Enthalpy of incongruent decomposition of $3CaO \cdot Al_2O_3$

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Using a precursor method tricalcium aluminate (C_3A) and peritectic melt formed at the incongruent decomposition of this compound at 1808 K were prepared. The peritectic melt consisted of 59.15 mass % CaO + 40.85 mass % Al_2O_3. Calcium oxide used in the study was prepared by thermal decomposition of $CaCO_3$.

Temperature dependence of the specific relative enthalpy of the peritectic melt was determined combining the measurements of a "drop calorimetry" with the data obtained using a calorimeter for determination of heat of dissolution. Temperature dependences of the specific relative enthalpy of C_3A and CaO were determined on the basis of literature data and measurements of their heats of dissolution. Values of the specific relative enthalpies of C_3A, CaO, and peritectic melt at the temperature of 1808 K were used together with the material balance of the decomposition of C_3A for determination of the specific enthalpy of the incongruent decomposition of C_3A

$$\Delta h_{\mathrm{in.dis}}(C_3A\,;\,1808\ \mathrm{K}) = (306 \pm 31)\ \mathrm{kJ\ kg^{-1}}$$

Until now value of this quantity has not been calorimetrically determined.

Используя метод прекурсора, были получены трикальциевый алюминат (C_3A) и перитектический расплав, образующийся при инконгруэнтном разложении этого соединения при 1808 K. Перитектический расплав состоял из 59,15 % по массе CaO и 40,85 % по массе Al_2O_3. Окись кальция, используемая в данной работе, приготовлялась посредством термического разложения $CaCO_3$.

Используя метод измерения с помощью «капельной калориметрии» в сочетании с результатами калориметрического измерения теплот растворения, была установлена температурная зависимость специфической относительной энтальпии перитектического расплава. Температурные зависимости специфической относительной энтальпий C_3A и CaO были установлены на основе литературных данных и измерений их теплот растворения. Величины специфических относительных энтальпий C_3A, CaO и перитектического расплава при температуре 1808 K были использованы вместе с материальным балансом разложения C_3A для определе-

ния специфической энтальпии инконгруэнтного разложения C_3A

$$\Delta h_{\mathrm{in.dis}}(C_3A\,;\,1808\ \mathrm{K}) = (306 \pm 31)\ \text{кДж кг}^{-1}$$

До сих пор величина этого параметра не была калориметрически определена.

Tricalcium aluminate (C_3A) is one of the most important clinker minerals in portland cement. (In the formula C_3A C stands for CaO and A for Al_2O_3.) Determination of the heat of its incongruent decomposition is a contribution to the enthalpic analysis of the system $CaO—Al_2O_3—SiO_2$ which is important in technology of cement, glass, and formation of slags in blast furnaces.

C_3A decomposes incongruently at the equilibrium temperature 1808 K into CaO and a peritectic melt. Composition of the peritectic melt (per. melt) was taken from the phase diagrams of the systems $CaO—Al_2O_3$ [1] and $CaO—Al_2O_3—SiO_2$ [2], respectively. It follows that the peritectic melt contains 59.15 mass % CaO + 40.85 mass % Al_2O_3. It should be pointed out that this composition is influenced by the presence of water vapours in the atmosphere. If the atmosphere contains no water vapours [3] the content of Al_2O_3 in the peritectic melt increases approximately by 2 mass % and content of CaO lowers by 2 mass % in comparison with the composition given above. In this paper we shall use the composition of peritectic melt corresponding to the presence of water vapours because this is closer to the conditions met in corresponding technologies.

For determination of the heat of incongruent decomposition of C_3A undirect calorimetric method was used. At this method we need to know the material balance of the decomposition reaction and the values of relative enthalpies of C_3A, peritectic melt, and CaO at the equilibrium temperature 1808 K. Decomposition of 1 kg of C_3A into peritectic melt and CaO is represented by the reaction scheme

$$1\ \mathrm{kg}\ C_3A \rightarrow 0.9238\ \mathrm{kg\ per.\ melt} + 0.0762\ \mathrm{kg\ C} \qquad (A)$$

According to (A) the specific enthalpy of decomposition of C_3A at the temperature of 1808 K (it is denoted $\Delta h_{\mathrm{in.dis}}(C_3A\,;\,1808\ \mathrm{K})$) can be calculated on the basis of the Hess law

$$\frac{\Delta h_{\mathrm{in.dis}}(C_3A\,;\,1808\ \mathrm{K})}{\mathrm{kJ\ kg^{-1}}} = 0.9238\,\frac{h_{\mathrm{rel}}(\mathrm{per.\ melt}\,;\,1808\ \mathrm{K})}{\mathrm{kJ\ kg^{-1}}} + \\ + 0.0762\,\frac{h_{\mathrm{rel}}(\mathrm{C}\,;\,1808\ \mathrm{K})}{\mathrm{kJ\ kg^{-1}}} - 1\,\frac{h_{\mathrm{rel}}(C_3A\,;\,1808\ \mathrm{K})}{\mathrm{kJ\ kg^{-1}}} \qquad (1)$$

The values of the specific relative enthalpy (h_{rel}) of C_3A, of the peritectic melt, and of CaO at the equilibrium temperature $T_{\mathrm{eq}} = 1808$ K were calculated from the temperature dependences of the specific relative enthalpies of corresponding phases. Temperature dependence of the specific relative enthalpy of the peritectic melt was derived from experimental data which were obtained by the method of "double calorimetry applied to the same sample".

This method [4, 5] consists in summing the changes in specific enthalpy (taken with reverse sign) measured at cooling of the sample from chosen temperature to 298 K in a drop calorimeter (Δh_{cool}) and the change in enthalpy at the dissolution of the same cooled sample at the temperature of 298 K in a calorimeter for determination of the heat of dissolution (Δh_{sol})

$$h_{\text{rel}} = -(\Delta h_{\text{cool}} + \Delta h_{\text{sol}}) \tag{2}$$

Temperature dependences of specific relative enthalpies of C_3A and CaO were determined from the temperature dependences of their specific enthalpic content [6] and from their heats of dissolution measured in the same solvent as was used for determination of the specific heat of dissolution of the peritectic melt.

Relationship (*1*) provides also a background for calculation of the error in the determination of the value of the specific enthalpy of the incongruent decomposition of C_3A ($\delta(\Delta h_{\text{in.dis}}(C_3A))$). This quantity was calculated from errors in determination of the specific relative enthalpies of the phases coexisting at decomposition of C_3A on the basis of the Gauss law of propagation of error

$$\delta(\Delta h_{\text{in.dis}}(C_3A)) = \sqrt{\sum_X [w(X) \cdot \delta(h_{\text{rel}}(X))]^2} \tag{3}$$

where $w(X)$ is the mass fraction of the corresponding phase X in the reaction scheme (*A*).

Experimental

Preparation of samples

The samples used for measurements in this work were prepared (with exception of CaO) by a precursor method [7].

Preparation of aluminate phases

For preparation of C_3A and of the peritectic melt the following chemicals were used: $CaCO_3$ (Specpure, JMC) and metallic aluminium (purity for semiconductors — 99.999 mass % Al, produced by the Research Institute of Metals, Panenské Břežany). C_3A was prepared from mixture of amorphous solid oxides (these were prepared by precursor method) by heating the mixture first at the temperature of 1000 °C for 1 h and then at 1300 °C for 4 h.

The peritectic melt (composition: 59.15 mass % $CaO + 40.85$ mass % Al_2O_3) was prepared by heating the homogeneous mixture of solid oxides in the sealed crucible (PtRh10) at the temperature of 1650 °C for 4 h.

Preparation of CaO

For preparation of calcium oxide $CaCO_3$ (Specpure, JMC) was used. The samples of $CaCO_3$ were gradually heated to 900 °C and the obtained product was further once or twice heated at 1300 °C for 4 h. One value of the heat of dissolution of CaO was obtained with the once heated sample (denoted as A) and three values of Δh_{sol} of calcium oxide were obtained with the twice heated sample (denoted as B). Prepared calcium oxide was stored in desiccator filled with P_2O_5 in argon atmosphere.

Apparatus

For the measurement of the change in enthalpy at cooling the sample of the peritectic melt from the chosen temperature to 298 K a drop calorimeter was used [8]. Heats of dissolution of the products obtained by cooling the peritectic melt (after measurement in the drop calorimeter) as well as the heats of dissolution of C_3A and CaO were measured in the calorimeter designed for the determination of the heats of dissolution at the temperature of 298 K [9]. Diluted hydrochloric acid (1 volume part of HCl ($w(\mathrm{HCl}) = 35$—38 %) was mixed with 1 volume part of H_2O) was used as the solvent.

Results and calculations

Determination of the temperature dependence of the specific relative enthalpies of C_3A ($h_{\mathrm{rel},\varphi}$ (C_3A; T)) *and of* CaO ($h_{\mathrm{rel},\varphi}$ (C; T))

Temperature dependences of the enthalpic content of C_3A and CaO were calculated by using data from tables [6]

$$C_m(T, p_{\mathrm{atm}}) = A + B \quad 10^{-3}T + C \cdot 10^5 T^{-2} + D \quad 10^{-6}T^2 \qquad (4)$$

where C_m is the molar heat capacity and A, B, C, D are the constants. By integration of eqn (4) in the temperature limits $T_0 = 298$ K and T the following relationships for the temperature dependences of $\Delta h_{\mathrm{cool},\varphi}(C_3A; T)$ and $\Delta h_{\mathrm{cool},\varphi}(C; T)$ were obtained (the symbol φ indicates that the values correspond to the mean of experimental data)

$$\frac{-\Delta h_{\mathrm{cool},\varphi}(\mathrm{C_3A}; T)}{\mathrm{kJ\,kg^{-1}}} = -3.434\times10^{2} + 9.291\times10^{-1}\frac{T}{\mathrm{K}} + $$
$$+5.803\times10^{-5}\frac{T^{2}}{\mathrm{K}^{2}} + 1.8284\times10^{4}\frac{T^{-1}}{\mathrm{K}^{-1}} \qquad (5)$$

$$\frac{-\Delta h_{\mathrm{cool},\varphi}(\mathrm{C}; T)}{\mathrm{kJ\,kg^{-1}}} = -3.090\times10^{2} + 8.855\times10^{-1}\frac{T}{\mathrm{K}} + $$
$$+4.0316\times10^{-5}\frac{T^{2}}{\mathrm{K}^{2}} + 1.2393\times10^{4}\frac{T^{-1}}{\mathrm{K}^{-1}} \qquad (6)$$

The heats of dissolution of C_3A and CaO at 298 K were determined with the dissolution calorimeter. The negative values of the heats of dissolution ($-\Delta h_{\mathrm{sol}}(\mathrm{C_3A})$ and $-\Delta h_{\mathrm{sol}}(\mathrm{C})$), the arithmetic mean of the experimental values of the specific heat of dissolution of C_3A ($-\Delta h_{\mathrm{sol},\varphi}(\mathrm{C_3A})$) and of CaO ($-\Delta h_{\mathrm{sol},\varphi}(\mathrm{C})$) and the errors in the determination of these quantities $\delta(\Delta h_{\mathrm{sol},\varphi}(\mathrm{C_3A}))$, $\delta(\Delta h_{\mathrm{sol},\varphi}(\mathrm{C}))$ are presented in Tables 1 and 2.

The errors in $\Delta h_{\mathrm{sol},\varphi}(\mathrm{C_3A})$ and $\Delta h_{\mathrm{sol},\varphi}(\mathrm{C})$ were determined as errors of the

Table 1

Experimental values of the specific heat of dissolution of C_3A at $T = 298$ K and error in determination of this quantity

$\frac{-\Delta h_{\mathrm{sol}}(\mathrm{C_3A})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{-\Delta h_{\mathrm{sol},\varphi}(\mathrm{C_3A})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{\delta(\Delta h_{\mathrm{sol},\varphi}(\mathrm{C_3A}))}{\mathrm{kJ\,kg^{-1}}}$
3115	3130	18
3128		
3134		
3141		

Table 2

Experimental values of the specific heat of dissolution of CaO (samples A and B) at $T = 298$ K and error in determination of this quantity

$\frac{-\Delta h_{\mathrm{sol}}(\mathrm{C})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{-\Delta h_{\mathrm{sol},\varphi}(\mathrm{C})}{\mathrm{kJ\,kg^{-1}}}$	$\frac{\delta(\Delta h_{\mathrm{sol},\varphi}(\mathrm{C}))}{\mathrm{kJ\,kg^{-1}}}$
3536 (A)	3533	26
3523 (B)		
3518 (B)		
3555 (B)		

arithmetic mean of the specific heat of dissolution using the "Student distribution of errors". The Student coefficient for the corresponding number of measurements on the level of reliability $(1-\alpha)=0.95$ was taken from tables.

After adding the negative value of the arithmetic mean of the specific heat of dissolution of C_3A from Table 1 to the right hand side of eqn (*5*) we obtain for the temperature dependence of the specific relative enthalpy of C_3A the relationship (*7*). Adding corresponding value for CaO from Table 2 to eqn (*6*) we obtain the relationship (*8*)

$$\frac{h_{\mathrm{rel},\varphi}(\mathrm{C_3A}\,;\,T)}{\mathrm{kJ\,kg^{-1}}}=2.7866\times10^{3}+9.291\times10^{-1}\frac{T}{\mathrm{K}}+ +5.803\times10^{-5}\frac{T^2}{\mathrm{K}^2}+1.8284\times10^{4}\frac{T^{-1}}{\mathrm{K}^{-1}} \qquad (7)$$

$$\frac{h_{\mathrm{rel},\varphi}(\mathrm{C}\,;\,T)}{\mathrm{kJ\,kg^{-1}}}=3.224\times10^{3}+8.855\times10^{-1}\frac{T}{\mathrm{K}}+ +4.0316\times10^{-5}\frac{T^2}{\mathrm{K}^2}+1.2393\times10^{4}\frac{T^{-1}}{\mathrm{K}^{-1}} \qquad (8)$$

The errors in the experimental determination of the specific relative enthalpy of C_3A and CaO are

$$\frac{\delta(h_{\mathrm{rel},\varphi}(\mathrm{C_3A}\,;\,T))}{\mathrm{kJ\,kg^{-1}}}=23 \quad \text{and} \quad \frac{\delta(h_{\mathrm{rel},\varphi}(\mathrm{C}\,;\,T))}{\mathrm{kJ\,kg^{-1}}}=30$$

respectively. The errors were calculated from the errors in determination of Δh_{cool} and Δh_{sol} of corresponding phases using the Gauss law of propagation of errors. As in the tables [6] the coefficients of the temperature dependence of the molar heats are presented without information on error, it was assumed that the relative error of Δh_{cool} is 1 % for both C_3A and CaO.

Determination of the temperature dependence of the specific relative enthalpy of peritectic melt ($h_{\mathrm{rel},\varphi}$(per. melt; T))

For determination of the temperature dependence of $h_{\mathrm{rel},\varphi}$(per. melt; T) it was necessary to measure the changes in enthalpy Δh_{cool} at cooling the melt from chosen temperatures to 298 K in the drop calorimeter. Because of the changes in phase composition of the peritectic melt during cooling it was also necessary to determine the heat of dissolution of products of its cooling.

The negative values of Δh_{cool}(per. melt) measured in the temperature interval $\langle 1845\ \mathrm{K};\ 1944\ \mathrm{K}\rangle$ are presented in Table 3.

Table 3

Measured values of $-\Delta h_{\mathrm{cool}}, -\Delta h_{\mathrm{sol},\varphi}$, and h_{rel} of the peritectic melt and calculated values of $h_{\mathrm{rel},\varphi}$(per. melt) at chosen temperatures in the interval ⟨1845 K; 1944 K⟩

$\frac{T}{\mathrm{K}}$	$-\Delta h_{\mathrm{cool}}$(per. melt) / kJ kg^{-1}	$-\Delta h_{\mathrm{sol},\varphi}$(per. melt) / kJ kg^{-1}	h_{rel}(per. melt) / kJ kg^{-1}	$h_{\mathrm{rel},\varphi}$(per. melt) / kJ kg^{-1}
1845	1978	3039	5017	5023
1876	2054	3029	5083	5064
1896	2070	3018	5088	5091
1913	2093	3004	5097	5114
1944	2191	2972	5163	5155

For each sample heat content of which was measured in the drop calorimeter three or four values of the heat of dissolution were determined. (The cooled samples were crushed and sifted through the screen having diameter of the mesh of 0.04 mm.) The negative values of the arithmetic means of the specific heats of dissolution of products of cooling of the peritectic melt ($-\Delta h_{\mathrm{sol},\varphi}$(per. melt)) are presented for given temperatures in Table 3.

The values of the specific relative enthalpies (h_{rel}(per. melt)) at each temperature of the studied temperature range (which are presented in Table 3) are calculated as a sum of changes of enthalpies measured with the drop calorimeter ($-\Delta h_{\mathrm{cool}}$(per. melt)) and the arithmetic means of the heats of dissolution ($-\Delta h_{\mathrm{sol},\varphi}$(per. melt)).

On the basis of the values of h_{rel}(per. melt) measured at different temperatures the temperature dependence of the specific relative enthalpy of the peritectic melt was calculated using the least-squares method

$$\frac{h_{\mathrm{rel},\varphi}(\text{per. melt};\, T)}{\mathrm{kJ\ kg^{-1}}} = 2.5515 \times 10^{3} + 1.3395\,\frac{T}{\mathrm{K}} \qquad (9)$$

The values $h_{\mathrm{rel},\varphi}$(per. melt) calculated for chosen temperatures from the relationship (*9*) are given in Table 3. The error in determination of the specific relative enthalpy of the peritectic melt was determined as the error of the regression equation (*9*) considering "Student's coefficient" and it equals

$$\frac{\delta(h_{\mathrm{rel},\varphi}(\text{per. melt};\, T))}{\mathrm{kJ\ kg^{-1}}} = 23$$

Calculation of the enthalpy of incongruent decomposition of C_3A *at the equilibrium temperature* $T_{eq} = 1808$ K

The values of the specific relative enthalpies of C_3A, peritectic melt, and CaO, respectively, calculated according to the relationships (*7*), (*9*), and (*8*) at the temperature 1808 K are presented in Table 4. Introducing the values of $h_{\mathrm{rel},\varphi}(\mathrm{X};\ 1808\ \mathrm{K})$ of corresponding phases into the relationship (*1*) we obtain the value of the specific enthalpy of incongruent decomposition of C_3A at the temperature $T_{eq} = 1808$ K

$$\Delta h_{\mathrm{in.dis},\varphi}(\mathrm{C_3A};\ 1808\ \mathrm{K}) = (306 \pm 31)\ \mathrm{kJ\ kg^{-1}} \qquad (10)$$

After converting this result to the amount of substance we obtain the value of the molar enthalpy of incongruent decomposition of C_3A

$$\Delta H_{\mathrm{m,in.dis},\varphi}(\mathrm{C_3A};\ 1808\ \mathrm{K}) = (83 \pm 8.4)\ \mathrm{kJ\ mol^{-1}} \qquad (10a)$$

Table 4

Values $h_{\mathrm{rel},\varphi}(\mathrm{X};\ 1808\ \mathrm{K})$ of C_3A, peritectic melt, and CaO

X	$h_{\mathrm{rel},\varphi}(\mathrm{X};\ 1808\ \mathrm{K})$ / kJ kg^{-1}
C_3A	4666 ± 23
Peritectic melt	4973 ± 23
C	4964 ± 30

Fig. 1 shows the temperature dependences of the specific relative enthalpies of single phases multiplied by corresponding coefficients following from the reaction scheme of the incongruent decomposition of C_3A (*A*) and the measured values of h_{rel}(per. melt) multiplied by the mass fraction 0.9238, respectively. The value of $\Delta h_{\mathrm{in.dis}}(\mathrm{C_3A})$ is given as a difference of the specific relative enthalpy of products of decomposition (point *4*) (w(per. melt) · h_{rel}(per. melt; 1808 K) + w(C) · h_{rel}(C; 1808 K)) and of the specific relative enthalpy of C_3A at the temperature of 1808 K.

Dividing eqn (*10*) by T_{eq} we obtain the value of specific entropy of the incongruent decomposition of C_3A

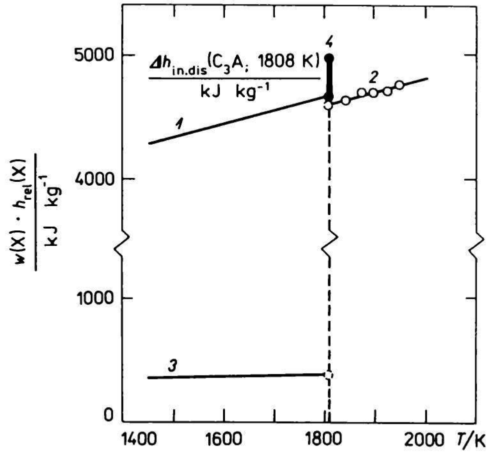
$$\Delta s_{\mathrm{in.dis},\varphi}(\mathrm{C_3A};\ 1808\ \mathrm{K}) = \frac{\Delta h_{\mathrm{in.dis},\varphi}(\mathrm{C_3A};\ 1808\ \mathrm{K})}{1808\ \mathrm{K}} =$$

$$= (169 \pm 17)\ \mathrm{J\ kg^{-1}\ K^{-1}} \qquad (11)$$

Fig. 1. Temperature dependence of the term $w(\mathrm{X}) \cdot h_{\mathrm{rel}}(\mathrm{X})$.

1. C_3A; *2.* peritectic melt; *3.* CaO

The value of $\Delta h_{\mathrm{in.dis}}(C_3A)$ is given as the difference of the sum of specific relative enthalpies of products of decomposition multiplied by corresponding mass fractions ($w(\text{per.melt}) \cdot h_{\mathrm{rel}}(\text{per. melt};\ 1808\ \mathrm{K}) + w(\mathrm{C}) \cdot h_{\mathrm{rel}}(\mathrm{C};\ 1808\ \mathrm{K})$) (point *4*) and of the specific relative enthalpy of C_3A at the temperature of 1808 K.



Similarly the molar entropy of the incongruent decomposition of C_3A equals

$$\Delta S_{\mathrm{m,in.dis},\varphi}(C_3A;\ 1808\ \mathrm{K}) = \frac{\Delta H_{\mathrm{m,in.dis},\varphi}(C_3A;\ 1808\ \mathrm{K})}{1808\ \mathrm{K}} = (46 \pm 4.6)\ \mathrm{J\ mol^{-1}\ K^{-1}} \tag{11a}$$

Discussion

The values of the specific relative enthalpies of C_3A and CaO at the temperature 1808 K are determined both by the sum of Δh_{cool} of these phases and their heats of dissolution Δh_{sol}. The values of the specific heats of dissolution of these phases determined in this work are as follows

$$-\Delta h_{\mathrm{sol},\varphi}(C_3A) = (3130 \pm 18)\ \mathrm{kJ\ kg^{-1}}$$

$$-\Delta h_{\mathrm{sol},\varphi}(\mathrm{C}) = (3533 \pm 26)\ \mathrm{kJ\ kg^{-1}}$$

These values can be compared with the data presented in paper [10]

$$-\Delta h_{\mathrm{sol},\varphi}(C_3A) = (3089.8 \pm 0.6)\ \mathrm{kJ\ kg^{-1}}$$

$$-\Delta h_{\mathrm{sol},\varphi}(\mathrm{C}) = (3541.9 \pm 2.2)\ \mathrm{kJ\ kg^{-1}}$$

In the work [10] the heats of dissolution of C_3A and CaO were measured in diluted HCl of another concentration (approximately 1 volume part of HCl ($w(\mathrm{HCl}) \approx 35\ \%$) in 2 volume parts of water) than that used in this work. Also the temperature of the solvent was different, *viz.* 303 K. Despite that the agreement between these two sets of data is good.

Choice of the data for estimation of the temperature dependence of the molar heat used for determination of the function $\Delta h_{\mathrm{cool},\varphi}(\mathrm{X}) = \mathrm{f}(T)$ of C_3A and CaO (the data from tables [6] were used) also influences the values of h_{rel} of these phases at the equilibrium temperature 1808 K. When the temperature dependence of $C_m(\mathrm{C};\ T,\ p_{\mathrm{atm}})$ was taken from tables [11] we obtained for specific enthalpy of CaO at 1808 K the value $h_{\mathrm{rel},\varphi}(\mathrm{C};\ 1808\ \mathrm{K}) = 4952\ \mathrm{kJ\ kg^{-1}}$ which differs from the value $h_{\mathrm{rel},\varphi}(\mathrm{C};\ 1808\ \mathrm{K}) = 4964\ \mathrm{kJ\ kg^{-1}}$ given in Table 4. However, with respect to the low mass fraction of CaO in the material balance of the decomposition of C_3A this difference would influence the value of $\Delta h_{\mathrm{in.dis},\varphi}(\mathrm{C_3A};\ 1808\ \mathrm{K})$ only by 1 kJ $\mathrm{kg^{-1}}$.

Also choice of the regression relationship for representation of the temperature dependence of $h_{\mathrm{rel},\varphi}(\mathrm{per.\ melt};\ T)$ influences the value of $h_{\mathrm{rel},\varphi}(\mathrm{per.\ melt};\ 1808\ \mathrm{K})$. In this work a linear regression was chosen because the values of $h_{\mathrm{rel}}(\mathrm{per.\ melt})$ were measured in a relatively narrow temperature interval $\langle 1845\ \mathrm{K}—1944\ \mathrm{K}\rangle$.

Calculated value of the enthalpy of incongruent decomposition of C_3A depends however, also on the material balance of decomposition of C_3A. This balance is determined by the composition of the peritectic melt. In this work we considered the composition of peritectic melt as it is presented in [1] and [2], respectively, as these data are closer to technological conditions than those presented in [3] which were measured in the atmosphere containing no moisture. If the calculation of $\Delta h_{\mathrm{in.dis},\varphi}(\mathrm{C_3A})$ was carried out with the composition of peritectic melt and equilibrium temperature presented in [3] ($T_{\mathrm{eq}} = 1812$ K) (and assuming that for the temperature dependence of $h_{\mathrm{rel},\varphi}(\mathrm{per.\ melt};\ T)$ still the relationship (*9*) can be used) we would obtain $\Delta h_{\mathrm{in.dis},\varphi}(\mathrm{C_3A};\ 1812\ \mathrm{K}) = 307\ \mathrm{kJ\ kg^{-1}}$. This value differs only negligibly from the value of $\Delta h_{\mathrm{in.dis},\varphi}(\mathrm{C_3A};\ 1808\ \mathrm{K}) = 306\ \mathrm{kJ\ kg^{-1}}$ (see eqn (*10*)), which can be explained by the fact that the values of the relative enthalpies of products of decomposition of C_3A, *i.e.* CaO and peritectic melt, are rather close at the temperature of decomposition of C_3A (Table 4).

The value of $\Delta h_{\mathrm{in.dis},\varphi}(\mathrm{C_3A})$ was determined in this work with relative error of 10 % (relationship (*10*)) despite of that the relative error of determination of the specific relative enthalpies of single phases taking part in the decomposition of C_3A is lower than 1 % (the biggest relative error corresponds to CaO, *viz.* 0.6 %).

The values of $\Delta H_{\mathrm{m,in.dis}}(\mathrm{C_3A})$ presented in literature differ substantially from the value of this parameter determined in this work. In paper [12] the value $\Delta H_{\mathrm{m,in.dis}}(\mathrm{C_3A})$ of 150.7 kJ $\mathrm{mol^{-1}}$ is given. It is not clear, however, if this value was estimated or taken from literature. Close to the latter value are the data from the recent work [13]. These authors found $\Delta H_{\mathrm{m,in.dis}}(\mathrm{C_3A}) = 157\ \mathrm{kJ\ mol^{-1}}$, which differs from the value of $\Delta H_{\mathrm{m,in.dis}}(\mathrm{C_3A})$ determined in this work by 82 %—90 %. (In the cited paper also the values for CA and CA_2 are presented.) All these data were calculated from liquidus curves of the system CaO—$AlO_{1.5}$ and no information about error of these data is given.

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