The coexistence of crystalline phases in the MgO-rich part of the system $CaO—MgO—SiO_2—Na_2O—P_2O_5$

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The phase coexistence in the concentration part $CaO—MgO—2MgO \cdot SiO_2—2CaO \cdot SiO_2—2CaO \cdot Na_2O \cdot P_2O_5$ of the system $CaO—MgO—SiO_2—Na_2O—P_2O_5$ was determined at subsolidus temperatures, *i.e.* the elementary tetrahedra in the system were defined. The crystalline phases present were identified by the X-ray powder diffraction.

The only phosphate phase in the system is $CaNaPO_4$, which forms solid solutions with adjacent silicate phases at high temperatures and which is responsible for bonding properties in the basic refractory materials from the phosphate bond point of view.

In order to remain in the narrow, technologically most effective composition region, defined by

$$S = \frac{n_{CaO}}{n_{SiO_2}} \geq 2,$$

corresponding to the subsystem $3CaO \cdot SiO_2—2CaO \cdot SiO_2—2CaO\ Na_2O \cdot P_2O_5$, of the model system $CaO—SiO_2—Na_2O \cdot P_2O_5$, the amount of $Na_2O\ P_2O_5$ has to be kept within certain limits, the relations for which are also given.

The phosphate bond in the basic refractory materials has been the subject of considerable interest in recent research. In the works [1—4] it was stated unanimously that the chemical bonding of sodium metaphosphate $NaPO_3$ in the "system" sodium metaphosphate—magnesite (rich in CaO and SiO_2) influences favourably the thermomechanical properties of refractory materials if compared with chemical bondings used so far.

There are, however, considerable discrepancies concerning the mechanism of phosphate bond in such "system". *Lyon et al.* [5] suppose the phosphate glass to be the main bonding phase, *Di Bello* and *Pradel* [6] assign the same function to the calcium magnesium phosphate. *Foessel* and *Treffner* [3] established in the system a narrow region with low contents of SiO_2, in which the phosphate bonding occurs by means of a "well-defined" compound. *Venable* and *Treffner* [7] as well as the present authors in their previous paper [8], however, identified the calcium sodium orthophosphate $CaNaPO_4$ as the main

bonding phase that causes in a narrow composition region of the system, high modulus of rupture of basic refractory materials at high temperatures.

The aim of this study was to establish the coexistence of solid phases of the system $CaO—MgO—SiO_2—Na_2O \cdot P_2O_5$ which is a part of the oxide system $CaO—MgO—SiO_2—Na_2O—P_2O_5$, to subdivide it into elementary subsystems and to estimate their thermal stability.

The subsystem $CaO—MgO—SiO_2—Na_2O \quad P_2O_5$

The available data on the coexistence of MgO with crystalline phases in the ternary systems $CaO—MgO—SiO_2$ [9] and $CaO—MgO—Na_2O \cdot P_2O_5$ [8] made it possible to localize (in the investigated basic subsystem $CaO—MgO—SiO_2—Na_2O \cdot P_2O_5$) a composition region between the figurative points C, M, M_2NP, C_2NP, C_2S, and M_2S* (Fig. 1).

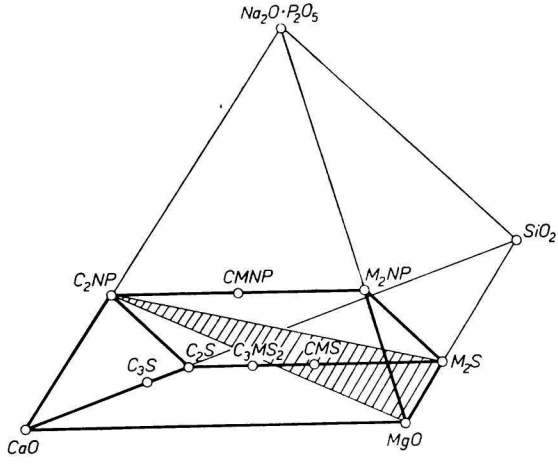

Fig. 1. Compatibility region of MgO with other crystalline phases of the system $CaO—MgO—SiO_2—Na_2O \quad P_2O_5$.

MgO coexists with all crystalline phases of the system C—M—S that constitute the subsystem C—M—M_2S—C_2S and, similarly, with all crystalline phases of the system C—M—NP that constitute the subsystem C—M—M_2NP—C_2NP.

Furthermore, in investigating the system C—M—NP [8] it has been found that the joins M—C_2NP and M_2NP—C_2NP divide it into three subsystems: C—M—C_2NP, M—C_2NP—CMNP, and M—CMNP—M_2NP. In the latter two subsystems MgO coexists with the low-melting phosphates $CaO \cdot MgO \cdot Na_2O \cdot P_2O_5$ (CMNP) and $2MgO \cdot Na_2O \cdot P_2O_5$ (M_2NP) that are undesired in the "system" sodium metaphosphate—magnesite as they unfavourably influence its thermal stability (defined arbitrarily by the first appearance of liquid). On the other hand, the subsystem C—M—C_2NP is thermally

* In order to simplify the notation of chemical compounds in the figures as well as in the text, the shortened, commonly accepted symbols as *e.g.* C for CaO, M for MgO, S for SiO_2, N for Na_2O, P for P_2O_5, C_2S for $2CaO \cdot SiO_2$ *etc.* will be used throughout.

the most stable. Hence, for the study of phase relations only that part of the system C—M—S—NP is of importance, which is limited to the composition region C—M—M_2S—C_2S—C_2NP and, simultaneously, to the composition triangle M—M_2S—C_2NP (Fig. 1).

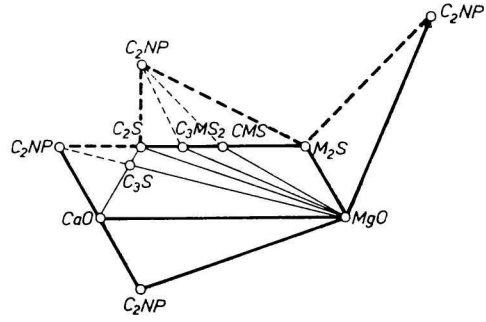

Fig. 2. Phase coexistence in the composition region CaO—MgO—$2MgO \cdot SiO_2$—$2CaO \cdot SiO_2$—$2CaO \cdot Na_2O \cdot P_2O_5$.

The composition region C—M—M_2S—C_2S—C_2NP in an "unfolded" form is shown in Fig. 2. It can be seen that MgO coexists in this region with all respective phases (fully drawn joins). The data concerning the phase coexistence of C_2NP along the binary joins C_3S—C_2NP, C_2S—C_2NP, C_3MS_2—C_2NP, CMS—C_2NP, and M_2S—C_2NP (joins drawn with broken lines) are, however, either incomplete or missing at all. And it is just the knowledge of the phase relations along the corresponding joins that is indispens-

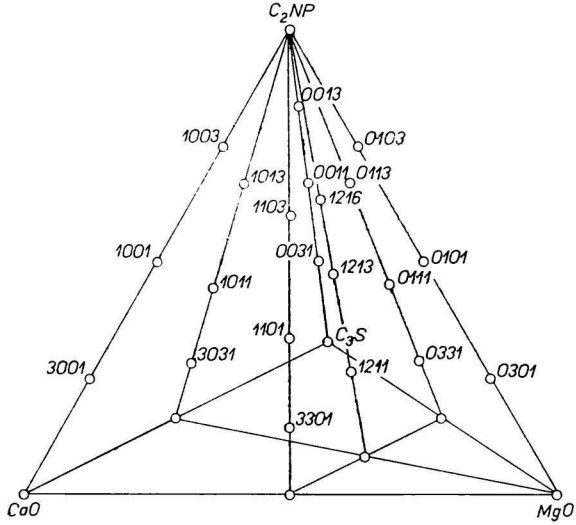

Fig. 3. Figurative points of samples in the system CaO—MgO—$3CaO \cdot SiO_2$—$2CaO \cdot Na_2O \cdot P_2O_5$.

able for the subdivision of the system C—M—M_2S—C_2S—C_2NP into elementary composition tetrahedra which can, as far as the phase relations are concerned, be considered as independent quaternary regions with differing thermophysical properties.

Experimental

For the preparation of individual samples, 0.3 M water solutions of $NaNO_3$, $NH_4H_2PO_4$, $Mg(NO_3)_2$, $Ca(NO_3)_2$ as well as the sol of SiO_2 have been used. These solutions were mixed in desirable proportions, so that the compositions of the samples corresponded to the beforehand selected figurative points on the joins in the system C—M—M_2S—C_2S—C_2NP. Fig. 3 can serve as an example of such selection of figurative points for the subsystem C—M—C_3S—C_2NP.

The solutions were dried, heated up to 600°C for decomposition of nitrates and afterwards homogenized in an agate mortar. The samples were heated in platinum crucibles for 20 hours at 1350°C first and then kept for 40 hours at 500°C in order to stabilize

Table 1

Composition, heating temperatures and crystalline phases present in the binaries of the system $CaO-MgO-2MgO\ SiO_2-2CaO \cdot SiO_2-2CaO\ Na_2O \cdot P_2O_5$

Composition of the sample [mole %]		Heating temperature [°C/hrs]	Phases
C_3S	C_2NP		
75.0	25.0	1350/10	α-C_2NP(s.s.) + C_3S
50.0	50.0	1350/10	α-C_2NP(s.s.) + C_3S
25.0	75.0	1350/10	α-C_2NP(s.s.) + C_3S
C_2S	C_2NP		
75.0	25.0	1350/20	α_0'-C_2S(s.s.)*
50.0	50.0	1350/20	α_0'-C_2S(s.s.)
25.0	75.0	1350/20	α_0'-C_2S(s.s.)
C_3MS_2	C_2NP		
75.0	25.0	1350/10	α-C_2NP(s.s.) + C_3MS_2
50.0	50.0	1350/10	α-C_2NP(s.s.)
25.0	75.0	1350/10	α-C_2NP(s.s.)
CMS	C_2NP		
75.0	25.0	1350/10	β-C_2NP(s.s.) + CMS
50.0	50.0	1350/10	β-C_2NP(s.s.) + CMS
25.0	75.0	1350/10	β-C_2NP(s.s.)
M_2S	C_2NP		
75.0	25.0	1350/10	α-C_2NP(s.s.) + M_2S
50.0	50.0	1350/10	α-C_2NP(s.s.) + M_2S
25.0	75.0	1350/10	α-C_2NP(s.s.) + M_2S

* α_0'-C_2S(s.s.) = $Ca_{2-x}Na_x(PO_4)_x(SiO_4)_{1-x}$, $0 \leq x \leq 1$.

Table 2

Composition, heating temperatures and crystalline phases present in the composition tetrahedra of the system $CaO-MgO-2MgO \cdot SiO_2-2CaO \cdot SiO_2-2CaO \cdot Na_2O \cdot P_2O_5$

Composition of the sample [mole %]				Heating temperature [°C]/[hrs]	Phases
CaO	MgO	C_3S	C_2NP		
20.0	40.0	20.0	20.0	1350/10	α-C_2NP(s.s.) + C + M
14.3	28.6	42.8	14.3	1350/10	α-C_2NP(s.s.) + C + M + C_3S
10.0	20.0	60.0	10.0	1350/10	α-C_2NP(s.s.) + C + M + C_3S
C_3S	MgO	C_2S	C_2NP		
20.0	40.0	20.0	20.0	1350/10	α_0'-C_2S(s.s.)* + M
14.3	28.6	42.8	14.3	1350/10	α_0'-C_2S(s.s.) + M
10.0	20.0	60.0	10.0	1350/10	α_0'-C_2S(s.s.) + M
C_2S	MgO	C_3MS_2	C_2NP		
20.0	40.0	20.0	20.0	1350/10	α-C_2NP(s.s.) + M
14.3	28.6	42.8	14.3	1350/10	α-C_2NP(s.s.) + M
10.0	20.0	60.0	10.0	1350/10	α-C_2NP(s.s.) + M + C_3MS_2
C_3MS_2	MgO	CMS	C_2NP		
20.0	40.0	20.0	20.0	1350/10	β-C_2NP(s.s.) + M + CMS
14.3	28.6	42.8	14.3	1350/10	β-C_2NP(s.s.) + M + CMS
10.0	20.0	60.0	10.0	1350/10	β-C_2NP(s.s.) + M + CMS
CMS	MgO	M_2S	C_2NP		
20.0	40.0	20.0	20.0	1350/10	α-C_2NP(s.s.) + M + M_2S
14.3	28.6	42.8	14.3	1350/10	α-C_2NP(s.s.) + M + M_2S
10.0	20.0	60.0	10.0	1350/10	α-C_2NP(s.s.) + M + M_2S

* α_0'-C_2S(s.s.) = $Ca_{2-x}Na_x(PO_4)_x(SiO_4)_{1-x}$, $0 \leq x \leq 1$.

the lowest-temperature modifications** of C_2S in the presence of C_2NP. The compositions of individual samples are summarized in Tables 1 and 2. The preparation of samples from water solutions, used in this study is very similar to that described previously [10, 11].

The phase composition of each sample was determined by the X-ray powder diffraction; the temperature, at which the first liquid appeared was determined using a Leitz heating microscope and a Griffin 6000 hot-stage microscope. Both equipments facilitated direct observation of samples up to 1750°C.

** It is not always the same modification of C_2S that coexists with C_2NP at 500°C, but it depends on the concentration of C_2NP in the particular sample. This question is presently being investigated in detail.

Results and discussion

The experimental study in the subsolidus region of the system C—M—M_2S—C_2S—C_2NP yields results concerning the phase coexistence, presence of solid solutions and thermal stability in its binaries as well as in its elementary composition tetrahedra.

The phases present in the systems C_3S—C_2NP, C_2S—C_2NP, C_3MS_2—C_2NP, CMS—C_2NP, and M_2S—C_2NP, respectively, investigated at 75, 50, and 25 mole % of C_2NP each, are given in Table 1. It has been found that in these binaries a formation of solid solutions occurs, which is caused most probably by mutual substitution of PO_4^{3-} and SiO_4^{4-} anions, mainly in the structure of C_2NP. C_2S and C_2NP form a continuous series of solid solutions of the type $Ca_{2-x}Na_x(PO_4)_x(SiO_4)_{1-x}$ with orthorhombic structure of α_0'-C_2S type, which is in agreement with the literature [12]. There is a limited formation of solid solutions in the systems C_3S—C_2NP, C_3MS_2—C_2NP, CMS—C_2NP, and M_2S—C_2NP. The phase equilibria in the binaries of the system C—M—M_2S—C_2S—C_2NP, however, are fairly complicated and they need a separate study.

The solidus temperatures of the equimolar mixtures in the binary systems were estimated by high-temperature microscopy, in observing the first appearance of liquid. In the system (C_3S + C_2NP) the liquid phase did not appear even if heated up to 1760°C. The solidus temperatures in the other binaries were determined as follows: (C_2S + + C_2NP) 1760°C, (C_3MS_2 + C_2NP) 1330°C, (CMS + C_2NP) 1300°C, and (M_2S + C_2NP) 1380°C (it should be noted here that the solidus temperature in the last system, measured by a hot-stage microscope Griffin 6000 was 1335°C). These solidus temperatures are of great importance for the thermal stability of the respective systems at high temperatures. Obviously, the systems C_3S—C_2NP and C_2S—C_2NP are thermally most stable, whereas the systems C_3MS_2—C_2NP, CMS—C_2NP, and M_2S—C_2NP represent the low-melting regions in the system C—M—M_2S—C_2S—C_2NP.

The phase compositions determined in the five elementary composition tetrahedra of the system C—M—M_2S—C_2S—C_2NP (Fig. 4) are given in Table 2. It turns out that Na_2O P_2O_5 reacts only with CaO (either free or in the form of calcium silicates or calcium magnesium silicates) yielding thus C_2NP. This phase forms at high temperatures substitutional solid solutions with C_3S, C_2S, C_3MS_2, CMS, and M_2S as mentioned above. MgO does not react with $Na_2O \cdot P_2O_5$ in the composition region C—M—M_2S—C_2S—C_2NP and only MgO and C_2NP coexist with each phase present in this region. The investigated tetrahedra C—M—C_3S—C_2NP, C_3S—M—C_2S—C_2NP, C_2S—M—C_3MS_2—C_2NP, C_3MS_2—M—CMS—C_2NP, and CMS—M—M_2S—C_2NP can be, at subsolidus temperatures, considered as independent elementary composition tetrahedra.

The solidus temperatures in the elementary quaternary subsystems of the system C—M—M_2S—C_2S—C_2NP were also measured in order to estimate their thermal stability at high temperatures. In the quaternary subsystem of the composition (C + C_3S + + 2M + C_2NP) the liquid phase did not appear up to 1760°C. The solidus temperatures of the other subsystems were determined as follows: (C_3S + C_2S + 2M + C_2NP) 1710°C, (C_2S + C_3MS_2 + 2M + C_2NP) 1380°C, (C_3MS_2 + CMS + 2M + C_2NP) 1360°C, and (CMS + M_2S + 2M + C_2NP) 1280°C.

Taking the solidus temperatures in the elementary composition tetrahedra as a criterion, we can divide the system C—M—M_2S—C_2S—C_2NP into two composition regions differing markedly in their thermal stability: the regions M—M_2S—C_2S—C_2NP and C—M—C_2S—C_2NP, respectively. The boundary plane between them is given by the composition triangle C_2S—C_2NP—M, which is important not only from the viewpoint of thermophysical properties, but also from the viewpoint of polymorphic transforma-

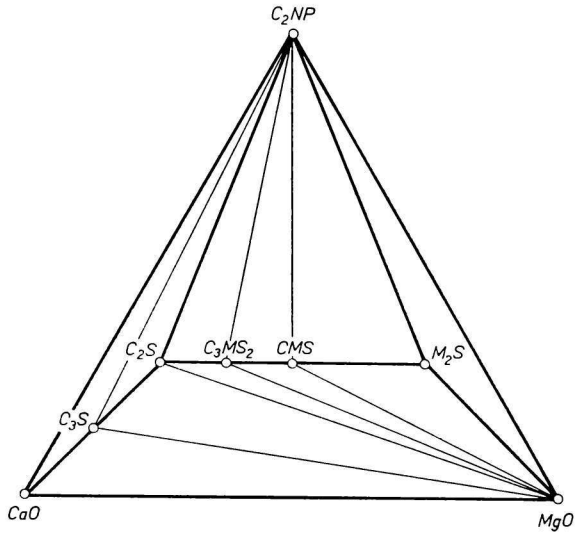

Fig. 4. Elementary tetrahedra in the system
$CaO—MgO—2MgO \cdot SiO_2—2CaO \cdot SiO_2—2CaO \cdot Na_2O\ P_2O_5$.

tions of solid solutions. There exist, in the composition region $M—M_2S—C_2S—C_2NP$, low-melting phases that influence very unfavourably the thermal stability of the "system" sodium metaphosphate—magnesite (rich in CaO and SiO_2) at high temperatures. The composition region $C—M—C_2S—C_2NP$, on the other hand, is thermally the most stable and hence very important portion of the system C—M—S—NP. It is true that this region includes the free CaO with its technologically unwanted properties (hydration), but this negative influence can be completely removed by admixing an appropriate amount of $Na_2O \cdot P_2O_5$. Thus, as a final consequence of this study, a narrow, technologically most effective composition region in the "system" sodium metaphosphate—magnesite (rich in CaO and SiO_2) for admixtures of $Na_2O\ P_2O_5$ can be established. Such region is defined by the molar ratio

$$S = \frac{n_{CaO}}{n_{SiO_2}} \geq 2$$

and by

$$(n_{NP})_{min} \leq (n_{NP}) \leq (n_{NP})_{max}$$

and refers to the elementary tetrahedron $C_3S—C_2S—M—C_2NP$ of the system C—M—S—NP (see Appendix).

Conclusion

The results of this study made it possible to explain qualitatively the problem of the phosphate bonding in the subsolidus region of the "system" sodium metaphosphate—magnesite (rich in CaO and SiO_2). At the same time, however, a whole series of theoretical

questions emerged, such as the problem of the influence of SiO_4^{4-}—PO_4^{3-} substitution in the structures of calcium silicates on the stability of their modifications, the localization of phase boundaries of the solid solutions with polymorphic transformations at subsolidus temperatures, the volume changes caused by polymorphic transformations, the phase relations in the subliquidus regions of the partial systems, *etc.* This study is, therefore, to be considered as the first contribution to a systematic investigation of phase equilibria in the composition region C—M—M_2S—C_2S—C_2NP of the basic system C—M—S—NP.

Appendix

In order to calculate the effective amounts $(G_{NP})_{min}$ and $(G_{NP})_{max}$ in the "system" sodium metaphosphate—magnesia (rich in CaO and SiO_2) the model system C—S—NP can be used.

This model system can be demonstrated using the oblique-angle coordinate system $y-x$ with the 60° angle and unit coordinates on both axes (Fig. 5). The unit coordinates on both axes express the molar ratios N_{SiO_2} and $N_{Na_2O\,.\,P_2O_5}$, respectively. The compounds C_2NP, C_3S, and C_2S limit in the system C—S—NP a composition triangle $\triangle B_1B_2B_3$. The straight line p_1 passing through the points B_1 and B_2 is identical with the join C_2NP—C_3S and, similarly, the straight line p_2 passing through the points B_1 and B_3 is identical with the join C_2NP—C_2S of the composition triangle C_2NP—C_3S—C_2S. The straight line p_a is defined by one fixed point B_4 (in the corner of the composition triangle, with y-coordinate equal to 1) and one variable point B_a (where "a" is the molar ratio N_{SiO_2} in the original system C—S) that can lie on the x-axis anywhere within limits $0 < N_{SiO_2} < 1/3$. This straight line (see Fig. 5) intersects the straight lines p_1 and p_2 at the points NP_{min} and NP_{max}, respectively, showing thus in the system C—S—NP the region of effective admixtures of $Na_2O \cdot P_2O_5$, defined by

$$S = \frac{n_{CaO}}{n_{SiO_2}} \geq 2$$

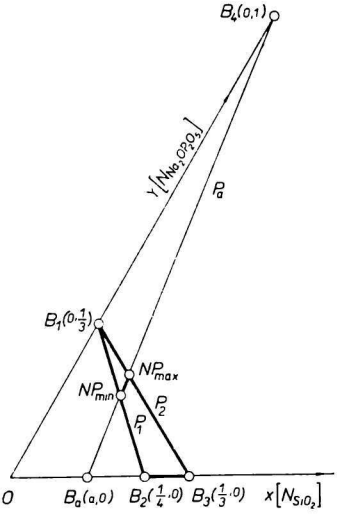

Fig. 5. Graphical method for determining the effective composition interval $\langle (NP)_{min}, (NP)_{max} \rangle$ in the model system CaO—SiO_2—$Na_2O \cdot P_2O_5$.

and

$$(N_{NP})_{min} \leq (N_{NP}) \leq (N_{NP})_{max}.$$

The amount of $Na_2O \cdot P_2O_5$, needed to shift the composition B_a (Fig. 5) of the original system $CaO—SiO_2$ into the demanded composition interval $\langle NP_{min}, NP_{max}\rangle$ of the system C—S—NP, can be calculated as follows:

Let the equations of the straight lines p_1 and p_2, and p_a be

$$p_1\,(B_1, B_2): \quad y = -\frac{4}{3}x + \frac{1}{3},$$

$$p_2\,(B_1, B_3): \quad y = -x + \frac{1}{3},$$

$$p_a\,(B_4, B_a): \quad y = -\frac{1}{a}x + 1.$$

The intersection point of p_1 and p_a corresponds then to the point $NP_{min}\left(\frac{2a}{3-4a}, \frac{1-4a}{3-4a}\right)$ the coordinates of which are the molar ratios N_{SiO_2} and $N_{Na_2O \cdot P_2O_5}$ in the system C—S—NP, so that $N_{CaO} = 1 - N_{SiO_2} - N_{Na_2O \cdot P_2O_5} = 2(1-a)/(3-4a)$.

In a similar way, the intersection point of p_2 and p_a corresponds to the point NP_{max} $\left(\frac{2a}{3(a-1)}, \frac{3a-1}{3(a-1)}\right)$ and to $N_{CaO} = 2/3$.

The two extreme values of the ratio $n_{Na_2O \cdot P_2O_5}/(n_{CaO} + n_{SiO_2})$ can be then evaluated, using the equations

$$\left(\frac{N_{Na_2O \cdot P_2O_5}}{N_{CaO} + N_{SiO_2}}\right)_{NP_{min}} = \left(\frac{n_{Na_2O \cdot P_2O_5}}{n_{CaO} + n_{SiO_2}}\right)_{NP_{min}} = \frac{1-4a}{2}, \tag{1}$$

$$\left(\frac{N_{Na_2O \cdot P_2O_5}}{N_{CaO} + N_{SiO_2}}\right)_{NP_{max}} = \left(\frac{n_{Na_2O \cdot P_2O_5}}{n_{CaO} + n_{SiO_2}}\right)_{NP_{max}} = \frac{1-3a}{2}, \tag{2}$$

where $n_{Na_2O \cdot P_2O_5}$, n_{CaO}, and n_{SiO_2} are the respective numbers of moles of Na_2O P_2O_5, CaO, and SiO_2 in the system C—S—NP, whereas a is the molar ratio N_{SiO_2} in the original system C—S.

$$a = \frac{n_{SiO_2}}{n_{CaO} + n_{SiO_2}} = \frac{1}{\frac{n_{CaO}}{n_{SiO_2}} + 1} = \frac{1}{S+1}$$

if substituting

$$\frac{n_{CaO}}{n_{SiO_2}} = S. \tag{3}$$

The effective composition of the system C—S—NP with given $S \geq 2$ lies then in the interval $(n_{NP})_{min} \leq (n_{NP}) \leq (n_{NP})_{max}$ if

$$(n_{NP})_{min} = (n_{CaO} + n_{SiO_2}) \frac{S - 3}{2(S + 1)}, \quad (4)$$

$$(n_{NP})_{max} = (n_{CaO} + n_{SiO_2}) \cdot \frac{S - 2}{2(S + 1)}. \quad (5)$$

The equations (*4*) and (*5*) can be re-written using the mass percentages $(G_{NP})_{min}$ and $(G_{NP})_{max}$ for the given percentages G_{CaO} and G_{SiO_2} in the original system.

$$(G_{NP})_{min} = A \frac{S - 3}{2(S + 1)}, \quad (6)$$

$$(G_{NP})_{max} = A \frac{S - 2}{2(S + 1)}, \quad (7)$$

where

$$A = 3.636\ G_{CaO} + 3.394\ G_{SiO_2}$$

and

$$S = 1.0714 \frac{G_{CaO}}{G_{SiO_2}}.$$

The values G_{CaO} and G_{SiO_2} have to be determined by the chemical analysis of the original system.

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