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ALGORITHMIZING THE CALCULATION OF EQUILIBRIUM PHASE COMPOSITION OF MULTICOMPONENT SYSTEMS IN THE SUBSOLIDUS REGION II

(Computed Phase Composition of Belite Clinkers)

JÁN MAJLING, VIKTOR JESENÁK

Faculty of Chemical Technology Slovak, Technical University
Department of the Chemical Technology of Silicates, Jánska 1, 812 37 Bratislava

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In the system $CaO—SiO_2—Al_2O_3—Fe_2O_3—MgO—SO_3$* *it is possible to identity 6 different equilibrum phase associations relevant to the production of belive cement clinker. On the basis of the algorithm given in [1], the qualitative and quantitative phase composition of the equilibrium product is determined in terms of the composition of the raw material mix containing model limestone and clay. The sensitive dependence of the hydration properties of the product on the parameters of clinker preparation is given by the large number of various phase associations within the narrow range of raw material composition and by kinetic factors.*

INTRODUCTION

Calculation of the phase composition of belite clinkers

The phase composition of Portland clinker has so far been calculated by the procedure of Bogue or by modified calculatin methods [2]. These procedures can only be applied when the phase composition of the clinker belongs to one of the two phase associations characteristic of Portland clinker, i.e. $C_3S—C_2S—C_3A—C_4AF—M$, or $C_3S—C_2S—C_2F—C_4AF—M$. The quantitative phase composition of other types of clinker is usually calculated in a similar way on the basis of experimentally identified phase composition of the products [3].

In contrast to the above alternatives, use of the algorithm described in a previous study [1] allows the equilibrium phase association and quantitative representation of the individual mineralogical components in the product of reactions in multicomponent systems in the subsolidus region to be determined on the basis of information on the phase equilibrium of the subsystems in the system being studied.

The present work is concerned with the determination of equilibrium phase associations in the system $C—S—A—F—M—\overline{S}$, of interest in the manufacture of belite cements, namely in terms of composition of a two-component raw material mix, i.e. limestone and clay. The computation result provides a picture of qualitative and quantitative changes of the individual mineralogical components in the equilibrium product.

THE PHASE COEXISTENCE MATRIX (PCM) OF THE SYSTEM $C—S—A—M—F—\overline{S}$

The data on the coexistence of phase couples in the system in question, as taken over from the literature [4 through 8] are summarized in the PCM in Table I. From the standpoint of belite clinker manufacture, the relevant region of the

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*) Further on, the abbreviated symbols are used: $CaO—C$, $SiO_2—S$, $Al_2O_3—A$, $MgO—M$, $Fe_2O_3—F$, $SO_3—\overline{S}$

phase diagram of the six-component system is only the part containing the 19 phases listed in the PCM, i.e. the 18 phases coexisting with C_2S. The table relates to the subsolidus region of the system in question, above the equilibrium temperature of the formation of C_3S, i.e. 1250 °C: (the first line of PCM specifies that C_2S does not coexist with CaO). The data on the coexistence of C_2S with C and C_3S show a change in the sequence of the 0,1 symbols in the first two columns of the first line.

Table I

The phase coexistence matrix of the system C—S—A—F—M—$\bar{S}$.

0 — coexistence, 1 — no coexistence, 2 — no data available on phase coexistence

	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1 . C_2S	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2 . C_3S	.	0	1	0	1	1	0	1	1	0	1	1	0	0	1	1	1	0
3 . C	.		1	0	1	1	0	1	1	0	1	1	0	0	1	1	1	0
4 . C_3S_2	.		.	1	1	1	1	1	1	1	1	0	0	2	0	1	0	1
5 . C_3A	.		.		0	1	1	1	1	0	1	1	1	0	1	1	1	0
6 . $C_{12}A_7$	.		.		.	0	1	1	1	0	1	1	1	0	1	1	1	0
7 . CA	.		.		.		1	0	0	0	0	1	1	0	0	1	1	0
8 . C_2F	.		.		.		.	0	1	0	1	0	0	0	1	1	1	0
9 . CF	.		.		.		.		0	0	0	0	0	0	1	1	1	1
10 . CF_2	.		.		.		.		.	1	0	0	0	0	0	1	1	1
11 . C_4AF	.		.		.		.		.		0	0	1	0	1	1	1	0
12 . MA	.		.		.		.		.		.	0	1	0	0	0	0	0
13 . MF	.		.		.		.		.		.		1	0	0	0	0	0
14 . $C_5S_2\bar{S}$	.		.		.		.		.		.		.	0	1	2	2	0
15 . $C_4A_3\bar{S}$	.		.		.		.		.		.		.		0	2	2	0
16 . C_2AS	.		.		.		.		.		.		.		.	0	0	1
17 . C_3MS_2	.		.		.		.		.		.		.		.		0	0
18 . C_2MS_2	.		.		.		.		.		.		.		.		.	1
19 . M	.		.		.		.		.		.		.		.		.	

The symbol 2 in the PCM indicates that no data are so far available on the coexistence of the respective phases. The computation was carried out on the assumption of coexistence of the respective phases.

IDENTIFICATION OF THE REAL PHASE ASSOCIATIONS

Using the DUPOL program [1], combinations of 6 phases were generated from the 19 phases of the PCM. Associations not containing the C_2S phase were eliminated from combinations of 6 phases. This yielded 27 real associations listed in Table II. As alkali metal oxides are not considered in the system, the sulphates present can combine only into two sulphate phases which coexist in equilibrium with C_2S, i.e. $C_5S_2\bar{S}$ and $C_4A_3\bar{S}$. Associations 1 and 2 in Table II are then equivalent with the phase associations of Portland clinker. Belite clinkers can be realized most advantageously on the basis of associations in which all the phases present exhibit hydration properties.

Table II

Real phase associations in the revelant concentration region of the system C—S—A—F—M—$\bar{S}$

1	C_2S	C_3S	C_3A	C_4AF	$C_4A_3\bar{S}$	M
2	C_2S	C_3S	C_2F	C_4AF	$C_4A_3\bar{S}$	M
3	C_2S	C_3S	C_2F	$C_5S_2\bar{S}$	$C_4A_3\bar{S}$	M
4	C_2S	C_3S_2	MF	$C_5S_2\bar{S}$	$C_4A_3\bar{S}$	C_2MS_2
5	C_2S	C_3S_2	MF	$C_4A_3\bar{S}$	C_2AS	C_3MS_2
6	C_2S	C_3A	$C_{12}A_7$	C_4AF	$C_4A_3\bar{S}$	M
7	C_2S	$C_{12}A_7$	CA	C_4AF	$C_4A_3\bar{S}$	M
8	C_2S	CA	CF	CF_2	MA	$C_4A_3\bar{S}$
9	C_2S	CA	CF	C_4AF	MA	$C_4A_3\bar{S}$
10	C_2S	CA	CF_2	MA	$C_4A_3\bar{S}$	C_2AS
11	C_2S	CA	C_4AF	MA	$C_4A_3\bar{S}$	M
12	C_2S	C_2F	CF	C_4AF	MF	$C_4A_3\bar{S}$
13	C_2S	C_2F	CF	MF	$C_5S_2\bar{S}$	$C_4A_3\bar{S}$
14	C_2S	C_2F	C_4AF	MF	$C_4A_3\bar{S}$	M
15	C_2S	C_2F	MF	$C_5S_2\bar{S}$	$C_4A_3\bar{S}$	M
16	C_2S	CF	CF_2	MA	MF	$C_4A_3\bar{S}$
17	C_2S	CF	CF_2	MF	$C_5S_2\bar{S}$	$C_4A_3\bar{S}$
18	C_2S	CF	C_4AF	MA	MF	$C_4A_3\bar{S}$
19	C_2S	CF_2	MA	MF	$CA_3\bar{S}$	C_2AS
20	C_2S	C_4AF	MA	MF	$C_4A_3\bar{S}$	M
21	C_2S	MA	MF	$C_4A_3\bar{S}$	C_2AS	C_3MS_2
22	C_2S	MA	MF	$C_4A_3\bar{S}$	C_2AS	C_2MS_2
23	C_2S	MA	MF	$C_4A_3\bar{S}$	C_3MS_2	C_2MS_2
24	C_2S	MA	MF	$C_4A_3\bar{S}$	C_3MS_2	M
25	C_2S	MF	$C_5S_2\bar{S}$	$C_4A_3\bar{S}$	C_3MS_2	C_2MS_2
26	C_2S	MF	$C_5S_2\bar{S}$	$C_4A_3\bar{S}$	C_3MS_2	M
27	C_2S	$C_5S_2\bar{S}$	$C_4A_3\bar{S}$	C_2AS	C_3MS_2	C_2MS_2

COMPUTING THE PHASE COMPOSITION OF CLINKERS ON THE BASIS OF TWO-COMPONENT RAW MATERIAL MIXES

The phase composition of belite clinkers based on a twocomponent raw material mix was computed according to algorithm [1]. The raw material components considered were limestone and clay currently extracted for the Stupava Cement Works (Table III). While neglecting the content of alkalies and TiO_2, model compositions of the raw material components were obtained (Table III) and considered in the calculation. This is based on selection of that real phase association for which, at the given raw material composition, a positive proportion by weight of each phase in the association is obtained. At the same time, determination of the proportion of each phase in the equilibrium association yields the quantitative composition of the system (Table IV).

Table III

Chemical composition of raw materials for the computation of clinker phase composition

Oxides	Content of raw material mix components w/mass. %			
	Stupava limestone	Model composition	Stupava clay	Model composition
CaO	48.7	89.36	7.9	9.90
SiO_2	—	—	46.3	58.02
Al_2O_3	0.8	1.47	15.1	18.92
Fe_2O_3	0.4	0.73	5.8	7.27
MgO	4.6	8.44	3.9	4.89
SO_3	—	—	0.8	1.00
Na_2O	0.2	—	0.8	—
K_2O	0.1	—	3.0	—
TiO_2	0.1	—	0.6	—
ign. loss	43.2	—	15.6	—

Table IV

Computed quantitative clinker composition in terms of limestone content in the raw material mix

Limestone w/mass. %	Computed phase composition w/mass. %					
61.25	65.1 C_2S	3.8 $C_4A_3\bar{S}$	11.2 MA	4.9 MF	14.2 C_3MS_2	0.8 M
62.00	73.0	3.8	11.0	4.8	5.4	1.9
63.00	76.9	3.7	10.1	3.8	2.4 C_4AF	3.1
64.00	75.1	3.6	8.6	1.8	6.8	4.0
65.00	73.3	3.5	6.9	0.2 CA	11.1	4.8
66.00	71.5	3.4	1.3	6.3	10.9	6.5
67.50	68.8	3.3	3.5 C_3A	6.9 $C_{12}A_7$	10.6	6.9
68.00	67.8	3.3	7.9	3.6	10.5	6.9
69.00	62.3	3.2	12.5	4.5 C_3S	10.2	7.0
73.00	24.8	2.8	11.3	44.5	9.4	7.1

The computation results are shown in Fig. 1, which illustrates the changes in qualitative and quantitative composition of equilibrium clinkers in terms of the composition of the initial raw material mix. The individual phase associations, coming into consideration for the individual regions of raw materials composition (1, 2 ... 6), are listed in Table V. The arrows indicate phase substitutions due to exceeding the existence boundary of the respective association.

DISCUSSION

The results given above concern equilibrium phase composition of the given systems at subsolidus temperatures. Some types of belite clinkers are prepared at about or below 1250 °C. The reactions proceed in solid phase and according to the X-diffraction analysis, the equilibrium is established within several tens of

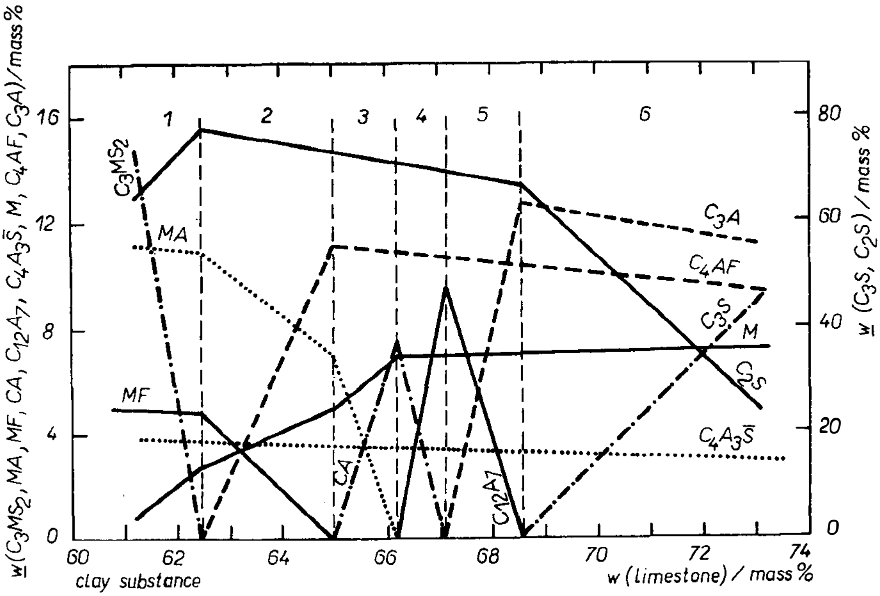

Fig. 1. Dependence of the computed content of phases in belite clinker on the ratio of raw material mix components.

Table V

Phase association of the system C—S—A—F—M—$\bar{S}$ relevant for the individual regions (Table IV) of a raw material mix composition

1	2	3	4	5	6
C_2S	C_2S	C_2S	C_2S	C_2S	C_2S
$C_4A_3\bar{S}$	$C_4A_3\bar{S}$	$C_4A_3\bar{S}$	$C_4A_3\bar{S}$	$C_4A_3\bar{S}$	$C_4A_3\bar{S}$
M	M	M	M	M	M
MA	$\to C_4AF$	C_4AF	C_4AF	C_4AF	C_4AF
MF	MA	$\to CA$	$\to C_{12}A_7$	$\to C_3A$	$\to C_3S$
C_3MS_2	MF	MA	CA	$C_{12}A_7$	C_3A

*) The arrows indicate phase disappearance at the boundaries of phase associations (Fig. 1).

minutes. The reaction products are a sintered material so that the liquid phase content is indiscernible and does not invalidate the computation results [8].

The results appear useful for technical practice as they represent the extent of changes in phase composition of clinkers due to changes in the composition of the raw material mix. The procedure allows the effect of additional or changed raw material components on the equilibrium phase composition of products to be evaluated quantitatively.

The quantitative phase composition provides the first approximation of the product „structure", determining its physico-chemical properties [9]. In the given case, the hydraulic properties of belite clinkers are of interest. Essentially, the actual information will differ from the ideal one, as provided by the calculation, in the following two ways:

a) As a result of the formation of solid solutions, the actual equilibrium composition of the individual phases differs from the nominal one, given by the stoichiometric composition; (if data on the real phase composition in the individual associations are available, the computation can be modified).

b) In the manufacture or laboratory preparation of clinkers, the reactions do not reach completely a state of equilibrium. Attainment of degrees of reactions beyond the limits detectable by the quantitative phase analyses methods may distinctly change the properties of the product by eliminating the last remaining intermediates and producing equilibrium solid solutions in the given equilibrium phase association.

The experimentally established great sensitivity of the hydration properties of belite clinkers [10] — regardless of the known effects of the conditions of their cooling — is associated with the account given above and follows from the fact that six different phase associations arise within a relatively narrow composition range, i.e. between 62.5 and 68.5 wt. % of limestone. As a result of this, a small change in the raw material mix composition will bring about a significant change in the quality and content of phases in the equilibrium association (e.g. an increase in limestone content in the raw material mix from 66.0 wt. % by 1 % will be responsible for a substitution of 6.3 wt. % CA by about 9 wt. % of $C_{12}A_7$ in the equilibrium phase association).

With respect to the effects of the oscillation phenomenon [11], the properties of incompletely reacted reaction mixes can show a great variability with solid phase reactions, namely in dependence on

- mineralogical constitution of raw material components,
- granulometric composition of the raw material components,
- granulometric composition of the mineralogical components in the individual raw material components,
- firing atmosphere,

even at a constant chemical composition of the raw material mix.

These effects may be responsible for

- a variable quality of the intermediate product,
- a variable morphological structure of the product,
- and a variable chemical composition of the individual phases, i.e. the proportions of the individual components in solid solutions.

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ALGORITMIZÁCIA VÝPOČTU ROVNOVÁŽNEHO FÁZOVÉHO ZLOŽENIA MNOHOZLOŽKOVÝCH SÚSTAV V SUBSOLIDUSOVEJ OBLASTI II.

(Výpočet fázového zloženia belitových slinkov)

Ján Majling, Viktor Jesenák

Chemickotechnologická fakulta SVŠT, Katedra chemickej technológie silikátov, 812 37 Bratislava

Analýzou koexistencie fáz v relevantnej oblasti 6-zložkovej sústavy oxidov (C—S—A—M—F—S̄) ktorá sa študovala z hľadiska výroby belitových slinkov — sa zistilo — že kľúčová mineralogická zložka C_2S koexistuje s 18-timi fázami sústavy. Výpočtom sa identifikovalo 27 reálnych rovnovážnych 6-fázových asociácií obsahujúcich kľúčovú zložku. Výpočtom podľa [1] sa identifikovali aktuálne rovnovážne asociácie fáz belitových slinkov pri ich syntéze z bežnej dvojzložkovej cementárskej surovinovej zmesi. Výsledky sa interpretujú ako zmeny kvalitatívneho fázového zloženia (rovnovážna asociácia fáz) a ako vývoj kvantitívneho fázového zloženia v závislosti od obsahu surovinových zložiek vo východiskovej zmesi. Výsledky analýzy spolu s dôsledkami kinetických úvah [9] vysvetľujú experimentálne pozorovanú veľkú citlivosť hydratačných vlastností belitových slinkov v závislosti od vstupných parametrov reakcie.

Obr. 1. Závislosť počítaného obsahu fáz belitového slinku od pomeru zložiek surovinej zmesi.

АЛГОРИТМИЗАЦИЯ РАСЧЕТА РАВНОВЕСНОГО ФАЗОВОГО СОСТАВА МНОГОКОМПОНЕНТНЫХ СИСТЕМ В СУБСОЛИДУСОВОЙ ОБЛАСТИ II.

Расчет фазового состава белитовых клинкеров

Ян Майлинг, Виктор Есенак

Химико-технологический факультет Словацкого политехнического института,
кафедра химической технологии силикатов,
812 37 Братислава

На основании анализа сосуществоания фаз в релевантной области шестикомпонентной системы оксидов (C—S—A—M—F—S̄), которую исследовали с точки зрения получения белитовых клинкеров, установили, что ключевой минералогический компонент C_2S сосуществует с 18 фазами системы. С помощью расчета идентифицировали 27 реальных равновесных шестифазных ассоциаций, содержащих ключевой компонент. Расчетом согласно [1] идентифицировали актуальные равновесные ассоциации фаз белитовых клинкеров при их синтезе из обычной двухкомпонентной цементационной сырьевой смеси. Результаты объясняются как изменения качественного фазового состава (равновесная ассоциация фаз) и как развитие количественного фазового состава в зависимости от содержания сырьевых компонентов в исходной смеси. На основании анализа и кинетических соображений [9] объясняется наблюдаемая большая чувствительность гидратационных свойств белитовых клинкеров в зависимости от входных параметорв реакции.

Рис. 1. Зависимость рассчитываемого содержания фаз белитового клинкера от соотношения компонентов сырьевой смеси.