The above system in comparison with a pure one (KH_2PO_4–NaH_2-PO_4) differed in the fraction of individual P_2O_5 forms.

By condensation of a KH_2PO_4 and $Ca(H_2PO_4)_2$ mixture (mole ratio of the substrates accordingly 1:0.5 and 1:0.25) the water solubility of products was much higher in comparison with the condensation products of the individual constituents (Figure 3a; Table 3). This value was temperature-dependent. For the first ratio with the rise of temperature a decrease from 85% to 40% was observed and for the other one from 96% to 60%. With the increase of temperature, the fraction of water-soluble higher condensed phosphates increased rapidly from 6% to 90% in the first case and from 3% to 76% in the second one. The product obtained at 300 °C contained a small amount of crystalline phase, but the interpretation of results was difficult (Table 4). In compositions produced in the temperature range from 350 to 450 °C the following crystalline phases were identified: $KCa(PO_3)_3$, $(KPO_3)_n$, $\delta Ca(PO_3)_2$.

The condensation of potassium and calcium dihydrogen phosphate mixture, in which $Ca(H_2PO_4)_2$ was an intermediate of $NH_4H_2PO_4$ and $CaCO_3$ reaction, was carried out as previously mentioned with two different mole ratios of substrates. The degree of calcium carbonate decomposition was high (residue of CO_2 equal to 0.4%). In the final phases (with mole ratio of substrates 1:1:0.5), however, a considerable amount of

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Figure 3. Influence of temperature on the fraction of individual water-soluble condensation products in the systems (a) $KH_2PO_4-0.5Ca(H_2PO_4)_2$, (b) $KH_2PO_4-NH_4H_2PO_4-0.5CaCO_3$, and (c) $KH_2PO_4- NH_4H_2PO_4-0.5CaO$. 1, Water-soluble P_2O_5; 2, ortho, 3, pyro, 4, tripoly, 5, higher condensed phosphates; 6, water-soluble K^+; 7, water-soluble Ca^{2+}.

Table 5. Collection of Regression Equation Coefficients and Their Statistical Estimation for Particular Condensation Systems

| no.	system	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}	R^2	F	$F_{0.05}$
1	$KH_2PO_4-Ca(H_2PO_4)_2-H_2O$	762.63	−487.53	−3.61	730.47	0.0043	1.67	−522.49		−0.298	−0.0017	0.96	21	4.73
2	$KH_2PO_4-NH_4H_2PO_4-Na_2CO_3-H_2O$	609.19	770.69	−5.26	337.75	0.0168	−4.37	−234.27	−0.00002	−0.425	0.0059	0.98	53.43	5.14
3	$KH_2PO_4-NH_4H_2PO_4-CaCO_3-H_2O$	−337.79	600.63	2.12	701.37	−0.0027	−4.15	−435.33		−0.456	0.0056	0.97	29.31	4.74
4	$KH_2PO_4-NH_4H_2PO_4-CaO-H_2O$	599.54	867.64	−5.62	684.69	0.0185	−5.56	−546.94	−0.00002	0.166	0.0067	0.96	16.01	5.14

ammonia (3.5–4.8% NH_3) was found. The water solubility of P_2O_5 in the products obtained in this way was equal to 70–80% (Figure 3b). The condensation degree of dihydrogen phosphates was low in comparison with the pure system without ammonium ion. The prevailing water soluble form of P_2O_5 was orthophosphates, the fraction of which ranged from 55% to 34% depending on the process temperature, whereas the fraction of individual condensed phosphates changed only to a small degree with temperature. In the products as the main crystalline phases (Table 4), irrespective of dehydration temperature, there were identified $(NH_4,K)H_2PO_4$, KH_2PO_4, $K_2CaP_2O_7$, and $Ca_2KP_3O_{10}$ with trace contents of $(KPO_3)_n$, $KCa(PO_3)_3$, and $\delta Ca(PO_3)_2$.

The dehydration of the above mixture, with a lower mole ratio of $KH_2PO_4/NH_4H_2PO_4/CaCO_3$ of 1:0.5:0.25, proceeded similarly (Table 3). The residual content of ammonia in the produced compositions was equal to 1% NH_3 and CO_2 content to about 0.1%. The condensation degree was higher in comparison with previous ones. With increase of temperature a rise of higher condensed phosphate fraction was observed with a parallel de-

crease of pyro and tripoly form fractions. X-ray diffraction analysis showed (Table 4) that the products have contained, as previously, KH_2PO_4, $K_2CaP_2O_7$, Ca_2-KP_3O_{10}, and $(KPO_3)_n$ together with a small content of $(NH_4,K)H_2PO_4$, $KCa(PO_3)_3$, and $\delta Ca(PO_3)_2$.

In the next experiments, calcium carbonate in reagent mixture was replaced with calcium oxide with mole ratios of $KH_2PO_4/NH_4H_2PO_4/CaO$ as 1:1:0.5 and 1:0.5:0.25. The content of ammonia in the final products varied, depending on temperature, from 3% at 300 °C to 0.3% at 450 °C for the first case and, in the second, from 1.4% to 0.1%. The water solubility was temperature-dependent and with rise of temperature decreased: for the former ratio from 63% to 45% and for the latter one from 100% to 53% (Figure 3c; Table 3). The changes in condensed P_2O_5 forms composition with temperature were very clear: an increase of higher condensed phosphate fraction with a decrease of lower ones.

The degree of condensation of this mixture of phosphates was similar to that of the pure system: KH_2-$PO_4-Ca(H_2PO_4)_2$. The products obtained with a higher

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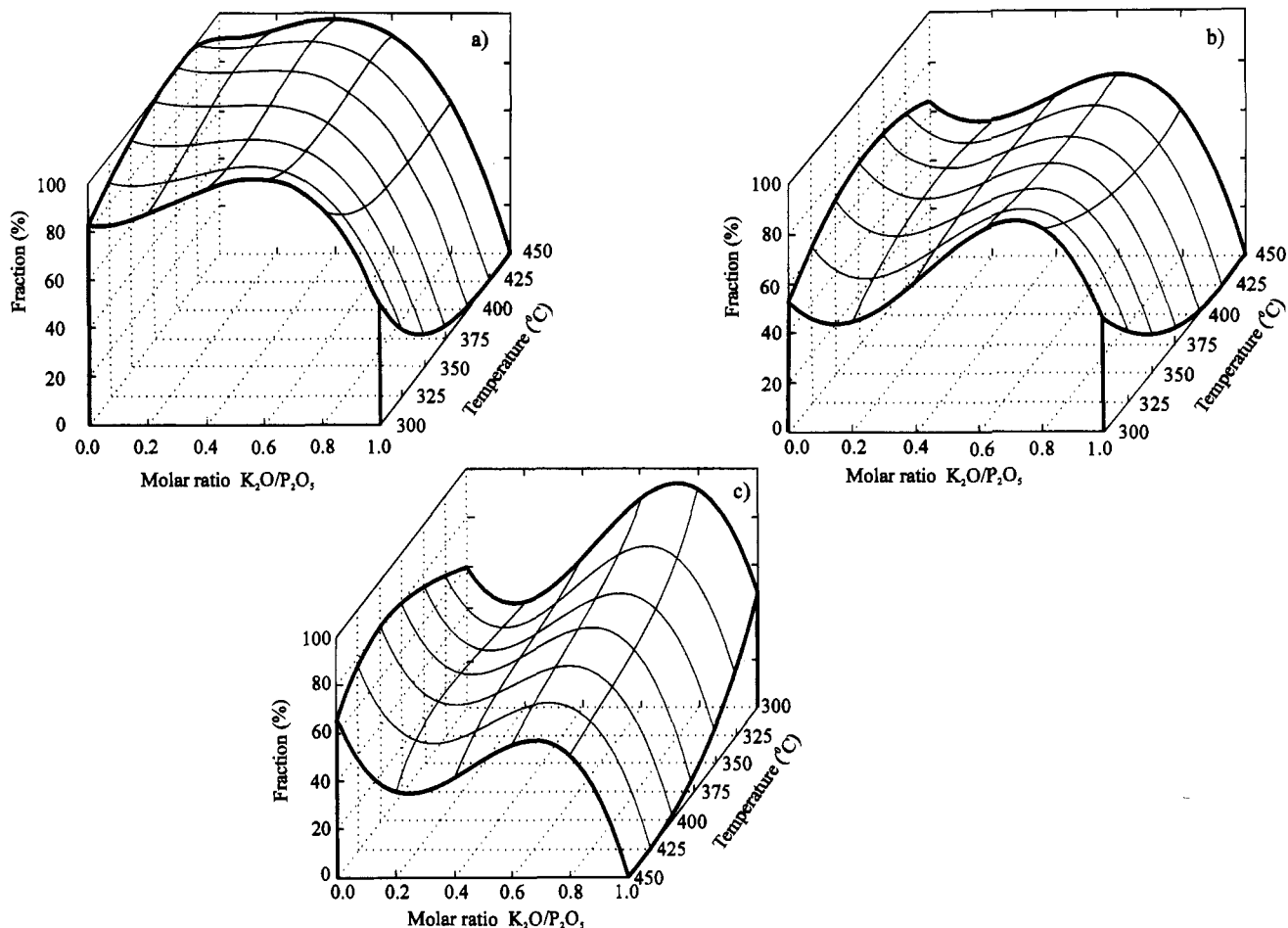
Figure 4. Influence of temperature and composition of initial mixture on the fraction of water-soluble P_2O_5 in condensation products in the systems (a) $KH_2PO_4-NH_4H_2PO_4-Na_2CO_3$, (b) $KH_2PO_4-NH_4H_2PO_4-CaCO_3$, and (c) $KH_2PO_4-NH_4H_2PO_4-CaO$.

fraction of additives ($NH_4H_2PO_4-CaO$) at 300–350 °C were amorphous with a small contribution of crystalline phase, whereas at the higher temperature the crystalline phase occurring in the products was mainly $KCa(PO_3)_3$ together with $(KPO_3)_n$ and $\delta Ca(PO_3)_2$ with trace contents of $(NH_4)_4H_2P_4O_{13}$ and $(NH_4)_2H_2P_2O_7$. In the latter case there was mainly identified $(KPO_3)_n$ along with $KCa(PO_3)_3$ and a small contribution of $\delta Ca(PO_3)_2$ at temperatures of 350–450 °C, while at 300 °C K_2-CaP_2O_7 was the dominant phase with trace contents of the compounds mentioned previously (Table 4).

The dependences obtained, determining the influence of the initial mixture composition and the dehydration temperature upon the most characteristic property of the products, i.e. their water solubilities, were expressed mathematically by an incomplete polynomial regression of the third order of two independent variables in the form

$$Y = b_1 + b_2X_1 + b_3X_2 + b_4X_1^2 + b_5X_2^2 + b_6X_1X_2 + \\ b_7X_1^3 + b_8X_2^8 + b_9X_1^2X_2 + b_{10}X_1X_2^2$$

where X_1 is the molar ratio of K_2O/P_2O_5 in substrates (0–1), X_2 is the temperature (300–450 °C), and Y is the fraction of water-soluble P_2O_5 in the products (%).

In Table 5 are compiled equation coefficients, for particular systems, calculated for independent variables and their statistical estimation where R^2 is the square of multiple correlation coefficients, F is the calculated value of Snedecor's F test for regression equation, and $F_{0.05}$ is the boundary value of F test for significance level $\alpha = 0.05$.

The values of regression function coefficients were determined by minimization of the squares of deviation sum. The correlation significance was verified with the use of Snedecor's F test.

The suitable dependence described by regression equations is exemplified in Figure 4. For a definite molar ratio of particular dihydrogen phosphates in a system (as K_2O/P_2O_5) a maximum of solubility was stated.

CONCLUSIONS

The results show that the solubility of condensed potassium–sodium phosphates was strictly connected with their structure. They were, depending on the mole ratio of both initial substances, amorphous products only with traces of crystalline phase in comparison with the insoluble Kurrol's salt $(KPO_3)_n$. At the lower temperature range (at 300 °C) pyro and tripoly phosphates and at higher temperatures (350–450 °C) tripoly and higher condensed forms were the main final reaction products. The fraction of higher condensed forms decreased with an increase of KH_2PO_4 in relation to NaH_2PO_4 in the initial mixture (350–450 °C). These statements refer to dehydration in both the $KH_2PO_4-NaH_2PO_4$ and $KH_2PO_4-NH_4H_2PO_4-Na_2CO_3$ systems.

In the case of replacement of NH_4^+ ion with Ca^{2+} (as $CaCO_3$ or CaO) the water solubility of the condensation products was much higher in comparison with those obtained from pure calcium dihydrogen phosphate. This positive influence can be attributed to the presence of some ammonium ion in final reaction products.

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By the condensation of KH_2PO_4 and $Ca(H_2PO_4)_2$ mixtures, there was observed a positive interaction of calcium and potassium ions upon water solubility of the produced polyphosphates. The compositions obtained from the dehydration process of single dihydrogen phosphates of K^+ and Ca^{2+} were insoluble in water (above 350 °C), while the solubility of potassium calcium polyphosphates produced from the mixture of both salts was significant higher.

A lower condensation degree was found in case of replacement of NH_4^+ ion with Ca^{2+} (as $CaCO_3$) in the mixture of KH_2PO_4 and $NH_4H_2PO_4$. Independent of process temperature the orthophosphate content of products was high. However, in this system there also appeared to be a positive interaction of K^+ and Ca^{2+} ions upon water solubility of produced double polyphosphates. More favorable results were obtained by replacing ammonium ion with Ca^{2+} ion in the form of CaO.

The results show that in most favorable dehydration conditions, that is, adequate mole ratio of K^+ ion to Na^+ ion in substrates mixture ($KH_2PO_4-NaH_2PO_4$ or $KH_2PO_4-NH_4H_2PO_4-Na_2CO_3$), all water-soluble compositions could be obtained suitable for manufacturing liquid PK fertilizers (Figure 4a). The identification of linear chain compounds as entire reaction condensation products shows the possibility of using them as complexing agents of nutrient microelements [initial investigation by Grzmil and Trojanowski (1992)].

By carrying out the dehydration process of potassium and ammonium dihydrogen phosphate in the presence of Ca^{2+} ion, it is possible to obtain products of controlled water solubility for use as controlled-release fertilizers (Figure 4b,c).

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