

Determination of the enthalpy of crystallization of eutectic melt in the system $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ — $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ — $2\text{CaO} \cdot \text{SiO}_2$

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The sample having composition of the eutectic melt in the system $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ — $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ — $2\text{CaO} \cdot \text{SiO}_2$ (51.97 mass % CaO, 41.34 mass % Al_2O_3 , 6.69 mass % SiO_2) and $\gamma\text{-Ca}_2\text{SiO}_4$ were prepared by reactions of components in solid phase. Next two phases formed at crystallization of the eutectic melt at equilibrium temperature of 1335 °C ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$) were prepared by a precursor method.

For determination of the temperature dependence of the specific relative enthalpy of the eutectic melt the combination of drop calorimetry with data obtained from the calorimeter for determination of heats of dissolution was used. Temperature dependences of specific relative enthalpies of C_3A , C_{12}A_7 , and $\beta\text{-C}_2\text{S}$ were determined on the basis of literature data and measured values of the specific heat of dissolution of C_3A , C_{12}A_7 , and $\gamma\text{-C}_2\text{S}$. Using the values of specific relative enthalpy of the eutectic melt, C_3A , C_{12}A_7 , and $\beta\text{-C}_2\text{S}$ related to the equilibrium temperature 1608 K and material balance of crystallization of the eutectic melt the specific enthalpy of crystallization of the eutectic melt was determined: $\Delta h_{\text{cryst}}(\text{eut.melt}; 1608 \text{ K}) = (-607 \pm 28) \text{ kJ kg}^{-1}$.

Посредством реакций в твердой фазе был приготовлен образец с составом эвтектического расплава из системы $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ — $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ — $2\text{CaO} \cdot \text{SiO}_2$ (51,97 вес. % CaO; 41,34 вес. % Al_2O_3 и 6,69 вес. % SiO_2) и $\gamma\text{-Ca}_2\text{SiO}_4$. Следующие две фазы, образующиеся при кристаллизации эвтектического расплава при равновесной температуре 1335 °C ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$ и $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$) были приготовлены методом прекурсора. С помощью сочетания измерений на вбрасываемом калориметре и калориметре, служащем для определения теплот растворения, была найдена температурная зависимость измеряемой относительной энтальпии эвтектического расплава. Температурные зависимости измеряемой относительной энтальпии C_3A , C_{12}A_7 и $\beta\text{-C}_2\text{S}$ были установлены на основании данных из таблиц и измеренных величин измеряемой теплоты растворения C_3A , C_{12}A_7 и $\gamma\text{-C}_2\text{S}$. Используя величины измеряемой относительной энтальпии эвтектического расплава, C_3A , C_{12}A_7 и $\beta\text{-C}_2\text{S}$ при равновесной температуре 1608 K и материальном балансе кристаллизации эвтектического расплава, была определена измеряемая энтальпия кристаллизации эвтектического расплава: $\Delta h_{\text{cryst}}(\text{eut.melt}; 1608 \text{ K}) = (-607 \pm 28) \text{ кДж кг}^{-1}$.

Composition and content of liquid phase formed at the production of cement clinker influences its technological properties. As the heat liberated at total or partial crystallization of these melts can influence the course of reactions in adjacent phases, its determination is of principle importance.

The aim of this work is the determination of the enthalpy and entropy of crystallization of C_3A , $C_{12}A_7$, and C_2S from eutectic melt of composition [1] 51.97 mass % CaO , 41.34 mass % Al_2O_3 , and 6.69 mass % SiO_2 at the equilibrium temperature 1335 °C and determination of the heat of crystallization of this melt when it is cooled from 1335 °C to 25 °C. (The symbols C, A, and S in formulas denote CaO , Al_2O_3 , and SiO_2 , respectively.) In the phase diagram of the system $C_3A-C_{12}A_7-C_2S$ the eutectic point at the temperature of 1335 °C is the invariant point with the lowest temperature [2].

For determination of the enthalpy of crystallization of C_3A , $C_{12}A_7$, and C_2S from the eutectic melt at 1335 °C an undirect calorimetric method was used. For applying this method knowledge of the values of relative enthalpies of single phases which take part in the crystallization process at the temperature of 1335 °C as well as the material balance of the process is needed. Masses of C_3A , $C_{12}A_7$, and $\beta-C_2S$ crystallizing from 1 kg of the eutectic melt (eut.melt) were determined on the basis of material balance of CaO , Al_2O_3 , and SiO_2 in the eutectic melt, C_3A , $C_{12}A_7$, and C_2S . It follows



With respect to this scheme we can write on the basis of the Hess law for calculation of the specific heat of crystallization of the eutectic melt at the equilibrium temperature $T_{eq} = 1608 \text{ K}$ ($\Delta h_{\text{cryst}}(\text{eut.melt}; 1608 \text{ K})$) the following relationship

$$\begin{aligned} \Delta h_{\text{cryst}}(\text{eut.melt}; 1608 \text{ K}) = & 0.0189 h_{\text{rel}}(C_3A; 1608 \text{ K}) + \\ & + 0.7893 h_{\text{rel}}(C_{12}A_7; 1608 \text{ K}) + 0.1918 h_{\text{rel}}(\beta-C_2S; 1608 \text{ K}) - \\ & - 1 h_{\text{rel}}(\text{eut.melt}; 1608 \text{ K}) \end{aligned} \quad (1)$$

Δh_i are given in kJ kg^{-1} .

The specific relative enthalpy (h_{rel}) of corresponding phase equals — with opposite sign — to the sum of values of specific changes in enthalpy of the phase at its cooling from given temperature to 298 K (Δh_{cool}) plus the heat of dissolution of this phase at 298 K (Δh_{sol}) [3, 4]

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

Thus this specific relative enthalpy is related to a reference state defined by the state of solution of the phase in suitably chosen dissolution mixture.

The values of h_{rel} of the eutectic melt, C_3A , $C_{12}A_7$, and $\beta-C_2S$ at $T_{eq} = 1608 \text{ K}$ were calculated from temperature dependences of h_{rel} of these phases determined

in suitably chosen temperature intervals. The temperature dependence of h_{rel} of the eutectic melt was obtained by measuring Δh_{cool} using the drop calorimeter and Δh_{sol} obtained in a dissolution calorimeter. The temperature dependences h_{rel} of the phases C_3A , $C_{12}A_7$, and $\beta\text{-}C_2S$ were determined on the basis of temperature dependences of the change of their specific enthalpy by heating [5] and from the values of their heats of dissolution measured in the same dissolution mixture which was used for the measurement of Δh_{sol} of the products resulting of cooling eutectic mixture.

The relationship (1) was also used as a basis for evaluation of the error in determination of the specific heat of crystallization of eutectic melt ($\delta(\Delta h_{\text{crist}}(\text{eut. melt}))$). This error was calculated from the errors in determination of h_{rel} of single phases X taking part in the process of crystallization (these are denoted as $\delta(h_{\text{rel}}(X))$) using the Gauss "law of spreading of errors"

$$\delta(\Delta h_{\text{crist}}(\text{eut. melt})) = \sqrt{\sum_X [w(X) \cdot \delta(h_{\text{rel}}(X))]^2} \quad (3)$$

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

Experimental

Preparation of samples

The samples used for calorimetric study were prepared either by reaction in solid phase (sample having composition of the eutectic melt and the phase $\gamma\text{-}C_2S$) or by a precursor method (C_3A , $C_{12}A_7$).

Preparation of the eutectic melt

Composition of the eutectic melt was determined from the phase diagram of the system $\text{CaO—Al}_2\text{O}_3\text{—SiO}_2$ at the equilibrium temperature 1335 °C [1]. For its preparation CaCO_3 , Al_2O_3 , and SiO_2 (Specpure, JMC) were used. Weighted mixture of these substances was homogenized in a platinum crucible with toluene for 8 h. After evaporation of toluene the platinum crucible was slowly heated for three days up to the temperature 1050 °C. At this temperature the sample was kept for 12 h. After sealing the crucible with the lid of the alloy PtRh10 the sample was heated for 4 h at temperature of 1600 °C and then quenched in liquid nitrogen. X-Ray diffraction of powdered product showed that the quenched sample of the eutectic melt did not crystallize. Spectral analysis of finely ground sample proved that the sample was not contaminated by melting, grinding or sifting.

Preparation of γ -C₂S

γ -C₂S was prepared by heating the homogenized mixture of CaO obtained from CaCO₃ (Specpure, JMC) and SiO₂ (Specpure, JMC) for 5 h at the temperature of 1450 °C and slow cooling of the sample. X-Ray analysis proved that the sample consists of γ -C₂S.

Preparation of C₃A and C₁₂A₇

C₃A and C₁₂A₇ were prepared using a precursor method modified according to [6]. Principle of the method consists in decomposition of organic glass prepared from calcium tartarate and aluminium tartarate. Starting materials were CaCO₃ (Specpure, JMC) and metal aluminium ($w(\text{Al}) = 0.999$). Both products were checked by X-ray analysis.

Apparatus

Changes in enthalpy at cooling of the melt having eutectic composition from given temperature to 298 K were measured in a drop calorimeter which was described in detail in paper [7]. Heats of dissolution of glasses which were formed at cooling of the eutectic melt and of the samples of C₃A, C₁₂A₇, and γ -C₂S were measured at temperature 298 K in a dissolution calorimeter described in paper [8]. A mixture of hydrochloric acid (1 volume part of 35–38 mass % HCl and 1 volume part of H₂O) with 40 mass % hydrofluoric acid in the volume ratio 10:1 was used as the solvent. Composition of the solvent was chosen on the basis of preliminary measurements of heats of dissolution of samples in mixtures of hydrofluoric and hydrochloric acids or in mixtures of hydrofluoric acid with nitric acid prepared in different ratios. The dissolving mixture was saturated with CaF₂ (this was prepared by dissolution of CaCO₃ in the mixture) in order to assure that all calcium from the dissolved samples will be precipitated as CaF₂.

Results

Determination of temperature dependence of the specific relative enthalpy of the eutectic melt ($h_{\text{rel}, \varphi}(\text{eut.melt}; T)$)

Determination of the temperature dependence of the quantity $h_{\text{rel}, \varphi}(\text{eut.melt}; T)$ (φ denotes the mean of the experimental values) is based on two sets of data. First the drop calorimeter was used for determination of the values Δh_{cool} corresponding to cooling of the melt having eutectic composition from temperature of the range 1631 K–1840 K to 298 K. The negative values of $\Delta h_{\text{cool}}(\text{eut.melt})$ for corresponding temperatures are summarized in Table 1. In the second step, for each sample used for determination of Δh_{cool} the heat of dissolution Δh_{sol} at the temperature of

Table 1

Experimental values of the change in specific enthalpy at cooling of the eutectic melt ($-\Delta h_{\text{cool}}(\text{eut.melt})$), its relative enthalpy $h_{\text{rel}}(\text{eut.melt})$ at given temperatures and calculated values of ($-\Delta h_{\text{cool},\varphi}(\text{eut.melt})$) and $h_{\text{rel},\varphi}(\text{eut.melt})$

$\frac{T}{\text{K}}$	$\frac{-\Delta h_{\text{cool}}(\text{eut.melt})}{\text{kJ kg}^{-1}}$	$\frac{-\Delta h_{\text{cool},\varphi}(\text{eut.melt})}{\text{kJ kg}^{-1}}$	$\frac{h_{\text{rel}}(\text{eut.melt})}{\text{kJ kg}^{-1}}$	$\frac{h_{\text{rel},\varphi}(\text{eut.melt})}{\text{kJ kg}^{-1}}$
1631	1579	1573	5086	5080
1678	1633	1644	5140	5151
1724	1717	1714	5224	5221
1782	1804	1802	5311	5309
1840	1890	1890	5397	5397

298 K was measured. (Before this measurement the samples were ground and sifted; mesh 0.04 mm was used.) The negative values of $\Delta h_{\text{sol}}(\text{eut.melt})$ (eut.melt denotes in this case products of cooling) are summarized in Table 2. In this table

Table 2

Values of the specific heat of dissolution of products of cooling of the eutectic melt at $T = 298$ K and error in its determination

$\frac{-\Delta h_{\text{sol}}(\text{eut.melt})}{\text{kJ kg}^{-1}}$	$\frac{-\Delta h_{\text{sol}, \varphi}(\text{eut.melt})}{\text{kJ kg}^{-1}}$	$\frac{\delta(\Delta h_{\text{sol}, \varphi}(\text{eut.melt}))}{\text{kJ kg}^{-1}}$
3519	3507	21
3524		
3487		
3514		
3492		

also the values of the arithmetic mean of the specific heat of dissolution ($-\Delta h_{\text{sol}, \varphi}(\text{eut.melt})$) and the error in determination of this value $\delta(\Delta h_{\text{sol}, \varphi}(\text{eut.melt}))$ are presented. At calculation of this error the "Student distribution of error" was considered. The value of $\Delta h_{\text{sol}, \varphi}(\text{eut.melt})$ was obtained on the basis of heats of dissolution of five glasses formed at cooling the melt having eutectic composition from five different temperatures to the temperature of 298 K. Comparison of these data shows that a possible change of properties of samples of this glass at transformation temperature is in the limits of experimental errors.

From the obtained values of $\Delta h_{\text{cool}}(\text{eut.melt})$ the temperature dependence of the change of enthalpy at cooling of the melt of eutectic composition was calculated using the least-squares method. It follows that

$$\frac{-\Delta h_{\text{cool}, \varphi}(\text{eut.melt}; T)}{\text{kJ kg}^{-1}} = -9.058 \times 10^2 + 1.5196 \frac{T}{\text{K}} \quad (4)$$

with error of

$$\frac{\delta(\Delta h_{\text{cool}, \varphi}(\text{eut.melt}; T))}{\text{kJ kg}^{-1}} = 11$$

The error was determined by dividing the error of regression dependence (4) with the square root of number of measurements and multiplying the result with the Student coefficient read from tables for the corresponding degree of freedoms of the residual sum of squares and for the reliability coefficient $(1 - \alpha) = 0.95$. The values of $(-\Delta h_{\text{cool}, \varphi}(\text{eut.melt}))$ calculated for chosen temperatures from eqn (4) are presented in Table 1.

Adding negative value of the arithmetic mean of the specific heat of dissolution of glass formed from the melt having eutectic composition (Table 2) and the experimental values of $(-\Delta h_{\text{cool}}(\text{eut.melt}))$ the values of $h_{\text{rel}}(\text{eut.melt})$ for given temperatures were obtained. The results are summarized in Table 1. Temperature dependence of h_{rel} of the melt having eutectic composition can be obtained by adding the negative value of the arithmetic mean of the heat of dissolution of cooled products of this melt to the right-hand side of eqn (4)

$$\frac{h_{\text{rel}, \varphi}(\text{eut.melt}; T)}{\text{kJ kg}^{-1}} = 2.6012 \times 10^3 + 1.5196 \frac{T}{\text{K}} \quad (5)$$

Error in determination of $h_{\text{rel}, \varphi}(\text{eut.melt}; T)$ was determined to be

$$\frac{\delta(h_{\text{rel}, \varphi}(\text{eut.melt}; T))}{\text{kJ kg}^{-1}} = 24$$

The latter value was determined from the error $\delta(\Delta h_{\text{cool}, \varphi}(\text{eut.melt}))$ and $\delta(\Delta h_{\text{sol}, \varphi}(\text{eut.melt}))$ on the basis of the "law of spreading of errors" The values of $h_{\text{rel}, \varphi}(\text{eut.melt})$ calculated according to relationship (5) are for given temperatures presented in Table 1.

Determination of the temperature dependence of the specific relative enthalpy of C_3A ($h_{\text{rel}, \varphi}(\text{C}_3\text{A}; T)$) and C_{12}A_7 ($h_{\text{rel}, \varphi}(\text{C}_{12}\text{A}_7; T)$)

Temperature dependences of the enthalpic content of C_3A and C_{12}A_7 , respectively, were calculated using the following equation for calculation of molar heat capacities

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

C_m is the molar heat capacity and A , B , C , and D are the constants taken from tables [5]. Introducing the values of the constants A , B , C ($D = 0$) and integrating in the limits $T_0 = 298$ K and T the temperature dependences of $\Delta h_{\text{cool}, \varphi}(\text{C}_3\text{A}; T)$ and $\Delta h_{\text{cool}, \varphi}(\text{C}_{12}\text{A}_7; T)$ were obtained

$$\begin{aligned} \frac{-\Delta h_{\text{cool}, \varphi}(\text{C}_3\text{A}; T)}{\text{kJ kg}^{-1}} &= -3.434 \times 10^2 + 9.291 \times 10^{-1} \frac{T}{\text{K}} + \\ &+ 5.803 \times 10^{-5} \frac{T^2}{\text{K}^2} + 1.8284 \times 10^4 \frac{T^{-1}}{\text{K}^{-1}} \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{-\Delta h_{\text{cool}, \varphi}(\text{C}_{12}\text{A}_7; T)}{\text{kJ kg}^{-1}} &= -3.365 \times 10^2 + 9.117 \times 10^{-1} \frac{T}{\text{K}} + \\ &+ 9.888 \times 10^{-5} \frac{T^2}{\text{K}^2} + 1.6697 \times 10^4 \frac{T^{-1}}{\text{K}^{-1}} \end{aligned} \quad (8)$$

Using a dissolution calorimetry the specific heats of dissolution of C_3A and $C_{12}A_7$ ($\Delta h_{\text{sol}}(C_3A)$, $\Delta h_{\text{sol}}(C_{12}A_7)$) at the temperature of 298 K were obtained. Negative values of the heats of dissolution, their arithmetic mean (denoted as $\Delta h_{\text{sol}, \varphi}(C_3A)$ and $\Delta h_{\text{sol}, \varphi}(C_{12}A_7)$, respectively) and the error in the arithmetic mean (denoted as $\delta(\Delta h_{\text{sol}, \varphi}(C_3A))$, $\delta(\Delta h_{\text{sol}, \varphi}(C_{12}A_7))$) are presented in Tables 3 and 4. The latter values were determined as the errors of the arithmetic mean of the specific heat of dissolution with consideration of the "Student distribution of errors" The Student coefficient was taken from tables for corresponding number of measurements and reliability coefficient $(1 - \alpha) = 0.95$.

Adding the negative value of the arithmetic mean of the specific heat of dissolution of C_3A to the right-hand side of eqn (7) the temperature dependence of h_{rel} was obtained

$$\begin{aligned} \frac{h_{\text{rel}, \varphi}(C_3A; T)}{\text{kJ kg}^{-1}} &= 3.2713 \times 10^3 + 9.291 \times 10^{-1} \frac{T}{\text{K}} \\ &+ 5.803 \times 10^{-5} \frac{T^2}{\text{K}^2} + 1.8284 \times 10^4 \frac{T^{-1}}{\text{K}^{-1}} \end{aligned} \quad (9)$$

Table 3

Values of the specific heat of dissolution of C_3A at $T = 298$ K and error in its determination

$\frac{-\Delta h_{\text{sol}}(C_3A)}{\text{kJ kg}^{-1}}$	$\frac{-\Delta h_{\text{sol}, \varphi}(C_3A)}{\text{kJ kg}^{-1}}$	$\frac{\delta(\Delta h_{\text{sol}, \varphi}(C_3A))}{\text{kJ kg}^{-1}}$
3617.9	3614.7	8.0
3618.2		
3607.4		
3615.3		

Table 4

Values of the specific heat of dissolution of $C_{12}A_7$ at $T = 298$ K and error in its determination

$\frac{-\Delta h_{\text{sol}}(C_{12}A_7)}{\text{kJ kg}^{-1}}$	$\frac{-\Delta h_{\text{sol}, \varphi}(C_{12}A_7)}{\text{kJ kg}^{-1}}$	$\frac{\delta(\Delta h_{\text{sol}, \varphi}(C_{12}A_7))}{\text{kJ kg}^{-1}}$
3174	3179	11
3180		
3183		

In a similar way the temperature dependence h_{rel} of C_{12}A_7 was obtained (in this case the heat of dissolution was added to eqn (8))

$$\begin{aligned} \frac{h_{\text{rel}, \varphi}(\text{C}_{12}\text{A}_7; T)}{\text{kJ kg}^{-1}} &= 2.8425 \times 10^3 + 9.117 \times 10^{-1} \frac{T}{\text{K}} + \\ &+ 9.888 \times 10^{-5} \frac{T^2}{\text{K}^2} + 1.6697 \times 10^4 \frac{T^{-1}}{\text{K}^{-1}} \end{aligned} \quad (10)$$

The errors in the values of the relative enthalpies of C_3A and C_{12}A_7 were determined to be

$$\frac{\delta(h_{\text{rel}, \varphi}(\text{C}_3\text{A}; T))}{\text{kJ kg}^{-1}} = 15 \quad \text{and} \quad \frac{\delta(h_{\text{rel}, \varphi}(\text{C}_{12}\text{A}_7; T))}{\text{kJ kg}^{-1}} = 18$$

respectively.

These errors were determined on the basis of determination of $\Delta h_{\text{cool}, \varphi}$ and $\Delta h_{\text{sol}, \varphi}$ of corresponding phases using the Gauss "law of spreading of errors" In the case of $\Delta h_{\text{cool}, \varphi}$ of both C_3A and C_{12}A_7 a one percent error was assumed because no data on precision of temperature dependence of molar heat capacities necessary for calculation of $\Delta h_{\text{cool}, \varphi}$ of C_3A and C_{12}A_7 were available [5].

Determination of the temperature dependence of the specific relative enthalpy of $\beta\text{-C}_2\text{S}$ ($h_{\text{rel}, \varphi}(\beta\text{-C}_2\text{S}; T)$)

At the equilibrium temperature of crystallization of the melt having eutectic composition ($T_{\text{eq}} = 1608 \text{ K}$) the stable modification of C_2S is its β -modification ($\beta\text{-C}_2\text{S}$). Because at cooling of $\beta\text{-C}_2\text{S}$ a phase transition at $T = 948 \text{ K}$ occurs [5] (the β -modification changes to γ -modification) this must be taken into account in the calculation of the temperature dependence of the change of enthalpy of C_2S . Using data [5] the temperature dependence of enthalpy of $\beta\text{-C}_2\text{S}$ in the temperature range $T - 948 \text{ K}$, the heat of phase transition $\beta\text{-C}_2\text{S} \rightarrow \gamma\text{-C}_2\text{S}$ at $T = 948 \text{ K}$, temperature dependence of enthalpy of $\gamma\text{-C}_2\text{S}$ in the range of $948 - 298 \text{ K}$ were calculated and then the temperature dependence of $\Delta h_{\text{cool}, \varphi}(\beta\text{-C}_2\text{S}; T)$ for the temperature interval $(948 \text{ K}, 1693 \text{ K})$ was obtained

$$\begin{aligned} \frac{-\Delta h_{\text{cool}, \varphi}(\beta\text{-C}_2\text{S}; T)}{\text{kJ kg}^{-1}} &= -2.782 \times 10^2 + 8.476 \times 10^{-1} \frac{T}{\text{K}} + \\ &+ 1.1838 \times 10^{-4} \frac{T^2}{\text{K}^2} + 1.5217 \times 10^4 \frac{T^{-1}}{\text{K}^{-1}} \end{aligned} \quad (11)$$

At the temperature 298 K the stable modification of dicalcium silicate is $\gamma\text{-C}_2\text{S}$. Therefore heats of dissolution of this modification of C_2S at 298 K were measured. The same dissolving mixture as in the case of glasses obtained by quenching of the

eutectic melts, C_3A and $C_{12}A_7$ was used. The experimental values of the specific heat of dissolution of $\gamma-C_2S$ as well as arithmetic mean of these values and the error in its determination are given in Table 5. Adding the value of $(-\Delta h_{\text{sol},\varphi}(\gamma-C_2S))$ to

Table 5

Values of the specific heat of dissolution of $\gamma-C_2S$ at $T = 298$ K and error in its determination

$-\Delta h_{\text{sol},\varphi}(\gamma-C_2S)$ kJ kg ⁻¹	$-\Delta h_{\text{sol},\varphi}(\gamma-C_2S)$ kJ kg ⁻¹	$\delta(\Delta h_{\text{sol},\varphi}(\gamma-C_2S))$ kJ kg ⁻¹
2445	2427	14
2419		
2419		
2423		
2431		

the right-hand side of eqn (11) the temperature dependence $h_{\text{rel}}(\beta-C_2S)$ was obtained

$$\begin{aligned} \frac{h_{\text{rel},\varphi}(\beta-C_2S; T)}{\text{kJ kg}^{-1}} &= 2.1488 \times 10^3 + 8.476 \times 10^{-1} \frac{T}{\text{K}} + \\ &+ 1.1838 \times 10^{-4} \frac{T^2}{\text{K}^2} + 1.5217 \times 10^4 \frac{T^{-1}}{\text{K}^{-1}} \end{aligned} \quad (12)$$

The error of this value

$$\frac{\delta(h_{\text{rel},\varphi}(\beta-C_2S; T))}{\text{kJ kg}^{-1}} = 20$$

This error was determined on the basis of $\delta(\Delta h_{\text{cool},\varphi}(\beta-C_2S))$ and $\delta(\Delta h_{\text{sol},\varphi}(\gamma-C_2S))$ using the Gauss "law of spreading of errors" In the case of $\Delta h_{\text{cool}}(\beta-C_2S)$ a one percent error was assumed.

Calculation of the specific enthalpy and entropy of crystallization of the melt having eutectic composition at $T_{\text{eq}} = 1608$ K

From the temperature dependences h_{rel} of single phases which take part in the process of crystallization of the eutectic melt (the relationships (5), (9), (10), and (12)) the values of h_{rel} at equilibrium temperature $T_{\text{eq}} = 1608$ K were determined (Table 6). After introducing the values of $h_{\text{rel},\varphi}(X; 1608 \text{ K})$ into eqn (1) the specific enthalpy of crystallization of the eutectic melt at $T_{\text{eq}} = 1608$ K can be calculated

$$\frac{\Delta h_{\text{cryst},\varphi}(\text{eut.melt}; 1608 \text{ K})}{\text{kJ kg}^{-1}} = -607 \pm 28 \quad (13)$$

Table 6

 Values of the relative enthalpy $h_{rel, \varphi}(X; 1608 \text{ K})$ of the eutectic melt, C_3A , $C_{12}A_7$, and $\beta\text{-}C_2S$

Phase	$\frac{h_{rel, \varphi}(X; 1608 \text{ K})}{\text{kJ kg}^{-1}}$
Eut.melt	5045 ± 24
C_3A	4927 ± 15
$C_{12}A_7$	4575 ± 18
$\beta\text{-}C_2S$	3827 ± 20

The experimental values of h_{rel} of the eutectic melt, temperature dependence h_{rel} of the eutectic melt (curve 1), C_3A (curve 2), $\beta\text{-}C_2S$ (curve 3), and $C_{12}A_7$ (curve 4) (all multiplied by the coefficients of the reaction scheme (A)) are plotted in Fig. 1. The value of $(-\Delta h_{cryst, \varphi}(\text{eut.melt}; 1608 \text{ K}))$ is given as the difference of h_{rel} of the eutectic melt at 1608 K (point 6) and $\sum_X w(X) \cdot h_{rel, \varphi}(X; 1608 \text{ K})$ ($X \equiv C_3A, \beta\text{-}C_2S$, and $C_{12}A_7$) (point 5).

The specific entropy of crystallization of the eutectic melt was obtained by dividing eqn (13) by the temperature $T_{eq} = 1608 \text{ K}$.

$$\begin{aligned} \Delta S_{cryst, \varphi}(\text{eut.melt}; 1608 \text{ K}) &= \frac{\Delta h_{cryst, \varphi}(\text{eut.melt}; 1608 \text{ K})}{1608 \text{ K}} = \\ &= (-377 \pm 17) \text{ J kg}^{-1} \text{ K}^{-1} \end{aligned} \quad (14)$$

Determination of the "total heat of crystallization" of the melt of eutectic composition

"Total heat of crystallization" which is liberated at crystallization of C_3A , $C_{12}A_7$, and C_2S from the melt of eutectic composition at $T_{eq} = 1608 \text{ K}$ and at cooling of these substances to 298 K related to mass unit will be denoted by the symbol $\Delta h_{\Sigma cryst, \varphi}(\text{eut.melt}; 1608 \text{ K})$. This heat can be calculated according to the relation

$$\begin{aligned} \frac{\Delta h_{\Sigma cryst, \varphi}(\text{eut.melt}; 1608 \text{ K})}{\text{kJ kg}^{-1}} &= 0.0189 \frac{h_{rel, \varphi}(C_3A; 298 \text{ K})}{\text{kJ kg}^{-1}} + \\ &+ 0.7893 \frac{h_{rel, \varphi}(C_{12}A_7; 298 \text{ K})}{\text{kJ kg}^{-1}} + 0.1918 \frac{h_{rel, \varphi}(\gamma\text{-}C_2S; 298 \text{ K})}{\text{kJ kg}^{-1}} - \\ &- 1 \frac{h_{rel, \varphi}(\text{eut.melt}; 1608 \text{ K})}{\text{kJ kg}^{-1}} \end{aligned} \quad (15)$$

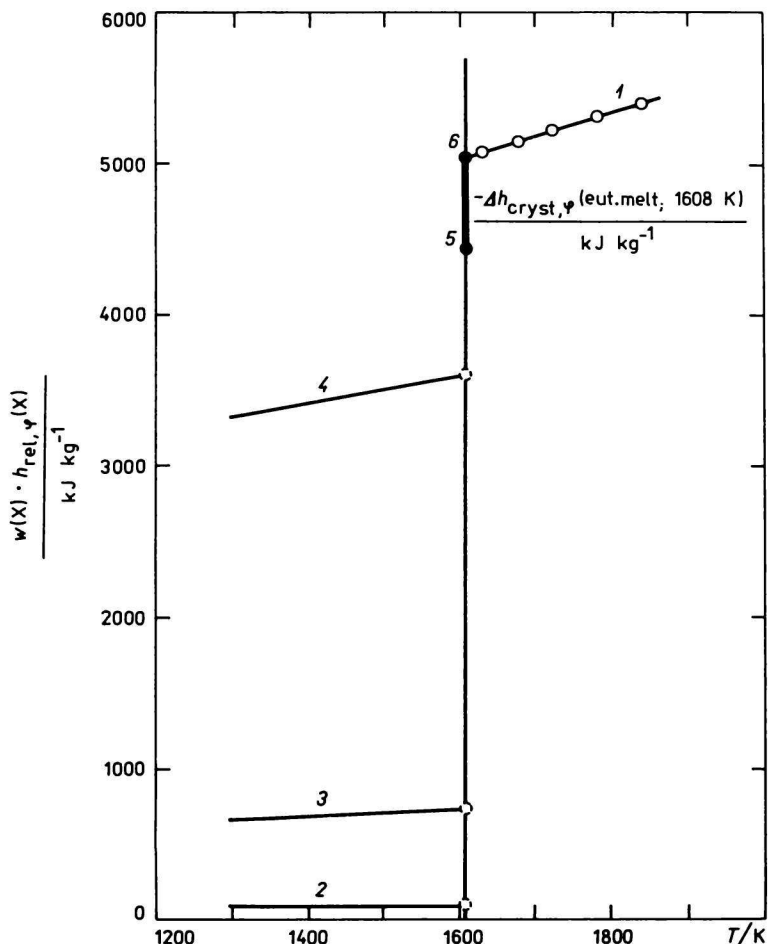


Fig. 1. Temperature dependences ($w(X) \cdot h_{rel, \varphi}(X)$).

1. Eut.melt; 2. C_3A ; 3. $\beta-C_2S$; 4. $C_{12}A_7$. The value of $(-\Delta h_{cryst, \varphi}(eut.melt; 1608 K))$ is given as the difference of the specific relative enthalpy of the eutectic melt at 1608 K (point 6) and the sum of specific relative enthalpies of products of crystallization of the eutectic melt at 1608 K, multiplied by corresponding mass fractions of the phases (point 5).

The values of h_{rel} of C_3A , $C_{12}A_7$, and $\gamma-C_2S$ at the temperature of 298 K correspond to the negative mean values of their specific heats of dissolution at this temperature. They are presented in Tables 3—5 ($-\Delta h_{sol, \varphi}(X)$). Inserting these values and the value of $h_{rel, \varphi}(eut.melt; 1608 K)$ from Table 6 into the relationship (15) we obtain the value of the specific total heat of crystallization of the melt of eutectic composition

$$\frac{\Delta h_{\Sigma \text{cryst. } \varphi}(\text{eut.melt}; 1608 \text{ K})}{\text{kJ kg}^{-1}} = -2002 \pm 26 \quad (16)$$

From comparison of the values of $\Delta h_{\text{cryst. } \varphi}(\text{eut.melt}; 1608 \text{ K})$ and $\Delta h_{\Sigma \text{cryst. } \varphi}(\text{eut.melt}; 1608 \text{ K})$ (the relationships (13) and (16)) it follows that at cooling of crystal phases C_3A , C_{12}A_7 , and C_2S from the temperature of 1608 K to temperature 298 K the amount of liberated heat is approximately twice as high as the heat of crystallization of these phases from the eutectic melt at $T_{\text{eq}} = 1608 \text{ K}$.

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