CO-EXISTENCE OF PHASES IN THE SYSTEM $CaO—Na_2O—P_2O_5$

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Co-existence of phases was studied in the CaO *and* Na_2O *- rich concentration region of the system by means of X-ray phase analysis. The results have not proved the existence of two phases described in literature as* $CaNa_4(PO_4)_2$ *and* $CaNa_6P_2O_9$.

INTRODUCTION

The present study is a part of a wider program dealing with the co-existence of phases in the five-component oxide system $CaO—MgO—Na_2O—P_2O_5—SiO_2$.

Table I

Melting temperatures of compounds present in the system $CaO—Na_2O—P_2O_5$

Compound	Abbreviated symbol a)	Character of melting b)	Melting point temperature °C	References
$NaPO_3$	NP	C	627	5, 6, 9, 14,15
$Ca(PO_3)_2$	CP	C	c	4, 13, 14, 15
$CaNa(PO_3)_3$	C2NP	I	749	15
$CaNa_4(PO_3)_6$	CN2P	C	738	14, 15
$Na_5P_3O_{10}$	N5P3	I	620	5, 6, 9
$Ca_7P_5O_{32}$	C7P5	I	d	1, 4
$Na_4P_2O_7$	N2P	C	955	5, 6, 7, 8, 9
$Ca_2P_2O_7$	C2P	C	1355	1, 2, 3, 16
$CaNa_2P_2O_7$	CNP	—	e	9, 12, 13,16
Na_3PO_4	N3P	C	f	7, 8, 9, 18, 19
$Ca_3(PO_4)_2$	C3P	C	g	1, 2, 3, 10
$CaNa_4(PO_4)_2$	CN2P	C	1750	9, 13, 16
$Ca_5Na_2(PO_4)_4$	C5NP2	S	h	10
$CaNaPO_4$	C2NP	C	1850	10, 16, 22
$Ca_4P_2O_9$	C4P	I	1720	1, 2, 3
$CaNa_6P_2O_9$	CN3P	C	1800	9, 13, 16

a) C = CaO, N = Na_2O, P = P_2O_5

b) C — congruent melting, I — incongruent melting, S — phase stable at subsolidus temperatures.

c) Considerable differences in melting temperatures: 965 °C [15], 984 °C [13].

d) The compound exists within the temperature interval of ca 800 °C—900 °C [1], the bottom existence limit is not specified.

e) Two independent descriptions of the melting of this substance are given: congruent melting at 1060 °C [12], incongruent melting at 814 °C [9], [13], [16].

f) Two independent data on the melting temperature are given: DTA — 1583 °C [8], [9], hot stage microscopy — 1512 °C [7].

g) Melting temperature is specified by values 1777 °C [2] and 1800 °C [3].

k) The substance is stable at subsolidus temperatures (1000 °C to 1400 °C) [10].

The three-component system $CaO—Na_2O—P_2O_5$ has so far been studied by numerous authors [1—16]. Some of the data given on the substances present in the system are summarized in Table I. The co-existence of phases is to be treated within the concentration range of up to 50 mol percent P_2O_5 only. The proper experimental work is concerned only with the CaO- and MgO-rich concentration range of the system.

As shown by literary data, the co-existence of phases in the system $CaO—Na_2O—P_2O_5$ can be illustrated by the diagram in Fig. 1. The binary subsystems $CaO—P_2O_5$ and $Na_2O—P_2O_5$ have already been well investigated [1—9]. Among the ternary compositions of the system $CaO—Na_2O—P_2O_5$, Ando and Matsuno [10] studied the connecting line $Ca_3(PO_4)_2—CaNaPO_4$. Kaprálik and Potančok [11] found that the $CaO—CaNaPO_4$ connecting line represents a quasi-binary system. The connecting line $Na_4P_2O_7—Ca_2P_2O_7$ was studied by Bergman and Goryacheva [12] as well as by Berak and Znamierowska [9], [13], the connecting line $NaPO_3—Ca(PO_3)_2$ by Morey [14] and Grenier, Martin and Durif [15]. Co-existence of phases in the other concentration ranges of the system $CaO—Na_2O—P_2O_5$ (Fig. 1) follows from the papers by Berak and Znamierowska [9], [13], [16], who carried out extensive studies of phase equilibria over numerous sections through the system within the concentration region limited by the compounds $Na_3PO_4—NaPO_3—Ca(PO_3)_2—Ca_2P_2O_7—CaNaPO_4—CaNa_6P_2O_9$.

Within the framework of their investigations of the system $Ca(PO_3)_2—Na_2O$, Berak and Znamierowska [9], [13] also described two new ternary compounds $CaNa_4(PO_4)_2$ and $CaNa_6P_2O_9$ which are also included in Fig. 1.

EXPERIMENTAL

The samples were prepared by evaporating the solutions obtained by mixing together aqueous solutions of $Ca(NO_3)_2$, $NaNO_3$ and $NH_4H_2PO_4$. The standard solutions were mixed in proportions by volume so as to ensure the required chemical composition of the sample.

The following reagents were employed in the preparation of the solutions:
$CaCO_3$ A.R., ignited at 450 °C,
$NaNO_3$ A.R., ignited at 250 °C,
$NH_4H_2PO_4$ A.R., dried at 100 °C
HNO_3 A.R.

The solutions were evaporated to dry residues. The intermediate product obtained was heated at 600 °C in order to eliminate volatile components and to decompose the nitrates present. The final heating was effected in air at temperaturs listed in Table II.

The crystalline phases arising in the samples were identified by means of powder diffraction patterns provided by the Philips 1540 diffractometer employing CuKα radiation. The lattice constants were refined by the least squares method using the Lindquist and Wengelin program [17].

RESULTS AND DISCUSSION

The samples investigated and the results of phase analyses together with the respective temperature regimes are specified in Table II. The chemical compo-

sition of samples was selected so as to maintain the simple molar ratios of the oxides in question. The chemical composition of each sample is expressed by means of the corresponding figurative point in the three-component system $CaO—Na_2O—P_2O_5$. Abbreviated symbols designating the respective compounds are employed in Table II.

Table II

Phase analysis results for the system $CaO—Na_2O—P_2O_5$

Sample	Sample composition a)	Stable connecting line b)	Temperature regime [°C/hr]	Identified crystalline phases
1	C2N3P2	C2NP-N2P	800/5	N2P, β C2NP
2	C2N9P5	C2NP-4N2P	600/5	N2P, βC2NP
3	CN12P4	4N3P-C	1000/3	α-N3P, C
4	CN6P2	2N3P-C	1000/3	α-N3P, C
5	CN3P	N3P-C	1000/3	α-N3P, C
6	C4N3P	N3P-4 C	1000/3	C, αN3P
7	CN2P	C3P-2 N3P	700/4	α-N3P, β-C2NP
8	C2NP	2C3P-N3P	700/4	β-C2NP
9	C6NP	C2NP-4 C	700/4	C, βC2NP
10	C6NP2	C5NP2-C	1050/2	C5NP2, C
11	C6NP2	C4P-C2NP	700/4	C4P*, βC2NP

a) The same form of abbreviated designation is used as in Table I and Fig. 1. The sample composition is specified by figurative points in the C-N-P system related to molar proportions of the components.

b) The concentrations of samples are 'visualized' by specifying the connecting line which has been proved stable. The ratio of the end terms of this connecting line characterizes a sample of chemical composition identical with the corresponding figurative point (column II of the Table).

*) The symbol C4P represents hydroxyl apatite in this case.

Various ignition temperatures were selected which ensured complete reacting of the components. The extent of solid solutions was not followed.

The results of the present study with respect to co-existence of phases in the sub-solidus region of the system $CaO—Na_2O—P_2O_5$ indicate to certain changes which are included in the revided diagram in Fig. 2.

In the concentration range of the system between the meta- and pyrophosphate connecting lines two connecting lines were formally supplemented, namely that for $CaNa_2P_2O_7—Ca_7P_5O_{32}$ (CNP—C7P5) and that for $CaNa_2P_2O_7—CaNa(PO_3)_3$ (CNP—C2NP3). The co-existence of none of the two couples of phases was proved; however , it follows from the phase co-existence known so far. The connecting line $CaNa_2P_2O_7—Ca_7P_5O_{32}$ is obviously significant only at those temperatures where the $Ca_7P_5O_{32}$ compound is stable.

Hill, Faust and Reynolds [4] reported that this compound exists within the temperature range of 915 °C to 980 °C only. Kreidler and Hummel [1] found this compound to be stable even at 800 °C, i.e. that its stability is not ruled out even at temperatures lower than 800 °C.

The connecting line $CaNa_2P_2O_7—CaNa(PO_3)_3$ is based on a study by Grenier, Martin and Durif [15] who described the compound $CaNa(PO_3)_3$ following a new evaluation of the $NaPO_3—Ca(PO_3)_2$ phase diagram.

The main difference between Figs. 1 and 2 is that the latter does not include compounds $CaNa_6P_2O_9$ and $CaNa_4(PO_4)_2$ described by Berak and Znamierowska

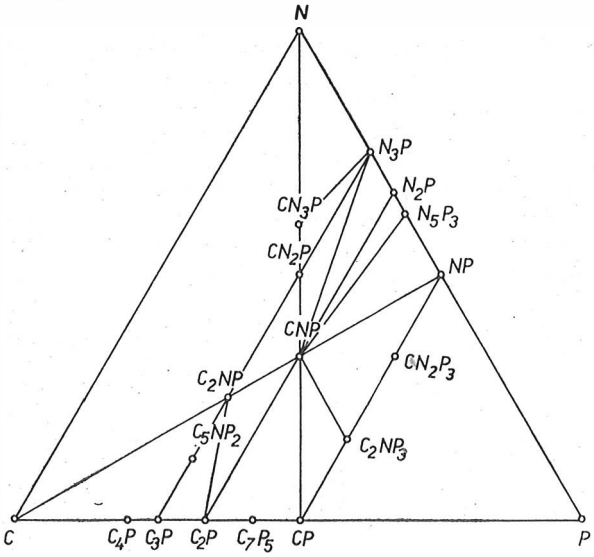

Fig. 1. Co-existence of phases in the system $CaO–Na_2O–P_2O_5$ *(on the basis of literary data);* *) *The compounds present in the system are designated by abbreviated symbols* (C = CaO, N = Na_2O, P = P_2O_5, C_2NP = 2CaO . Na_2O . P_2O_5 = $2CaNaPO_4$, *etc.*).

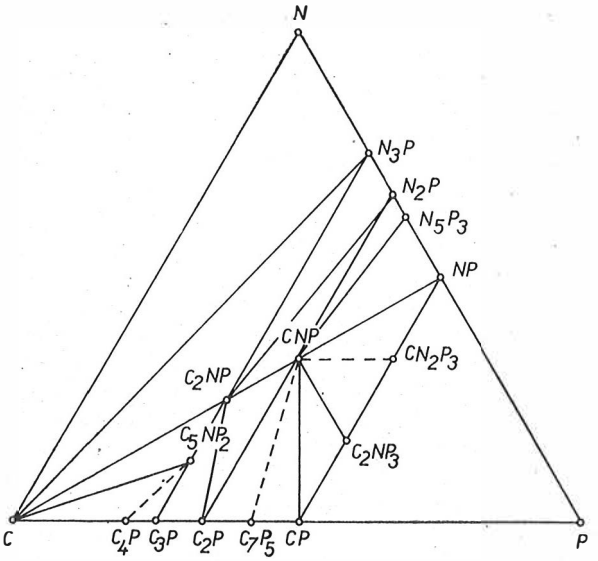

Fig. 2. Revised co-existence of phases in the system $CaO–Na_2O–P_2O_5$;
*) *Co-existence of phases marked by dashed connecting lines was not established exprimentally.*
**) *Phases* C5NP2 *co-exist when* C5NP2 *has its existence region* [*10*] *and when hydroxyl apatite is not stable* [*1*], [*20*].

[9], [13], [16]. For the compound $CaNa_6P_2O_9$, Berak and Znamierowska [13] even specify its indexed powder diffraction record, according to which the substance crystallized in the hexagonal system and has lattice constants $a = 12.06$ Å, $c = 18.85$ Å.

According to the present study the samples corresponding to the compounds considered by their compositions lie in the two-component regions. The sample having chemical composition $CaNa_6P_2O_9$ consists of CaO and α-Na_3PO_4. Both these phases are cubic with a face-centered unit cell and their mixture exhibits a relatively simple diffraction record. The error in the identification of this powder diffraction record by Berak and Znamierowska [13] is probably due to the fact that at the time of their work the diffraction data of α-Na_3PO_4 were not yet known.

This Na_3PO_4 modification was described by Palazzi and Rézy [18] who designated it as γ-Na_3PO_4, as well as by Majling [19]. Table III brings the so-far most complete list of its diffraction lines.

Table III

List of α-Na_3PO_4 diffraction lines ($a_0 = 7.419$ (1) Å)

hkl	d_{hkl} (exp.) [Å]	d_{hkl} (calc) [Å]	I/I_0	hkl	d_{hkl} (exp.) [Å]	d_{hkl} (calc) [Å]	I/I_0
111	4.2100	4.2837	50	620	1.1740	1.1731	4
200	3.7200	3.7097	15	533	1.1320	1.1315	< 1
220	2.6300	2.6232	100	444	1.0710	1.0709	1
222	2.1440	2.1418	5	551	1.0390	1.0389	< 1
400	1.8550	1.8458	22	624	0.9917	0.9915	1
422	1.5150	1.5145	17	731	0.9663	0.9659	< 1
333	1.4290	1.4279	3	660	0.8750	0.8743	< 1
440	1.3120	1.3116	5	840	0.8295	0.8294	< 1
531	1.2540	1.2541	2				

*) The powder diffraction record was taken using silicon as internal standard at a goniometer scanning rate of 1/4 ° 2 Θ/min. The Na_3PO_4 sample was heated for 5 hours at 800 °C. The phase stabilization was effected by adding 1 % by wt. of CaO. The intensities were measured by counting the pulses.

The authors of the present study have determined the lattice constants of the two phases comprising the sample having the chemical composition $CaNa_6P_2O_9$ and obtained the following values: $a_1 = 4.8107(5)$ Å, $a_2 = 7.401(3)$ Å. These values represent the lattice constants of CaO and α-Na_3PO_4 respectively. Na_3PO_4 was found in all the samples analyzed in its high-temperature modification α which means that the presence of Ca^{2+} ions has a stabilizing effect on this modification. The powder diffraction record presented by Corbridge and Tromans [21] represents the same Na_3PO_4 modification.

Another sample corresponding by its chemical composition to $CaNa_4(PO_4)_2$ was likewise found to comprise two phases, namely β-$CaNaPO_4$ and α-Na_3PO_4.

Fig. 2 includes still another change as compared with Fig. 1, i.e. that in place of the connecting line $CaNa_2P_2O_7$—Na_3PO_4 (CNP—N3P) given in Fig. 1, connecting line $CaNaPO_4$—$Na_4P_2O_7$ (C2NP—N2P) is given as a stable one

in Fig. 2. The co-existence of phases $CaNaPO_4$ and $Na_4P_2O_7$ was established according to phase analysis of samples 1 and 2 (Table II).

The co-existence of phases within the concentration region of the system delimited by the compounds CaO—$Ca_3(PO_4)_2$—$CaNaPO_4$ has not so far been investigated. One of the boundary systems, $Ca_3(PO_4)_2$—$CaNaPO_4$ was studied in detail by Ando and Matsuno [10]. Extensive formation of solid solutions between α and α-$Ca_3(PO_4)_2$ and α-$CaNaPO_4$ takes ploce in the sub-solidus region of this system. Above 1000 °C there is the existence region of a solid solution to which the composition $Ca_5Na_2(PO_4)$ has been ascribed and which has been designated as phase A by the above authors. Its indexed diffraction recording indicates that the structure of this phase may be regarded as a superstructure derived from α-$CaNaPO_4$.

When a sample of the figurative point C6NP2 (Table II), situated at the point of intersection of connecting lines $CaNaPO_4$—$Ca_4P_2O_9$ (C2NP—C4P) and $Ca_5Na_2(PO_4)_4$—CaO (C5NP2—C) had been ignited in vacuo ($p = 10^{-3}$ torr) at 1050 °C, the reaction product comprised CaO and a phase which has been identified as phase A [10].

The co-existence of phases implied in Fig. 2 is related to conditions where hydroxyl apatite is not stable [1], [20]. In such cases CaO will co-exist with the corresponding solid solution on the connecting line $Ca_3(PO_4)2$—$CaNaPO_4$ within this concentration region of the system. When the C6NP2 had been annealed in air the reaction product contained hydroxyl apatite and β-$CaNaPO_4$. Several unidentified low-intensity diffraction lines were present in the diffraction record of this sample.

The ignition temperatures had to be increased in order to ensure that the reactions would yield the required phases. The powder diffraction records from this concentration region of the system could therefore not be reliably identified owing to the similarities of the structures and the resulting extensive formation of solid solutions.

CONCLUSION

The paper deals with the co-existence of phases in the system CaO—Na_2O—P_2O_5 on the basis of results obtained so far in the studies of phase equilibria and phase co-existence in the system, as well as on the basis of experimental results obtained by the authors within the framework of the present study.

The conclusions of the present study are in disagreement with study [9] according to which the system includes two ternary compounds, namely $CaNa_6P_2O_9$ and $CaNa_4(PO_4)_2$. Both these compounds have been identified as mixtures of two phases.

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KOEXISTENCIA FÁZ V SÚSTAVE $CaO—Na_2O—P_2P_5$

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Predložená práca sumarizuje doterajšie poznatky o koexistencii fáz a fázových rovnováhach v sústave $CaO—Na_2O—P_2O_5$ v jej koncentračnej oblasti s obsahom $P_2O_5 \leqq 50$ mólových %. Práca tiež zahrňuje vlastné štúdium koexistencie fáz v niektorých zvolených a sporných rezoch sústavou (Tab. II) pri subsolidusových teplotách.

Výsledkom práce je diagram na obr. 2, ktorý zahrňuje koexistenciu fáz včetně vlastného štúdia a je konfrontovaný s diagramom koexistencie fáz podľa doterajších literárnych poznatkov (obr. 1).

Zmeny v koexistencii fáz vyplývajú hlavne zo skutočnosti, že v tejto práci, na základe difrakčnej analýzy práškových vzoriek, sa nepotvrdila existencia dvoch ternárnych zlúčenín doteraz v literatúre uvádzaných ako $CaNa_4(PO_5)_2$ a $CaNa_6P_2O_9$. Vzorky odpovedajúcich stechiometrií boli identifikované ako zmesi dvoch fáz a to β-$CaNaPO_4$ a α-Na_3PO_4 v prvom prípade a CaO a α-Na_3PO_4 v druhom prípade. Práškový difrakčný záznam α-Na_3PO_4 je uvedený.

K príprave vzoriek sa použili zriedené vodné roztoky ($Ca(NO_3)_2$, $NaNO_3$ a NH_4H_2PO). Výsledné roztoky, ktoré zabezpečovali požadované koncentrácie vzoriek sa odparovali do suchých zvyškov. Medzi produkty sa zahrievali pri 600 °C a neskoršie pri špecifikovaných teplotách.

Obr. 1. Koexistencia fáz v sústave $CaO–Na_2O–P_2O_5$ *(na základe literárnych údajov);*
*) *zlúčeniny prítomné v sústave sú označené skrátenými symbolmi* ($C = CaO$, $N = Na_2O$, $P = P_2O_5$, $C_2NP = 2CaO \cdot Na_2O \cdot P_2O_5 = 2CaNaOP_4$ *a pod).*

Obr. 2. Revidovaná koexistencia fáz v sústave $CaO–Na_2O–P_2O_5$;
*) *koexistencia fáz znázornená čiarkovanými spojnicami nebola exprimentálne určovaná,*
**) *fázy* C_5NP_2 *a* C *koexistujú za podmienok, kedy má oblasť existencie* C_5NP_2 [*10*] *a nie je stabilný hydroxylapatit* [*1*], [*20*].

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СОСУЩЕСТВОВАНИЕ ФАЗ В СИСТЕМЕ $CaO—Na_2O—P_2O_5$

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В предлагаемой работе суммируются до сих пор полученные данные о сосуществовании фаз и о фазовых равновесиях в системе $CaO—Na_2O—P_2O_5$ в области ее концентрации с содержанием $P_2O_5 \leqq 50$ молярных процентов. В работу включено также само рассмотрение сосуществования фаз в некоторых избранных и спорных сечениях системой (таб. 2) при температурах ниже солидуса.

Результатом работы является диаграмма на рис. 2, включающая сосуществование фаз и полученная на основе собственного изучения. Наша диаграмма сопоставляется с диаграммой сосуществования фаз согласно доступным данным по литературе (рис. 1).

Изменения сосуществования фаз вытекают прежде всего из факта, что в этой работе, на основе дифракционного анализа порошкообразных образцов, не подтвердилось существование двух тернарных соединений, приводимых до сих пор в литературе как $CaNa_4(PO_4)_2$ и $CaNa_6P_2O_9$. Образцы соответствующих стехиометрий были установлены как смеси двух фаз, а именно $\beta—CaNaPO_4$ и $\alpha—Na_3PO_4$ в первом случае, и CaO и $\alpha—Na_3PO_4$ во втором случае. Порошковая дифракционная запись $\alpha—Na_3PO_4$ приводится.

Для получения образцов применялись разбавленные водные растворы $Ca(NO_3)_2$, $NaNO_3$ и $NH_4H_2PO_4$. Полученные в конечном итоге растворы, обеспечивавшие требуемые концентрации образцов, упаривались до сухих остатков. Промежуточные продукты нагревались при 600 °C и позже при уточненных температурах.

Рис. 1. Сосуществование фаз в системе $CaO—Na_2O—P_2O_5$ *(на основе линейных данных); *) соединения, присутствующие в системе, обозначены сокращенными символами* ($C = CaO$, $N = Na_2O$, $P = P_2O_5$, $C_2NP = 2CaO \cdot Na_2O \cdot P_2O_5 = 22CaNaPO_4$ *и т. п.*).

Рис. 2. Пересмотренное сосуществование фаз в системе $CaO—Na_2O—P_2O_5$; **) сосуществование фаз, изображенное штрихованными соединяющими, экспериментально не определялось, **) фазы* C_5NP_2 и C *сосуществуют при условии наличия области сосуществования* C_5NP_2 [10] *и нестабильности гидроксилапатита* [1], [20].