Approximations of the Mineralogical Composition of Magnesite Clinkers

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Potential mineralogical compositions of basic refractories attainable by mixing of two magnesite clinkers of different composition have been computed. Redox conditions during burning were considered in calculations. The procedure used enables to choose the optimal proportion of both clinkers with respect to the presence and function of phases occurring in minor amounts in the planned product.

The mineralogical composition of magnesite clinkers is given in the first approximation by their chemical composition belonging to the five-component system MgO, CaO, SiO_2, Al_2O_3, Fe_2O_3. This set has to be extended to six components considering the possible presence of Fe^{2+} and the related phase FeO. As the influence of individual minor phases on the properties of magnesite refractories is known, it would be useful to elaborate a procedure determining the mineralogical composition of the product in dependence on the chemical composition of the raw mix and on conditions of the burning technology. The problem is in general topical both for the production of structural polyphase materials (alloys, ceramics) and for geochemistry as well. Obviously the solution of the problem can be divided into two stages: *1.* The calculation of equilibrium phase composition, *2.* consideration on the question — to what extent the product approximates equilibrium.

Possibilities to Calculate Subsolidus Equilibria

Calculation of subsolidus equilibria in multicomponent systems developed principally in two methodological directions:

1. Procedures based on direct experimental data summarized in phase diagrams.

2. Methods based on the data-base and procedures of equilibrium thermodynamics, *i.e.* on the search for the minimum of the Gibbs energy of the system.

Substantially elder are methods of the first group in applications for some technically significant systems as the *Bogue*'s method for portland cement clinkers [1] and that of *Rigby* [2] and *Rait* [3] for magnesite clinkers. These methods of equilibrium calculations are valid for specified sets of components (4—6), their limited portions in the raw mix and limited temperature interval given by conditions of technology.

Another alternative of this approach, suitable for the 2—3-component system, is the full mathematical description of the phase diagram by definition of singular points and expression of boundary lines and surfaces either by empirical regression relations or in agreement with general thermodynamic relations (*e.g.* with the LeChatelier—Shreder equation).

The second group of methods is characterized by sophisticated and extended calculations. Thus an interest of choosing this way of calculation originated just in the end of the sixties when computers allowed automation of calculations. At present there exist a multitude of computer programs differing in their strategies and limits of soluble situations [4].

The most competent *ab initio* approach is represented probably by the program VERTEX [5] suitable for equilibrium calculations of 3—7-component systems. Reliability of calculations of this type depends on the often discussed correctness of thermodynamic data of minerals.

A combination of both approaches mentioned above are the calculations based on the knowledge of the equilibrium phase assemblage (from phase diagrams) so that the calculation of minimizing the Gibbs energy is restricted to the determination of quantities of present phases [6] with respect to the equilibrium with the liquid phase and atmosphere composition.

Summarizing it could be stated that many problems of this type are accessible for solution. The coexistence of different philosophies of approaches is given on account of the specificity of the tasks and of their purpose. The bottleneck of the first group of methods is the reliability of quantitative phase analysis in multicomponent system, in the second one the question to what extent thermodynamic quantities of real minerals correspond to those of their tabulated data [7].

In this paper approximations of the mineralogical composition of magnesite clinkers were carried out by a procedure based on generalization and algo-

Table 1. Chemical Composition of Primary Magnesite Clinkers

	$w_i/\%$				
	MgO	CaO	Al_2O_3	Fe_2O_3	SiO_2
Clinker Jelšava	0.878	0.030	0.003	0.078	0.007
Clinker Košice	0.86	0.025	0.012	0.065	0.035
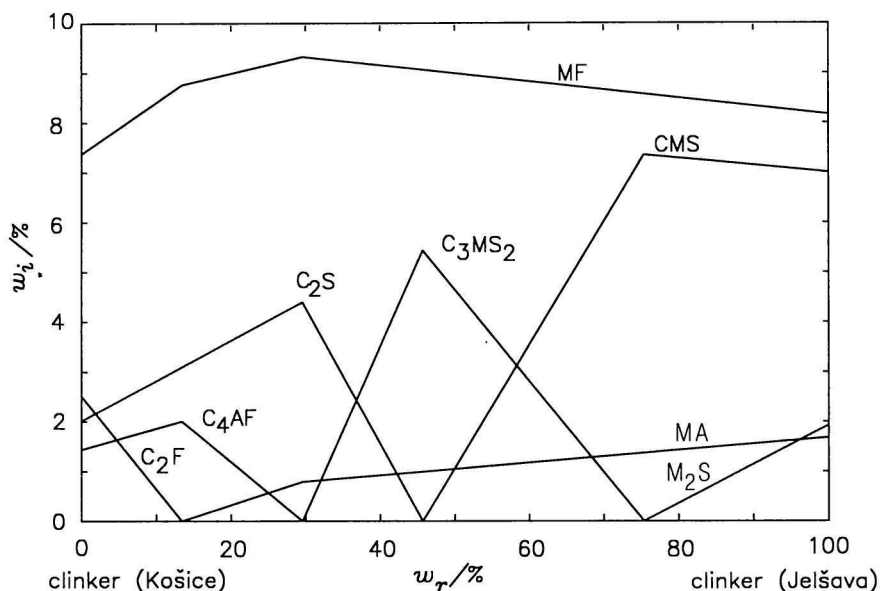
Fig. 1. Changes in mineralogical composition of BRM in dependence on the content of primary clinkers (0 % FeO).

rithmization of the Bogue and Rigby methods suitable for arbitrary 3—7-component system. Detailed description of the calculation procedure is given in [8]. The input data are the relatively reliable data on binary and pseudobinary phase compatibilities, available for a plenty of systems [9]. Calculations in their basic simplicity assume stoichiometric composition of minerals.

Survey of Mineralogical Compositions in the Binary Mixtures of Two Magnesite Clinkers

The use of two or more magnesite clinkers to prepare the green refractory composition is the common practice in the technology of basic refractory materials [10]. There can be advantageously mixed clinkers with *e.g.* elevated contents of CaO with clinkers low in CaO. This compromising should lower the content, or eliminate unwanted minor phases in the fired products.

For calculations two clinkers of the Slovak Magnesite Works (SMZ) were assumed: from Košice and Jelšava production plants. Original calculations on these systems are to be found in [11]. In this paper the results of calculations presented are based on modified computer programs enabling a continuous

survey of possible mineralogical compositions in consequence of changes of chemical composition of the mixtures, considering simultaneously changes of the oxidation state of Fe.

Chemical composition of the primarily assumed clinkers is given in Table 1.

Changes of the contents of minor phases in the burnt product obtained by mixing primary clinkers, in the whole composition range of both components, are shown in Fig. 1. For Figs. 1—3 it holds: $w(MgO) = 100 \% - \sum_i w_i$; w_i — mass fraction of the i-th compound. Figs. 2 and 3 present similar dependences of mineralogical compositions when a partial transformation of Fe_2O_3 to FeO was assumed.

Paragenesis of phases in the product has been defined by the Phase Compatibility Matrix (PCM) given in Table 2. Similarly as in the preceding paper [8] coexisting phases are there denoted by 0, incompatibles by 1. Published data [9, 12] were used as the source for the definition of PCM.

The basis of the computation is given by the setting up and solving systems of linear equations, expressing the materials balances for each of the 18 phase assemblages resulting from the PCM, summarized in Table 3. The result of the calculation is represented by identification of the "real"
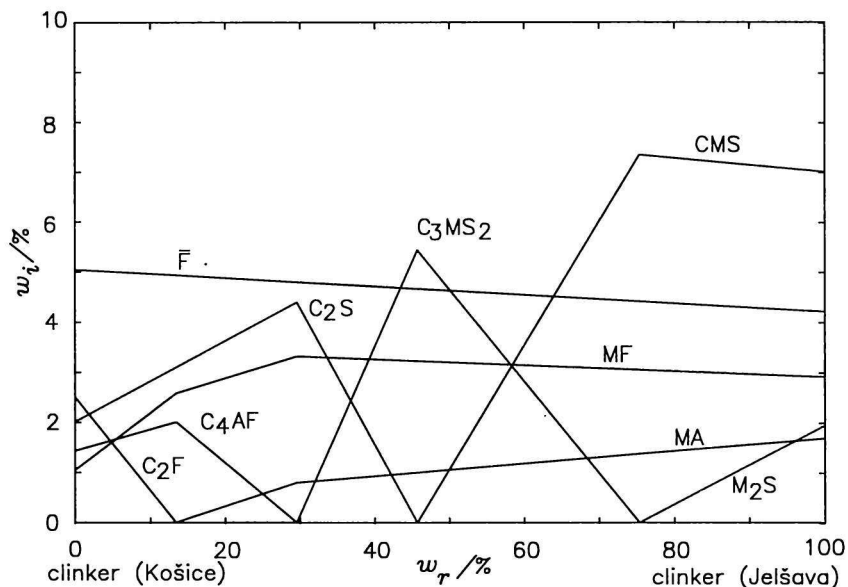
Fig. 2. Changes in mineralogical composition of BRM in dependence on the content of primary clinkers ($w(\text{FeO}) : \dot{w}(\text{Fe}_2\text{O}_3) = 0.2$).
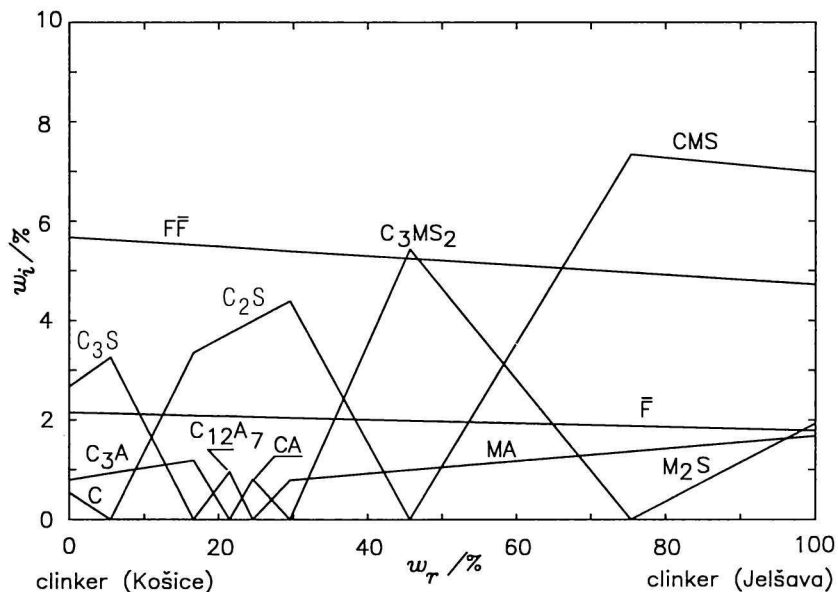

Fig. 3. Changes in mineralogical composition of BRM in dependence on the content of primary clinkers ($w(\text{FeO}) : w(\text{Fe}_2\text{O}_3) = 0.5$).

assemblage, where the calculated mass fraction of its each mineral component will appear being positive.

DISCUSSION

It is known that thermomechanical properties of basic refractory materials (BRM) are most severely damaged by eutectic melts of low viscosity — well wetting periclase at relatively low temperatures. Their presence depends on the quality and amounts of minor chemical components of the material, or in terms of our calculations, on minor phase components.

Thus calculations presented give a basis for the search of the optimal mixing ratio (ratios) of the primary clinkers. Of special interest in this respect are phase compositions of clinker mixtures at which the number of phases is decreased by 1 (transitions between phase polyhedra) (Table 4). The mixtures of present clinkers show four such singular cases. They can be considered as preferable for each further phase in the phase assemblage causes generally the decrease in the corresponding eutectic temperature. The speculation about the best ratio

Table 2. Phase Compatibility Matrix of Magnesite Clinkers

No.	Phase	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	M	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
2	M_2S		0	1	1	1	1	1	1	1	0	1	1	0	1	0	0
3	CMS			0	1	1	1	1	1	1	0	1	1	0	1	0	0
4	C_3MS_2				0	1	1	1	1	1	0	1	1	0	1	0	0
5	C_2S					0	1	0	0	0	0	0	0	0	0	0	0
6	C_3S						0	0	1	1	1	0	1	1	0	0	0
7	C							0	1	1	1	0	1	1	0	0	0
8	C_3A								0	1	1	1	1	1	0	0	0
9	$C_{12}A_7$									0	1	1	1	1	0	0	0
10	CA										0	1	0	1	0	0	0
11	MA											1	0	0	0	0	0
12	C_2F												0	0	0	1	0
13	CF													0	0	1	0
14	MF														0	1	0
15	C_4AF															1	0
16	$\bar{F}$																0
17	$F\bar{F}$																

0 — compatible phases; 1 — incompatible phases. M = MgO, S = SiO_2, C = CaO, A = Al_2O_3, F = Fe_2O_3, $\bar{F}$ = FeO, C_3MS_2 = 3CaO · MgO · $2SiO_2$ = $Ca_3Mg(SiO_4)_2$, etc.

(ratios) of clinkers can be then limited only to differentiating between these four particular cases.

Comparing the phase compositions in Figs.1 and 2 we can see that the assumed change of the ratio $w(FeO)/w(Fe_2O_3)$ did not change the positions at which particular silicate, or ferrite phases disappear, or are at the maximum, only the composition of the spinel phase changed.

At more reducing conditions of firing (Fig. 3) ferrites disappear and are replaced by calcium aluminates (CA, $C_{12}A_7$). But merwinite (C_3MS_2) appears at the same composition as in preceding cases.

It is to be pointed out that present calculations represent only an approximation of the equilibrium of the systems concerned, because of the presump-

Table 3. Equilibrium Phase Assemblages of Magnesite Clinkers in the Six-Component Oxide System MgO—CaO—SiO_2—Al_2O_3—Fe_2O_3—FeO (M—C—S—A—F—$\bar{F}$)

No.	Phase assemblage
1	M—M_2S—CMS—MA—MF—$F\bar{F}$
2	M—M_2S—CMS—MA—$\bar{F}$—$F\bar{F}$
3	M—C_3MS_2—C_2S—MA—MF—$F\bar{F}$
4	M—C_3MS_2—C_2S—MA—$\bar{F}$—$F\bar{F}$
5	M—C_2S—C_3S—C_3A—C_4AF—$F\bar{F}$
6	M—C_2S—C_3S—C_3A—$\bar{F}$—$F\bar{F}$
7	M—C_2S—C_3S—C_2F—C_4AF—$F\bar{F}$
8	M—C_2S—C_3A—$C_{12}A_7$—C_4AF—$F\bar{F}$
9	M—C_2S—C_3A—$C_{12}A_7$—$\bar{F}$—$F\bar{F}$
10	M—C_2S—$C_{12}A_7$—CA—C_4AF—$F\bar{F}$
11	M—C_2S—$C_{12}A_7$—CA—$\bar{F}$—$F\bar{F}$
12	M—C_2S—CA—MA—C_4AF—$F\bar{F}$
13	M—C_2S—CA—MA—$\bar{F}$—$F\bar{F}$
14	M—C_2S—MA—MF—C_4AF—$F\bar{F}$
15	M—C_2S—C_2F—MF—C_4AF—$F\bar{F}$
16	M—C_3S—C—C_3A—C_4AF—$F\bar{F}$
17	M—C_3S—C—C_3A—$\bar{F}$—$F\bar{F}$
18	M—C_3S—C—C_2F—C_4AF—$F\bar{F}$

tion of stoichiometric composition of phases. This premise is critical only in the case when limited solid solutions are formed in the system. Unfortunately there is a lack of data for definition of boundary lines of solid solutions — and thus also for possible corrections — by the introduction of the concept of pseudo-compounds.

Applying the results of suggested procedure to technical products it must be realized that these usually do not reach equilibrium at firing conditions. However, at stable conditions of technology relations can be found between calculated and real phase compositions, as it was done e.g. by modified calculations of the phase composition of cement clinkers [13].

Another problem to be considered is that the formed raw mixture consists of a coarse fraction and a fine grained matrix. At firing the BRM the matrix equilibrates first and subsequently (when ever) the bulk of the material. These effects are discussed in more detail in [10].

Table 4. Phase Composition (w_i) at Singular Ratios of Primary Clinkers (w_r) (Including Phase Compositions for Pure Clinkers)

Phase	w_r /%					
	0	13.5	29.6	45.7	75.4	100
	w_i /%					
M_2S						1.9
MA			0.7	0.9	1.3	1.6
MF	7.3	8.7	9.3	9.0	8.5	8.1
C_2S	2.0	3.0	4.3			
C_2F	2.5					
C_4AF	1.4	2.0				
CMS_2					7.3	6.9
C_3MS_2			5.4			

The advantage of the method presented is the rapid information on qualitative and quantitative changes of mineralogical composition of products in dependence on changes of the chemical composition. Analyzing the results, intervals of compositions can be estimated where advantageous or optimal properties of products can be expected. Necessary corrections are then to be carried out only in the specified, narrow composition ranges.

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