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THE EFFECT OF $NaPO_3$ ON PHASE COMPOSITION IN THE SYSTEM $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—Na_2O.P_2O_5$ IN RELATION TO BASIC REFRACTORIES

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The concentration part of the system $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—Na_2O . P_2O_5$, *which always contains the* MgO *phase, was found to contain 3 phosphate compounds, namely* $MgNaPO_4$, $MgCaNa_2(PO_4)_2$ *and* $CaNaPO_4$ *in co-existence with the adjacent phases at subsolidus temperatures.* $NaPO_3$ *reacts preferentially with* CaO, *either free or bound to low-melting* Ca*-phases and in the system there arises high-melting* $CaNaPO_4$ *which forms solid solution* $Ca_{2-x}Na_x(PO_4)_x(SiO_4)_{1-x}$.

In terms of rising $NaPO_3$ *concentration the system was found to contain 14 independent 6-phase combinations of univariant equilibria, the* MgO *phase of which is still thermodynamically stable with the phosphate phases mentioned above. The subsystem* $MgO—2CaO . SiO_2—MgO . Al_2O_3—MgO . Fe_2O_3—2CaO . Na_2O . P_2O_5$ *represents a limiting cross section through the optimum* $NaPO_3$ *concentrations in the main system* $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—Na_2O . P_2O_5$ *which is significant from the point of view of phosphate bond in basic refractories.*

Introduction

The study of phosphate phases in the oxide system $MgO—CaO—SiO_2—Al_2O_3—Fe_2O_3—Na_2O . P_2O_5$ is motivated by the use of $NaPO_3$ as an addition to sintered magnesite (containing CaO, Fe_2O_3, Al_2O_3, SiO_2) for the purpose of improving the thermomechanical properties of basic refractories.

Sintered magnesite can be simulated by means of the five-component oxide system $MgO—CaO—SiO_2—Fe_xO_y—Al_2O_3$. After adding $NaPO_3$ to the given system the former reacts with the components of the latter at high temperatures, producing phosphate phases. The presence of phosphate phases brings about changes in the initial phase composition and thus affects the physico-chemical properties of the system.

The present paper is concerned with determining the co-existence of the phases, namely in such a concentration volume of the system $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—Na_2O . P_2O_5$ in which MgO co-exists with the respective phases at subsolidus temperatures. A problem formulated in this manner would require investigation of a considerably large number of samples in the 6-component system. For this reason, on the basis of available literature data on the systems $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3$ [1], $Mg—CaO—Na_2O . P_2O_5$ [2] and $MgO—CaO—SiO_2—Na_2O . P_2O_5$ [3] it was suggested to study the co-existence of phases in its four 4-component subsystems $MgO—CaO—SiO_2—Na_2O . P_2O_5$, $MgO—CaO—Al_2O_3—Na_2O . P_2O_5$, $MgO—CaO—Fe_2O_3—Na_2O . P_2O_5$ and $CaO—Al_2O_3—Fe_2O_3—Na_2O . P_2O_5$ using the simplified thermodynamic assumption of phase stability on the basis of change in standard free enthalpy ΔG°_T for reaction between the phases in the subsystems in question.

When assuming that ΔC_p for the reactions is equal to zero, then $\Delta H^\circ_T \doteq \Delta H^\circ_{298\,\mathrm{K}}$ and similarly $\Delta S^\circ_T \doteq \Delta S^\circ_{298\,\mathrm{K}}$. Then

$$\Delta G^\circ_T \doteq \Delta H^\circ_{298\,\mathrm{K}} - T\Delta S^\circ_{298\,\mathrm{K}}.$$

The change in entropy $\Delta S^\circ_{298\,\mathrm{K}}$ in reactions between solid phases only is relatively small so that $T\Delta S^\circ_{298} \to 0$, and then $\Delta G^\circ_T \doteq \Delta H^\circ_{298\,\mathrm{K}}$, and spontaneous courses are exhibited only by exothermic reactions for which $\Delta H^\circ_{298\,\mathrm{K}} < 0$ (the Jandera rule).

The stability of the compounds in the four-component subsystems was assessed by means of the heats of formation ΔH°_f from oxides [1], [4], [5]. Since the values of heats of formation ΔH°_f for the phosphate compounds M_2NP ($2MgO \cdot Na_2O \cdot P_2O_5$) and CMNP ($CaO \cdot MgO \cdot Na_2O \cdot P_2O_5$) are unknown, their approximate values were derived on the assumption of the analogy

$$\frac{\Delta H^\circ_\mathrm{f}(M_2NP)}{\Delta H^\circ_\mathrm{f}(C_2NP)} \doteq \frac{\Delta H^\circ_\mathrm{f}(M_2S)}{\Delta H^\circ_\mathrm{f}(C_2S)};$$

then

$$\Delta H^\circ_\mathrm{f}(M_2NP) \doteq -413.6\ \mathrm{kJ/mol}.$$

Similarly,

$$\frac{\Delta H^\circ_\mathrm{f}(CMNP)}{\Delta H^\circ_\mathrm{f}(C_2NP)} \doteq \frac{\Delta H^\circ_\mathrm{f}(CMS)}{\Delta H^\circ_\mathrm{f}(C_2S)}$$

and thus

$$\Delta H^\circ_\mathrm{f}(CMNP) = -755.3\ \mathrm{kJ/mol}$$

Then, for example for the reaction

$$3\,MgO + SiO_2 + 1/2\,[Na_2O + P_2O_5] = M_2S + 1/2\,M_2NP$$

$$\Delta H^\circ_{298\,\mathrm{K}}\ \text{(from the left to the right)} = \Delta H^\circ_\mathrm{f}(M_2S) + 1/2\Delta H^\circ_\mathrm{f}(M_2NP)$$

$$\Delta H^\circ_{298\,\mathrm{K}} = -269.9\ \mathrm{kJ}.$$

The negative value of $\Delta H^\circ_{298\,\mathrm{K}}$ implies stability of both compounds on the right-hand side of the equation.

Using the possible reaction courses chosen for the individual subsystems it was possible to estimate the most probable phases assumed to be stable for a given oxidic composition (zero approximation). This assumption of phase stability was then verified experimentally in each particular case. The procedure has been proved highly effective.

EXPERIMENTAL

The samples of the required compositions were prepared by evaporation from solutions of $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Al(NO_3)_3$, $Fe(NO_3)_3$, $NaH_2PO_4 \cdot H_2O$ and SiO_2 sol (all of AR purity) which were mixed in the corresponding propor-

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* The following abbreviations were used in the present paper: M = MgO, S = SiO_2, C = CaO, F = Fe_2O_3, A = Al_2O_3, N = Na_2O, P = P_2O_5.

tions by volume. The solutions were evaporated dry and the resulting intermediate products were heated at 700 °C for the purpose of eliminating all the volatile components and decomposing the nitrates. The final heating of the samples was carried out in air at 1200 °C for a period of 10 hours (both temperature and time of heating were found satisfactory for the reactions to proceed completely).

The crystalline phases in the slowly cooled samples were identified by means of diffraction patterns of powdered samples, obtained at room temperature on the Philips 1540 diffractometer (CuKα radiation, scanning rate $\frac{1}{2}$ ° 2ϑ/min. The system MgO—CaO—SiO_2—Na_2O . P_2O_5.

The co-existence of the phsophate phases in the system MgO—CaO—SiO_2—NP was investigated in studies [2], [3]. The results have shown that in the given system MgO co-exists with three phosphate phases, M_2NP, CMNP and C_2NP. On the basis of thermodynamic calculations the authors of the present paper derived the probable existence of connecting lines C_3S—C_2NP, C_2S—C_2NP, C_3MS_2—C_2NP, CMS—C_2NP, M_2S—C_2NP, M_2S—CMNP, M_2S—M_2NP, MgO—M_2NP, MgO—CMNP, MgO—C_2NP and CaO—C_2NP using a comparison of the ΔH°_{298K} values for all the reactions considered in the system, and proving experimentally the thermodynamic stability of the compounds at the connecting lines. The experimental-results were used in the construction of a diagram of the co-existing phases in the region of the system MgO—CaO—SiO_2—NP characteristic by the presence of MgO at subsolidus temperatures (Fig. 1). The diagram does not concern solid solutions which are formed in the system by substitution of the PO_4^{3-} anions [3], [6], [7].

The diagram in Fig. 1 implies the existence of 7 possible 4-phase combina-

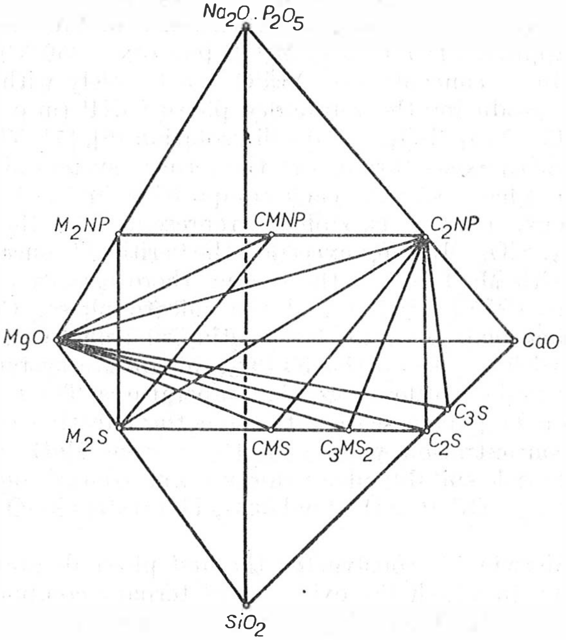

Fig. 1. Phase co-existence diagram for the concentration region of the system MgO—CaO—SiO_2—Na_2O . P_2O_5 *adjacent to the* MgO *peak.*

tions including the MgP phase and arising in the system $MgO—CaO—SiO_2—NP$ in dependence on the increasing $NaPO_3$ addition to the system $MgO—CaO—SiO_2$:
Initial phase composition

$MgO + CaO + C_3S$
↓
I. $MgO + CaO + C_3S + C_2NP$
↓
II. $MgO + C_3S + C_2S + C_2NP$
↓
III. $MgO + C_2S + C_3MS_2 + C_2NP$
↓
IV. $MgO + C_3MS_2 + CMS + C_2NP$
↓
V. $MgO + CMS + M_2S + C_2NP$
↓
VI. $MgO + M_2S + C_2NP + CMNP$
↓
VII. $MgO + M_2S + CMNP + M_2NP$

Among the discrete compositions in the $MgO—CaO—SiO_2—NP$ system there arise, apart from the 4-phase combinations, also 3-phase ones of univariant equilibria; of these, the concentration triangle $MgO—C_2S—C_2NP$ is significant with respect to the system $NaPO_3$ — magnesite (containing CaO and SiO_2). The concentration triangle $MgO—C_2S—C_2NP$ already includes the "critical" concentrations of $NaPO_3$ in the system $MgO—CaO—SiO_2—NP$, beyond which there is the region of co-existence of low-melting phosphate phases CMNP (approx. 1185 °C) and M_2NP (approx. 1050 °C) [2], [3].

Up to the "critical" concentration $NaPO_3$ reacts solely with CaO either free or bound to C_3S, producing the refractory phase C_2NP (m.p. 1830 °C) beside C_2S, or a type $(Ca, Na)_2 (PO_4, SiO_4)$ solid solution [6], [7]. The solid solution $(Ca, Na)_2 (PO_4, SiO_4)$ exists throughout the ternary system $MgO—C_2S—C_2NP$ as a homogeneous phase, so that each composition in the ternary system is reduced to a co-existence of two phases represented by the system $MgO—(Ca, Na)_2 (PO_4, SiO_4)$. Having exceeded the "critical" concentration, $NaPO_3$ reacts likewise with MgO and in the system there already arise low-melting phosphate phases CMNP, M_2NP and the silicate phases C_3MS_2 and CMS. The phase combinations containing low-melting phosphate and silicate phases are undesirable with respect to the $NaPO_3$—magnesite system as the phases form equilibrium regions of low eutectic temperatures. The subsystem $MgO—C_2S—C_2NP$ is a boundary section through the effective concentrations of $NaPO_3$ in the concentration volume of the system $MgO—CaO—SiO_2—NP$ and represents the sole suitable phase composition, comprising only the refractory phases MgO, C_2S, C_2NP as the final ones. The system $MgO—CaO—Al_2O_3—Na_2O . P_2O_5$.

Rankin and Merwin [8] constructed the first phase diagram of the system $MgO—CaO—Al_2O_3$ in which the existence of ternary compounds was not yet specified. More recently, Welch [9], using hot stage microscopy, determined in the system two new ternary compounds having the compositions $Ca_7MgAl_{10}O_{23}$ and $Ca_{25}Mg_8Al_{34}O_{84}$ (or $Ca_3MgAl_4O_{10}$). However, Majumdar [10] has not proved the existence of $Ca_7MgAl_{10}O_{23}$ and in his phase diagram specifies only the ternary compound $Ca_3MgAl_4O_{10}$ (C_3A_2M) with an incongruent point. Glasser and Marr [11] found that the ternary phase C_3A_2M does not co-exist in the system $CaO—MgO—SiO_2—Al_2O_3$ with C_2S and MA, so that the phase C_3A_2M cannot arise in phase composition in the magnesite system containing CaO and SiO_2.

A survey of studies [3], [8], [9], [10], [11] showed that in the system $MgO—CaO—Al_2O_3—NP$ the phase relationships along the connecting lines $MA—M_2NP$, MA—CMNP, $MA—C_2NP$, $CA—C_2NP$, $C_{12}A_7—C_2NP$ and $C_3A—C_2NP$

Table I

X-ray phase analysis of samples examined in the system $MgO—CaO—Al_2O_3—Na_2O \cdot P_2O_5$.

Connecting line	Sample composition mol %				Temperature regime °C/hr	Phases present
	MgO	CaO	Fe_2O_3	NP		
$MF—M_2NP$	60.0	—	20.00	20.00	850/10	MF, M_2NP
MF—CMNP	40.0	20.00	20.00	20.00	1200/10	MF, CMNP
$MF—C_2NP$	20.0	40.00	20.00	20.00	1200/10	MF, β C_2NP
$C_2F—C_2NP$	—	66.66	16.66	16.66	1200/10	C_2F, βC_2NP
$CF—C_2NP$	—	60.00	20.00	20.00	1200/10	CF, βC_2NP
$CF_2—C_2NP$	—	49.99	33.33	16.66	1200/10	CF_2, βC_2NP
$Fe_2O_3—C_2NP$	—	50.00	25.00	25.00	1200/10	Fe_2O_3, βC_2NP

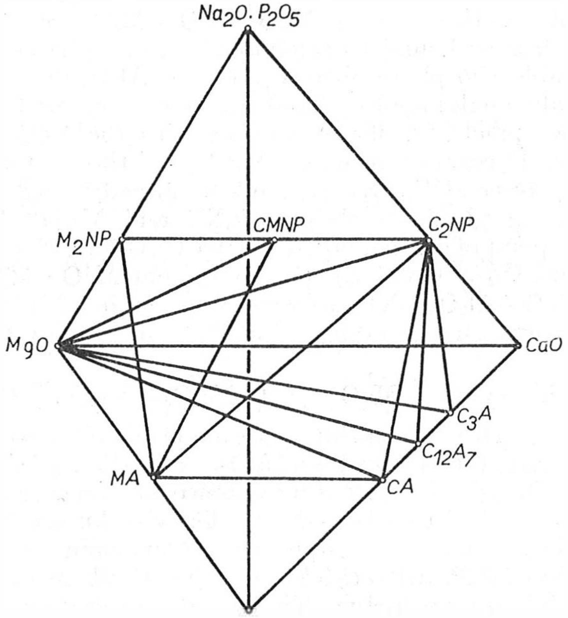

Fig. 2. Phase co-existence diagram for the concentration region of the system $MgO—CaO—Al_2O_3—Na_2O \cdot P_2O_5$ *adjacent to the* MgO *peak.*

were not known. The initial composition, temperature exposure and the phases present in the investigated samples from the binary parts of the system MgO—CaO—Al_2O_3—NP are listed in Tab. I. A diagram of the system of co-existing phases including the existence region of phase MgO is shown in Fig. 2.

The phase co-existence diagram in Fig. 2 allows to derive 6 possible 4-phase combinations of univariant equilibria, in all cases including the MgO phase, in terms of the increasing amount of $NaPO_3$ addition to the system MgO—CaO—Al_2O_3:

Initial phase composition

MgO + CaO + C_3A
↓
I. MgO + CaO + C_3A + C_2NP
↓
II. MgO + C_3A + $C_{12}A_7$ + C_2NP
↓
III. MgO + $C_{12}A_7$ + CA + C_2NP
↓
IV. MgO + CA + MA + C_2NP
↓
V. MgO + MA + C_2NP + CMNP
↓
VI. MgO + MA + CMNP + M_2NP

The change in the resulting phase composition in the system MgO—CaO—Al_2O_3—NP indicates that $NaPO_3$ within the concentration region MgO—CaO—CA—MA of the system MgO—CaO—Al_2O_3 reacts preferentially with CaO either free or bound to calcium aluminate phases CA, $C_{12}A_7$, C_3A, producing the stable phosphate phase C_2NP. The Al_2O_3 liberated by the reaction from the calciumaluminate phases further reacts with the MgO phase and the resulting spinel MA phase co-exists with the MgO and C_2NP ones. When this "critical" concentration of $NaPO_3$ in the system MgO—CaO—Al_2O_3—NP is exceeded the reaction begins already with the MgO phase, yielding low-melting phoshate phases CMNP and M_2NP. From the point of view of melting point of compounds MA (2105 °C), C_2NP (1830 °C), CA (1600 °C), C_3A (1535 °C) and $C_{12}A_7$ (1395 °C), the subsystem MgO—MA—C_2NP of the system MgO—CaO—Al_2O_3—NP appears very favourable with respect to eutectic temperatures in the system $NaPO_3$ —magnesite (containing CaO and Al_2O_3).

The system MgO—CaO—Fe_2O_3—Na_2O . P_2O_5

Berezhnoy [1], using his own and literature data [12]—[15], constructed a phase co-existence diagram for the system MgO—CaO—Fe_2O_3 in which the MgO co-exists with CaO, C_2F and MF. Co-existence of MgO with the phosphate phases in the system MgO—CaO—NP is likewise known [2]. An analysis of these studies has shown that the phase relations along the connecting lines MF—M_2NP, MF—CMNP, MF—C_2NP and C_2F—C_2NP in the system MgO—CaO—Fe_2O_3—NP are not known. The initial composition, the temperature exposure and the phases present in samples examined by X-ray phase analysis are listed in Table II. The diagram of phases co-existing at subsolidus temperatures in the system MgO—CaO—Fe_2O_3—NP is shown in Fig. 3.

Table II

X-ray phase analysis of samples examined in the system MgO—CaO—Fe_2O_3—$Na_2O \cdot P_2O_5$

Connecting line	Sample composition mol %				Temperature regime °C/hr	Phases present
	MgO	CaO	Al_2O_3	NP		
MA—M_2NP	60.0	—	20.00	20.00	850/10	MA, M_2NP
MA—$CMNP$	40.0	20.00	20.00	20.00	1200/10	MA, $CMNP$
MA—C_2NP	20.0	40.00	20.00	20.00	1200/10	MA, βC_2NP
CA—C_2NP	—	60.00	20.00	20.00	1200/10	CA, βC_2NP
$C_{12}A_7$—C_2NP	—	63.63	31.82	4.55	1200/10	$C_{12}A_7$, αC_2NP
C_3A—C_2NP	—	71.43	14.28	14.28	1200/10	C_3A, βC_2NP

The diagram of phase co-existence in the system MgO—CaO—Fe_2O_3—NP allows to derive 4 independent 4-phase combinations of univariant equilibria, always including the MgO phase in relation to the increasing amount of $NaPO_3$ addition to the system MgO—CaO—Fe_2O_3:
The initial phase composition

$$
\begin{array}{c}
MgO + CaO + C_2F \\
\downarrow \\
\text{I. } MgO + CaO + C_2F + C_2NP \\
\downarrow \\
\text{II. } MgO + C_2F + MF + C_2NP \\
\downarrow \\
\text{III. } MgO + MF + C_2NP + CMNP \\
\downarrow \\
\text{IV. } MgO + MF + CMNP + M_2NP
\end{array}
$$

The phase co-existence diagram in Fig. 3 also includes experimentally obtained results of phase co-existence along the connecting lines CF—C_2NP, CF_2—C_2NP and Fe_2O_3—C_2NP which in the system MgO—CaO—Fe_2O_3—NP delimitate the existence regions of the 4-phase combinations MF—C_2F—CF—C_2NP, MF—CF—CF_2—C_2NP and MF—CF_2—Fe_2O_3—C_2NP, but already without the MgO phase.

The change in the resulting phase composition in the system MgO—CaO—Fe_2O_3—NP implies that $NaPO_3$ reacts preferentially with CaO either free or bound to the calcium ferrite phase C_2F arising in the magnesite system (containing CaO and Fe_2O_3) as a low-melting undesirable phase. By reaction of $NaPO_3$ with the C_2F the latter is eliminated, liberating Fe_2O_3 which further reacts with the MgO phase yielding the spinel phase MF and C_2NP in co-existence with MgO. When this "critical" concentration of $NaPO_3$ in the system MgO—CaO—Fe_2O_3—NP is exceeded, $NaPO_3$ starts to react with the MgO phase only, yielding the low-melting phosphate phases $CMNP$ and M_2NP. On the basis of the melting points of the compounds MgO (2,825 °C), C_2NP (1.830 °C), MF (1,713°C) and C_2F (1.449 °C) the concentrations of $NaPO_3$ situated in the subsystem MgO—MF—C_2NP of the system MgO—CaO—Fe_2O_3—NP appear very favourable from the point of view of eutectic temperatures in the system $NaPO_3$ — magnesite (containing CaO and Fe_2O_3).

The system $CaO—Al_2O_3—Fe_2O_3—Na_2O \cdot P_2O_5$

Hansen, Brownmiller and Bogue [16] found in the system $CaO—Fe_2O_3—Al_2O_3$ the ternary compound C_4AF which had later on been called brownmillerite. According to [17]—[22] brownmillerite C_4AF forms a continuous series of solid solutions with C_2F. Sweyze [23] showed that within the concentration region $CaO—C_5A_3—C_2F$ of the system $CaO—Fe_2O_3—Al_2O_3$ the C_4AF phase was not a stoichiometrie compound, but merely one member of a series of solid solutions $Ca_2(Fe, Al)_2O_5$ stretching from composition C_2F up to composition C_6Al_2F. The terminal member od solid solutions C_6Al_2F exhibits the properties of a compound. Newkirk and Thwaite [24] studied the concentration region $CaO—CA—C_2F$ and found the main conclusions reached by Sweyze [23] as correct. On the other hand, Schlaudt and Roy [25] established in the $C_3A—C_3F$ section a solid solution having the composition $Ca_2Al_{1.08}Fe_{0.92}O_5$ in co-existence with CaO, which was very close to brownmillerite C_4AF. The composition C_4AF has so far been considered as an intermediate compound in a series of solid solutions along the connecting line between C_2F and the hypothetical compound C_2A, and this point od view has also been respected in the present study.

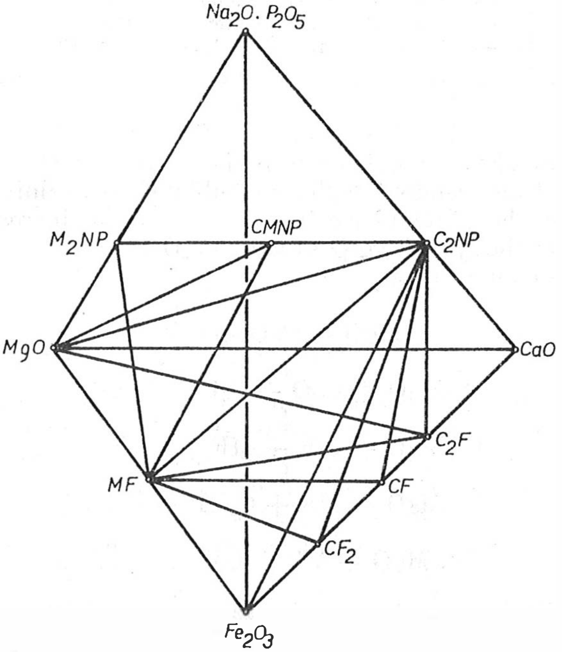

Fig. 3. Phase co-existence diagram for the concentration region of the system $MgO—CaO—Fe_2O_3—Na_2O \cdot P_2O_5$ *adjacent to the* MgO *peak.*

Literature [1] specifies co-existence of C_4AF with phases arising in the subsystem $MgO—CaO—SiO_2—Fe_2O—Al_2O_3$ of the main system MgO—CaO—

—SiO_2—Fe_2O_3—Al_2O_3—NP. It has been shown that in the concentration region of the main system, containing the MgO phase, it is necessary to determine the co-existence of C_4AF with the phosphate phases M_2NP, CMNP and C_2NP. Similarly to the previous cases the stability of phases was assessed according to the H_{298K} values of the reactions

$$2\,MgO + 4\,CaO + Al_2O_3 + Fe_2O_3 + Na_2O + P_2O_5 = C_4AF + M_2NP \qquad (1a)$$

$$\Delta H^\circ_{298K} = -\,445{,}0\ \mathrm{kJ}$$

$$\begin{aligned}2\,MgO + 4\,CaO + Al_2O_3 + Fe_2O_3 + Na_2O + P_2P_5 &= MgO + 1/2\,MA + \\ &+ 1/2\,MF + \\ &+ 1/2\,C_4AF + C_2NP \qquad (1b)\end{aligned}$$

$$\Delta H^\circ_{298K} = -\,868{,}0\ \mathrm{kJ}$$

$$MgO + 4\,CaO + Al_2O_3 + Fe_2O_3 + Na_2O + P_2O_5 = C_4AF + CMNP \qquad (2a)$$

$$\Delta H^\circ_{298K} = -\,796{,}7\ \mathrm{kJ}$$

$$\begin{aligned}MgO + 5\,CaO + Al_2O_3 + Fe_2O_3 + Na_2O + P_2O_5 &= 1/2\,MgO + 1/4\,MA + \\ &+ 1/4\,MF + \qquad (2b) \\ &+ 3/4\,C_4AF + C_2NP\end{aligned}$$

$$\Delta H^\circ_{298K} = -\,868{,}3\ \mathrm{kJ}$$

$$6\,CaO + Al_2O_3 + Fe_2O_3 + Na_2O + P_2O_5 = C_4AF + C_2NP \qquad (3)$$

$$\Delta H^\circ_{298K} = -\,868{,}8\ \mathrm{kJ}$$

The negative values of ΔH°_{298K} in equations [1b], [2b] and [3] imply the only co-existence of C_4AF with the phosphate phase C_2NP. X-ray phase analysis also indicated the co-existence of C_4AF with the single phosphate phase C_2NP.

The phase co-existence diagram for the subsolidus region of the system CaO—Al_2O_3—Fe_2O_3—NP in Fig. 4 allows to derive 6 independent 4-phase combinations of univariant equilibria in which C_4AF co-exists with C_2NP : CaO—C_2F—C_4AF—C_2NP, CaO—C_3A—C_4AF—C_2NP, C_3A—$C_{12}A_7$—C_4AF—C_2NP, $C_{12}A_7$—CA—C_4AF—C_2NP, CA—CF—C_4AF—C_2NP, and CF—CF_2—C_4AF—C_2NP. Among these only four are possible in which MgO co-exists with each phase: CaO—C_2F—C_4AF—C_2NP, CaO—C_3A—C_4AF—C_2NP, C_3A—$C_{12}A_7$—C_4AF—C_2NP and $C_{12}A_7$—CA—C_4AF—C_2NP.

In the magnesite system (containing CaO, Fe_2O_3 and Al_2O_3) the present C_4AF phase acts as a low-melting one (m.p. 1415 °C). Its total elimination from the system is attained by reaction between $NaPO_3$ and C_4AF which produces the refractory phosphate phase C_2NP, liberates oxides Fe_2O_3 and Al_2O_3 which subsequently react with the MgO phase producing refractory spinel phases MF and MA in co-existence with MgO and C_2NP. According to studies [26]—[31] the MA and MF spinel phases form a series of solid solutions of the type Mg (Al, Fe)$_2$O$_4$. The solid solution Mg(Al, Fe)$_2$O$_4$ then arises in the concentration volume of the quarternary system MgO—MA—MF—C_2NP as a homogenous phase and each composition in the system acquires the character of co-existence of three phases represented by the system MgO—Mg (Al, Fe)$_2$O$_4$—C$_2$NP.

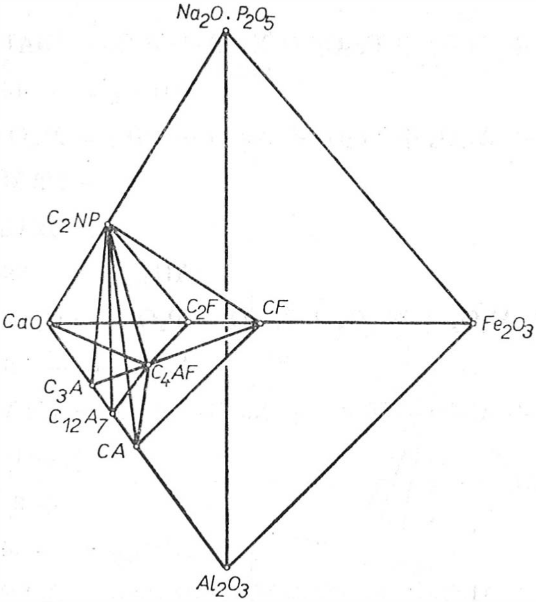

Fig. 4. Phase C$_4$AF *co-existence diagram for the concentration region of the system* CaO—Al$_2$O$_3$—Fe$_2$O$_3$—Na$_2$O . P$_2$O$_5$.

THE RESULTS AND DISCUSSION

The present study was concerned with determining the co-existence of phases in partial volumes of subsystems MgO—CaO—SiO$_2$—NP, MgO—CaO—Al$_2$O$_3$—NP, MgO—CaO—Fe$_2$O$_3$—NP and CaO—Al$_2$O$_3$—Fe$_2$O$_3$—NP of the main system MgO—CaO—Fe$_2$O$_3$—Al$_2$O$_3$—NP. An analysis of the results indicated to the existence of 14 independent 6-phase combinations of univariant equilibria in all the instances comprising the MgO phase. The C$_2$F phase is known not to co-exist with the calcium aluminate phases C$_3$A, C$_{12}$A$_7$ and CA. Then in the system MgO—CaO—SiO$_2$—Fe$_2$O$_3$—Al$_2$O$_3$—NP with a molar ratio CaO: :SiO$_2$ $>$ 2 there are two possible resulting subsystems including free MgO and CaO for the derivation of the mechanism of subsequent changes in phase composition in terms of increasing additions of NaPO$_3$ to the original system. For molar ratio Al$_2$O$_3$: Fe$_2$O$_3$ $\geqq$ 1 it is the subsystem MgO—CaO—C$_3$S—C$_3$A—C$_4$AF and for Al$_2$O$_3$: Fe$_2$O$_3$ $\leqq$ 1 the subsystem MgO—CaO—C$_3$S—C$_2$F—C$_4$AF.

Initial phase composition

$Al_2O_3 : Fe_2O_3 \geqq 1$
$MgO + CaO + C_3S + C_3A + C_4AF$
↓
1a $MgO + CaO + C_3S + C_3A + C_4AF + C_2NP$
↓
2a $MgO + C_3S + C_2S + C_3A + C_4AF + C_2NP$
↓
3a $MgO + C_2S + C_3A + C_{12}A_7 + C_4AF + C_2NP$
↓
4a $MgO + C_2S + C_{12}A_7 + CA + C_4AF + C_2NP$
↓
5a $MgO + C_2S + CA + MA + C_4AF + C_2NP$

$Al_2O_3 : Fe_2O_3 \leqq 1$
$MgO + CaO + C_3S + C_2F + C_4AF$
↓
1b $MgO + CaO + C_3S + C_2F + C_4AF + C_2$
↓
2b $MgO + C_3S + C_2S + C_4AF + C_2NP$
↓
3b $MgO + C_2S + C_2F + C_4AF + C_2NP$

↓
6 $MgO + C_2S + MA + MF + + C_4AF + C_2NP$
↓
7 $MgO + C_2S + C_3MS_2 + MA + MF + C_2NP$
↓
8 $MgO + C_3MS_2 + CMS + MA + MF + C_2NP$
↓
9 $MgO + CMS + M_2S + MA + MF + C_2NP$
↓
10 $MgO + M_2S + MA + MF + CMNP + C_2NP$
↓
11 $MgO + M_2S + MA + MF + CMNP + M_2NP$

The mechanism of subsequent changes in phase composition in the system $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—NP$ indicated that $NaPO_3$ in the system reacts preferentially with CaO either free or bound to Ca-phases, and that in co-existence with MgO there arise three phosphate phases C_2NP, CMNP and M_2NP. The number of occurences of the individual phases in the concentration range of the system $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—NP$ is as follows:

Phases	MgO	C_2NP	C_4AF	C_2S	MA,MF	C_3S	C_3A	other phases
Number of occurences	14	13	9	8	7	4	3	1—2

The number of occurences of the phases implies that within the concentration volume of the system $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—NP$, characterized by the presence of the MgO phase, the phosphate phase C_2NP covers the largest existence region second to that of MgO. When, in relation to the system $NaPO_3$—magnesite (containing CaO, SiO_2, Al_2O_3, Fe_2O_3) the points of phases C_3A, $C_{12}A_7$, CA, C_4AF, C_3MS_2, CMS, CMNP and M_2NP are regarded as relatively low as compared to the high-melting phases MgO, C_2S, MA, MF and C_2NP, then the 6-phase combination $MgO—C_2S—C_4AF—MA—MF—C_2NP$ (degree

6 in the schematic diagram) represents the terminal step of the subsequent changes in phase compositions which still include the low-melting C_4AF phase. When the last low-melting phase C_4AF has been eliminated by reaction of $NaPO_3$ with equivalent CaO contained in C_4AF from the system MgO—C_2S—MA—MF—C_4AF—C_2NP, the system then comprises solely high-melting phases represented by the 5-component subsystem MgO—C_2S—MA—MF—C_2NP. According to literature [6] [7], [32] the C_2S and C_2NP phases form a series of solid solutions of the type $(Ca,Na)_2$ $(PO_4.SiO_4)$ and similarly, according to [26]—[31] the phases MA and MF form solid solutions of the type $Mg(Al, Fe)_2O_4$. Then, in the concentration volume of the 5-component subsystem MgO—C_2S—MA—MF—C_2NP there arise solid solutions $(Ca, Na)_2$ (PO_4, SiO_4) and $Mg(Al, Fe)_2O_4$ as independent homogeneous phases and each composition in the section through the 5-component subsystem is reduced to the co-existence of three phases, expressed by the system MgO—$(Ca, Na)_2$ (PO_4, SiO_4)—$Mg(Al, Fe)_2O_4$.

These results have shown that the subsystem MgO—C_2S—MA—MF—C_2NP is a boundary section of "effective" concentrations of $NaPO_3$ in the concentration volume of the system MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—NP since their exceeding results in the formation of low-melting phosphate phases CMNP M_2NP and silicate phases C_3MS_2 and CMS. The optimum amount of $NaPO_3$ addition to the magnesite system (containing CaO, Fe_2O_3, Al_2O_3, SiO_2) and having the molar ratio CaO : $SiO_2 > 2$, is given by the following relationship:

$$YNaPO_3 = 1.82(a\ .\ CaO - 1.87b\ .\ SiO_2)$$

where $YNaPO_3$ is the amount of $NaPO_3$ addition in % by wt. related to the initial weight of the system,
a is the total CaO content in % by wt. in the original system,
b is the total SiO_2 content in % by wt. in the original system.

The amount of $NaPO_3$ calculated according to the above relationship is equivalent to the total CaO content in the system reduced by the CaO necessary for maintaining the high-melting C_2S phase. Under such conditions $NaPO_3$ reacts only with CaO either free or bound to relatively low-melting Ca-phases (C_3A, $C_{12}A_7$, CA, C_4AF, C_2F) and the phase composition is subject to changes. From the original low-melting Ca-phases, ions Fe_3^+ and Al^{3+} diffuse into periclase grains forming inclusions of high-melting spinels MA and MF, and/or solid solutions $Mg(Al,Fe)_2O_4$, while Ca^{2+} ions react with $NaPO_3$ producing C_2NP, or, in the presence of C_2S, the solid solution $(Ca,Na)_2(PO_4,SiO_4)$ taking up the intergranular space of the periclases. Under these conditions, in the system $NaPO_3$-magnesite there always arise only the high-melting phases of MgO, C_2S, MA, MF and C_2NP as the final ones.

CONCLUSION

The effect of $NaPO_3$ addition as a component of the system MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—NP has indicated implicitly that among the phosphate phases M_2NP, CMNP and C_2NP being formed in the partial section of the concentration volume of the given system, only the C_2NP phase exhibits very favourable refractory properties. The subsystem MgO—C_2S—MA—MF—C_2NP, including the phosphate phase C_2NP, is a boundary section of "effective" concentrations of $NaPO_3$ in the system $NaPO_3$ — magnesite, in which only high-melting phases of MgO, C_2S, MA, MF and C_2NP arise as final ones. The given phases represent the sole suitable phase composition from the point of view of marked improvement of refractory properties in the system $NaPO_3$—magnesite, containing a higher amount of CaO and Fe_2O_3 and a lower amount of SiO_2 and Al_2O_3 and having a molar ratio CaO : $SiO_2 > 2$.

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VPLYV $NaPO_3$ NA FÁZOVÉ ZLOŽENIE V SÚSTAVE $MgO-CaO-SiO_2-Fe_2O_3-Al_2O_3-Na_2O \cdot P_2O_5$ VO VZŤAHU K BÁZICKÝM ŽIARUVZDORNÝM MATERIÁLOM

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Štúdium koexistencie fosfátových fáz v koncentračnej časti sústavy MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—$Na_2O \cdot P_2O_5$, obsahujúcej vždy fázu MgO, objasňuje spôsob väzby $NaPO_3$ v magnezite (obohatený o CaO, FeO_3, Al_2O_3, SiO_2) s mólovým pomerom CaO : $SiO_2 > 2$.

V sústave sa našli tri fosfátové zlúčeniny $MgNaPO_4$, $MgCaNa_2(PO_4)_2$ a $CaNaPO_4$ v koexistencii s priľahlými fázami pri subsolidusových teplotách. $NaPO_3$ prednostne reaguje s CaO voľným alebo viazaným na nízkotaviteľné Ca-fázy (C_3A, $C_{12}A_7$, CA, C_4AF, C_2F). Z pôvodných nízkotaviteľných Ca-fáz difundujú ióny Fe^{3+} a Al^{3+} do zrn periklasu za vzniku inklúzií vysokotaviteľných spinelov $MgFe_2O_4$ a $MgAl_2O_4$, resp. tuhých roztokov $MgFe_xAl_{2-x}O_4$ a ióny Ca^{2+} reakciou s $NaPO_3$ tvoria vysokotaviteľný $CaNaPO_4$, ktorý v prítomnosti Ca_2SiO_4 tvorí tuhý roztok $Ca_{2-x}Na_x(PO_4)_x(SiO_4)_{1-x}$, vypĺňujúci intergranulárny priestor periklasov.

V závislosti od narastajúcej koncentrácie $NaPO_3$ určil sa v sústave mechanizmus následných zmien fázových zložení a existencia 14 nezávislých 6-fázových kombinácií univariantných rovnováh, v ktorých fáza MgO je ešte termodynamicky stabilná s fosfátovými fázami. Subsystém $MgO—2CaO . SiO_2—MgO . Al_2O_3—MgO . Fe_2O_3—2CaO . Na_2O . P_2O_5$ reprezentuje limitný rez optimálnych koncentrácií $NaPO_3$ v hlavnej sústave $MgO—CaO—SiO_2—Fe_2O_3—Na_2O_3 . P_2O_5$, z hľadiska fosfátovej väzby v bázických žiaruvzdorných materiáloch. Optimálne množstvo prídavku $NaPO_3$ do sústavy $NaPO_3$—magnezit (obsahujúci CaO, SiO_2, Fe_2O_3, Al_2O_3) s mólovým pomerom CaO : SiO_2 väčším ako 2 je dané vzťahom:

$$YNaPO_3 = 1{,}82\,(a\,.\,CaO — 1{,}87\,b\,.\,SiO_2)$$

kde $YNaPO_3$ — množstvo prídavku $NaPO_3$ vo váhových %, vztiahnuté na pôvodnú váhu sústavy,

a— celkový obsah CaO vo váh. % v pôvodnej sústave,

b — celkový obsah SiO_2 vo váh. % v pôvodnej sústave.

Takto vypočítané množstvo $NaPO_3$ podľa uvedeného vzťahu je ekvivalentné celkovému obsahu CaO v povôdnej sústave, zmenšenému o CaO, ktorý je nevyhnutný pre zachovanie vysokotaviteľnej fázy Ca_2SiO_4. Za takýchto podmienok vznikajú ako konečné len vysokotaviteľné fázy, reprezentované sústavou $MgO—2CaO . SiO_2—MgO . Fe_2O_3—MgO . Al_2O_3—2CaO . NaO . P_2O_5$.

Obr. 1. Diagram koexistence fáz v koncentračnej oblasti sústavy $MgO—CaO—SiO_2—Na_2O . P_2O_5$, *prilahlých k vrcholu* MgO.

Obr. 2. Digram koexistencie fáz v koncentračnej oblasti sústavy $MgO—CaO—Al_2O_3—Na_2O . P_2O_5$, *prilahlých k vrcholu* MgO.

Obr. 3. Diagram koexistencie fáz v koncentračnej oblasti sústavy $MgO—CaO—Fe_2O_3—Na_2O . P_2O_5$, *prilahlých k vrcholu* MgO.

Obr. 4. Diagram koexistencie fázy C_4AF *v koncentračnej oblasti sústavy* $CaO—Al_2O_3—Fe_2O_3—Na_2O . P_2O_5$.

ВЛИЯНИЕ $NaPO_3$ НА СОСТАВ ФАЗ В СИСТЕМЕ $Mg—CaO—SiO_2—Fe_2O_3—Al_2O_3—Na_2O . P_2O_5$ В ОТНОШЕНИИ К ОСНОВНЫМ ЖАРОУПОРНЫМ МАТЕРИАЛАМ

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Исследование сосуществования фосфатных фаз в концентрационной части системы $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—Na_2O . P_2O_5$, содержащей всегда фазу MgO, объясняет способ связи $NaPO_3$ в магнезите (с добавкой CaO, Fe_2O_3, Al_2O_3, SiO_2) с молярным отношением CaO : $SiO_2 > 2$.

В системе были установлены три фосфатных соединения $MgNaPO_4$, $MgCaNa_2(PO_4)_2$ и $CaNaPO_4$ в сосуществовании с соседними фазами при температуре субсолидус. $NaPO_3$ преимущественно реагирует со свободной или связанной CaO в низкокипящую Ca-фазу (C_3A, $C_{12}A_7$, CA, C_4AF, C_2F). Из первоначальных низкокипящих Ca-фаз диффундируют ионы Fe^{3} и Al^{3} в зерна перикласа с образованием включений жароупорных шпинелей $MgFe_2O_4$ и $MgAl_2O_4$, или твердых растворов $MgFe_xAl_{2-x}O_4$ и ионы Ca^{2+} взаимодействием с $NaPO_3$ образуют жароупорный $CaNaPO_4$, который в присутствии Ca_2SiO_4 образует твердый раствор $Ca_{2-x}Na_x(PO_4)_x(SiO_4)_{1-x}$, заполняющий межгранулярное пространство перикласов.

В зависимости от растущей концентрации $NaPO_3$ определяли в системе механизм следующих изменений составов фаз и существование 14 независимых 6-фазных комбинаций одновариантных равновесий, в которых фаза MgO является еще термодинамически устойчивой с фосфатными фазами. Подсистема $MgO—2\,CaO\,.\,SiO_2—MgO\,.\,Al_2O_3—MgO\,.\,Fe_2O_3—2\,CaO\,.\,Na_2O\,.\,P_2O_5$ представляет собой предельный разрез оптимальных концентраций $NaPO_3$ в основной системе $MgO—CaO—SiO_2—Fe_2O_3—Al_2O_3—Na_2O\,.\,P_2O_5$ с точки зрения жароупорности фосфатной связи в основных жароупорных материалах. Оптимальное количество добавки $NaPO_3$ в систему $NaPO_3$ — магнезит (содержащий CaO, SiO_2, Fe_2O_3, Al_2O_3) с молярным отношением $CaO : SiO_2 > 2$ дано отношением:

$$NaPO_3 = 1{,}82(a\,.\,CaO - 1{,}87\,b\,.\,SiO_2),$$

где a — общее содержание CaO в % по весу в первоначальной системе,
b — общее содержание SiO_2 в % по весу в первоначальной системе.

Таким образом рассчитанное количество $NaPO_3$ согласно приводимому отношению является эквивалентным к общему содержанию CaO в первоначальной системе, пониженному на CaO, которое необходимо для сохранения жароупорной фазы Ca_2SiO_4. При таких условиях образуются в виде окончательных фаз только жароупорные фазы, представляющие собой систему

$$MgO—2\,CaO\,.\,SiO_2—MgO\,.\,Fe_2O_3—MgO\,.\,Al_2O_3—2\,CaO\,.\,Na_2O\,.\,P_2O_5.$$

Рис. 1. Диаграмма сосуществования фаз в концентрационной области системы $MgO—CaO—SiO_2—Na_2O\,.\,P_2O_5$, *прилегающих к пику* MgO.

Рис. 2. Диаграмма сосуществования фаз в концентрационной области системы $MgO—CaO—Al_2O_3—Na_2O\,.\,P_2O_5$, *прилегающих к пику* MgO.

Рис. 3. Диаграмма сосуществования фаз в концентрационной области системы $MgO—CaO—Fe_2O_3—Na_2O\,.\,P_2O_5$, *прилегающих к пику* MgO.

Рис. 4. Диаграмма сосуществования фазы C_4AF *в концентрационной области системы* $CaO—Al_2O_3—Fe_2O_3—Na_2O\,.\,P_2O_5$.