

THERMOANALYTICAL EVENTS AND ENTHALPIES OF PHASES AND SYSTEMS OF THE CHEMISTRY AND TECHNOLOGY OF CONCRETE PART II. HYDRATED CEMENTS

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Essential focus of the study has been to acquire thermoanalytical events, incl. enthalpies of decompositions - ΔH , of technological materials based on two types of Portland cements. The values of thermoanalytical events and also ΔH of probes of technological compositions, if related with the data of a choice of minerals of calcium-silicate-sulfate-aluminate hydrates, served as a valued input for the assessment of phases present and phase changes due to the topical hydraulic processes. The results indicate mainly the effects of „standard humidity“ or „wet storage“ of the entire hydration/hydraulic treatment, but also the presence of cement residues alongside calcium-silicate-sulfate-aluminate hydrates (during the tested period of treatment). „A diluting“ effect of unhydrated cement residues upon the values of decomposition enthalpies in the studied multiphase system is postulated and discussed.

INTRODUCTION

Clinker minerals, and cement itself, are low cost materials composed of the most abundant elements on Earth and are easily converting at the specific chemical (technological) conditions to highly functionalized solid material, concrete [1, 2]. Portland cement, in which cementitious (clinker) calcium silicate and calcium aluminate minerals together with calcium sulfate are vital components, represents the most important materials base of concrete in construction industry. Minerals present in Portland cement react with water forming hydrates of basically two technological effects. Calcium-Aluminate-Silicate-Hydrate (*C-S-H*, *CASH*, but also *CH*) phases exert a key contribution to the progress of the development of mechanical properties of concrete, while phases with relationship to the sulfates, namely gypsum, ettringite and thaumasite are those responsible for weathering and degradation of properties (e.g. mechanical) of concrete. Numerous simultaneous hydration processes are proceeding during reactions of cement with water. These processes have different kinetic and thermodynamic features and affect the entire setting and hardening of concrete [1].

Owing to the specific importance of individual concerned phases these are intensively studied by various experimental methods in order to characterise their composition, structure and various physical-chemical

properties [3, 4]. Current models suppose that *C-S-H* phases are composed of microstructural crystalline regions containing disordered layer structures, which resemble hydrated calcium silicate aluminate minerals (e.g. tobermorite, jennite, ettringite) [2, 5]. High-resolution TEM studies showed that *C-S-H* paste contains tobermorite and jennite-like phases in a relatively high concentration [6]. Therefore, understanding the structural, chemical and physical properties of these minerals is a key to the understanding both properties of the individual phases and their role in the formation of concrete. The interface between the surface structure of tobermorite and water phase has been studied also by the FF-MD simulation with a focus on the adsorption and stability of Cl^- , Na^+ , and Cs^+ ions [7]. The iono-covalent bonding in *C-S-H* structures was described by ab initio calculations [8]. Ab initio MD has been used in the description of hydrogen bonding and the structural positions of water in the normal and anomalous 11 Å phases of tobermorite and jennite [9, 10]. The relation between chemical composition, chemical bonds and mechanical stability of tobermorite 9 Å phase has been explained by the DFT simulation [11]. Similar approach has been used in the explanation of structural, mechanical and reactivity properties of *C-A-H* phases originated from tricalcium aluminate (C_3A) [12].

Short-hand cement chemistry notation:

$C = \text{CaO}$, $S = \text{SiO}_2$, $\hat{S} = \text{SO}_3$, $A = \text{Al}_2\text{O}_3$, $c = \text{CO}_2$, $H = \text{H}_2\text{O}$

Another important issue in concrete chemistry is a weathering of cement-based building materials which usually leads to a degradation of properties (e.g. mechanical). During the weathering process new mineral phases are formed such as thaumasite under a sulfate attack. Sulfate attack on concretes and cement mortars is the phenomenon of occurrence of minerals with relationship to the sulfates, namely gypsum, ettringite and thaumasite. The interaction of sulfates with concrete is a spread of overlapping chemical and physical processes and so the detailed description of the actual course of sulfate corrosion process is very difficult [13, 14]. The identification of presence of these minerals in course of this process has relevance for the explanation of the scope of weathering and its effects. Experimental methods, like X-ray phase analysis, thermal analysis, spectroscopic (IR, Raman) and microscopies [1, 3, 4, 14], can characterize a progress of the changes of phase composition, but also indicate flexural strength development and length changes. In recent years molecular simulations became attractive also for concrete science. Molecular simulation approach integrates various molecular modelling methods ranging from classical interatomic potential-based (force field, FF) to methods of quantum chemistry (QC). Using these methods it is possible to study (and interpret) various properties such as structural, mechanical, spectroscopic, molecular diffusion and transport properties, equilibrium energetics, and the atomic-scale mechanisms controlling chemical reactivity and activation energies. As the example; the results of thermal analysis of mineral thaumasite and hydrogen bonding in it have been interpreted in details by the DFT method/calculation [14].

Among the experimental methods of studying the chemical changes during very complicated processes of the transformation of cement to concrete X-ray phase analysis, thermal analysis, spectroscopic (IR, Raman) and microscopic methods are of the key importance. Thermoanalytical characteristics, incl. enthalpies, of variety of cement-based technological compositions are correlated with molecular simulation approach/molecular modelling methods ranging from classical interatomic potential-based (force field, FF) to methods of quantum chemistry (QC). The known and verified data about pure minerals are a key reference source of the entire studies in this field. Quoted below are the basic information about structural and thermoanalytical data on minerals of the interest of the present paper, these comprise ettringite, thaumasite and tobermorite. Ettringite; its crystal structure has been reported in [15, 16]. Due to the presence of 46 mass % of water in the structure this phase specifically decomposes between 80 – 300°C. Mass loss of 33.5 % and $\Delta H \approx 500 - 930 \text{ J}\cdot\text{g}^{-1}$ are assigned to volatilization of 26 molecules of H_2O from the original composition of ettringite [1, 17, 18]. Crystal structure of thaumasite has been originally

reported in [19] and refined by [20]. Due to the presence of 41 mass % of water in the structure this phase specifically decomposes between 80 – 300°C. Observed and reported [1, 13, 14, 18, 21] are mass loss of 35.6 %, $\Delta H \approx 1030 - 1215 \text{ J}\cdot\text{g}^{-1}$, both indicating that 13 molecules of H_2O per unit of thaumasite are evolved. Tobermorite-like C–S–H phases comprise microstructural crystalline regions containing disordered layer structures of 11 Å tobermorite, 11 Å jennite and 9 Å tobermorite. Due to the presence of 13 – 23 mass % of water these phases specifically decompose between 80 – 300°C, $\Delta H \approx 600 - 750 \text{ J}\cdot\text{g}^{-1}$ [1, 17, 21].

The aim and essential focus of the present study has been to acquire thermoanalytical events, incl. heat released during the events – decomposition enthalpies ΔH , of technological compositions based on cementitious mineral-like components and compare these with characteristics and decomposition enthalpies ΔH of natural minerals – ettringite and thaumasite. Both phases are reported as those responsible for weathering and degradation of properties in matured concrete. The motivation should be seen also by fact that these (or similar) thermoanalytical data and knowledge of decomposition enthalpies of cement-based technological compositions may form a valued input for the assessment of phases present, phase changes, but also the key practical feature – strength development, due to the topical hydraulic processes in these systems.

EXPERIMENTAL

The series of technological mineral-like materials was chosen as a characteristic representative of widely used manmade hydraulic materials. Cements CEM I and CEM V are those that are frequently used in construction industry, these were selected also as a starting material for synthesis of tested probes. Principles and rules of the syntheses and treatment of individual probes are described/outlined below, more details can be found in [22]. The initial treatment with water has been in accord with the technological rules of cement and construction industry. Probes have been further kept at (i) standard conditions of humidity and (ii) the humidity of 100 % - ages, both for the durations of 90 and 365 days. In particular [22], the treatment comprised the following consecutive steps: Cements were mixed with water at the water-cement ratio $w/c = 0,48$ to produce pastes, a laboratory electric mixer was used to prepare these mixes. The duration of mixing procedure was constantly 3 minutes, the fresh pastes were then vibrated up to 30 seconds. Finally, a series of prisms with the proportions $20 \times 20 \times 120 \text{ mm}$ were cast for each mix. After 24 h of normal curing in wet environment the specimens were demoulded and divided in two identical groups, which were cured either in air at laboratory conditions (20 – 24°C, standard R.H., dry storage) or in water at

20 – 24°C (R.H. = 100 %, wet storage). The duration of curing before crushing and thermoanalytical study was 90 and 365 days for each regime.

Thermoanalytical curves (simultaneously TG and DTA/DSC curves) have been acquired on STA 449 F3 Jupiter® device of Netzsch, under the following conditions of measurements: atmosphere of N₂, heating rate 5°C·min⁻¹, from ambient temperature to 500°C. Events and characteristics on TG, DTG and DTA/DSC curves were evaluated by a standard software package of the device - NETZSCH Proteus Thermal Analysis software. The blank measurement (the reference and sample crucible empty, but all other conditions of measurements the same as the measurements with the sample) was executed to identify the correction of the background. This way both the level of zero mass loss (TG curves) and background level (DSC curves, when evaluating ΔH) were optimized to minimize any physically incorrect contribution towards the acquired and reported values. The software package executes the calculation of ΔH , from data of the DSC curve in a chosen temperature range, per total mass unit of the original probe.

RESULTS AND DISCUSSION

The thermoanalytical curves (both TG and DSC) of technological mineral-like hydraulic materials – probes of cements CEM I and CEM V treated with water in accord with the technological rules of cement and construction industry, exert complex shapes in general (cf. illustrated in Figure 1). However, two temperature regions of decomposition are obvious as on TG so on DSC curves. The first region is indicated by the overall step ranging from 80 to 300°C over the whole range of probes (Table 1) and corresponds [1, 14, 17, 21] to the sum of dehydration processes of calcium-silicate hydrates (*C-S-H*), calcium-silicate-aluminate-sulfate hydrates (*C-S-A-S-H*) and calcium-aluminate hydrates (*C-A-H*). The second region ranging from 400 to 500°C is a typical sign of the decomposition of portlandite – *CH* [1, 5].

Thermogravimetric mass losses and, especially, the shapes of TG curves confirm the earlier knowledge on complex and non-equilibrate state of the studied cement-based system during the technologically relevant conditions. The values of ΔH calculated from DSC curves in both distinguished temperature areas (80 to 300°C and 400 to 500°C), as reported in Table 1 and 2, and relations of these may exert a further input to discussion of the phase composition and phase changes in these and similar systems. The data extracted from DSC curves of technological hydraulic materials leading to the values of ΔH in these distinguished temperature regions give a statistically relevant and straightforward insight on the system. Moreover, these enable the interpretation of selected issues. The discussion below is focused on the influence and significance of effects

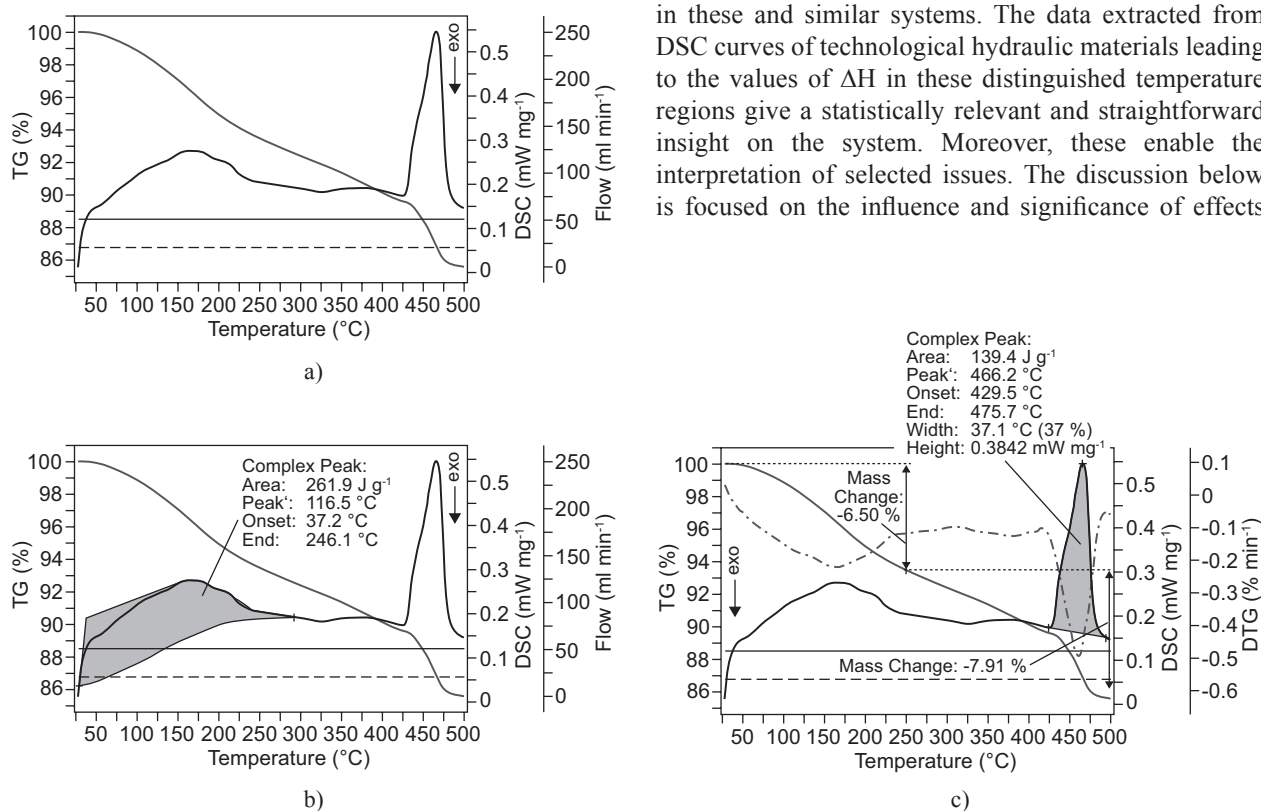


Figure 1. The representative thermoanalytical curves (both TG and DSC) of probes of technological mineral-like materials (exemplified are TG and DSC curves of the probe of the series denoted in Tables 1 and 2 as CEM I, RH = 100 %, 365 days); a) overall view, b) evaluation of the change of enthalpy ($\Delta H / \text{J}\cdot\text{g}^{-1}$) from DSC curve in the region 80 – 300°C, c) evaluation of the mass change ($\Delta m / \%$) and the change of enthalpy ($\Delta H / \text{J}\cdot\text{g}^{-1}$) from TG and DSC curves resp. in the region 400 – 500°C.

of initial compositions of cements, the entire conditions of cementitious hydraulic reactions and the presence and effects of residues of unreacted cements.

The data on overall decomposition enthalpies in the temperature interval of first decomposition step (80 to 300°C) have been extracted from DSC curves. Comparison of decomposition enthalpies of probes treated for 90 days and that treated for 365 days, cf. ΔH (365 – 90) in Table 1, has served as the issue differentiating phase changes due to simultaneous effect of both duration and dry vs. wet storage. Thus, the effects of the storage conditions of the studied technological mineral-like hydraulic materials are distinguished. The values of defined differences ΔH (365 – 90) fall in the interval $-40 - -150 \text{ J}\cdot\text{g}^{-1}$ for samples treated at standard conditions of humidity. Negative values (lower levels of ΔH after 365 days than that after 90 days) should be understood as the indication of the increased content of phases with low ΔH on the account of phases with the high ΔH in course of the hydraulic reactions. Specifically, and in accord with both the knowledge on the cement hydration [1-6] and values of ΔH of relevant minerals [1, 18, 21-24], the indicated differences of ΔH (365 – 90) relate with both the decreased content of ettringite and the increased content of tobermorite, while uncertain about thaumasite. The differences ΔH (365 – 90), defined as above, in samples treated at the humidity of 100 % -ages are in the interval $14 - 26 \text{ J}\cdot\text{g}^{-1}$. The positive values denoting the increase of ΔH from 90 days to 365 days display from point of view of phase changes, and in accord with [1-6], the overall increase of the content of hydrated phases due to the progress of reactions of cement

grains with abundantly present water molecules in “wet conditions” of the treatment of each studied probe of technological mineral-like hydraulic materials.

Due to fact that data have been acquired in the series of probes based on three different cements, besides the influence of storage (“dry” vs. “wet”) also the effects of cement type is outlined. The differences of enthalpies of probes treated 365 days and 90 days - ΔH (365 – 90) are for “dry” vs. “wet” conditions in the individual series as follows; -87 vs. 14 , -150 vs. 16 , -40 vs. 26 . This set confirms the tendencies in the appearance of $C-A-S-H$ hydrates over the whole range of studied compositions. The data are in accord with suggested course of hydraulic reactions [1, 3, 5, 13] of fine cements/clinkers already towards the hydrated phases with relatively rough surface. It coincides well also with the roughness of the surface of ettringite and thaumasite characterized by the interval of RMS ranging from 107 to 422 nm [18]. The important knowledge has arisen from the comparison of the relevant values of ΔH (mean) and ΔH (365 – 90) in the entire series, and especially of that data on two marks of CEM V type. There is indicated only slight change (increase from 16 to $26 \text{ J}\cdot\text{g}^{-1}$ reported in Table 1) of ΔH from 90 days to 365 days in “wet” conditions, most probably due to the unifying effect of abundantly present water upon the course of hydration reactions towards continuously increasing content of hydrated (and hydraulic) phases [1-5, 13]. In contrary, “dry” conditions exert the differences as follows: probe of mark 1 of CEM V is favourable to give rise of phases with low ΔH (tobermorite) on the account of phases with the high ΔH (ettringite, thaumasite), as seen by a huge decrease of ΔH from 90 days to 365 days, $-150 \text{ J}\cdot\text{g}^{-1}$ reported in Table 1), while in probe of mark 2 of CEM V this phenomenon is developed to a lesser extent (decrease of ΔH from 90 days to 365 days achieves $-40 \text{ J}\cdot\text{g}^{-1}$ only, cf. in Table 1). Thus, the results show that each mark of cement (also of the same general type, as illustrated here with two marks of CEM V) exerts specific details of its reactions to form technological mineral-like hydraulic materials comprising a variety of both formed hydrates relative ratio and materials parameters.

The data on ΔH related to the decomposition temperature $400 - 500^\circ\text{C}$ for samples of technological mineral-like hydraulic materials treated at standard conditions of humidity show that the duration of treatment from 90 to 365 days lowers the values of ΔH ($9 - 17 \text{ J}\cdot\text{g}^{-1}$ vs. $2 - 9 \text{ J}\cdot\text{g}^{-1}$). The decrease is due to slight decline of the content of portlandite (CH). It is also evidenced from the respective thermogravimetric data ($0.53 - 0.82 \%$ vs. $0.43 - 0.54 \%$), cf. values of Δm in Table 2. The observed issues are an evidence of those reactions during which $C-A-S-H$ phases form on the account of CH in the conditions of standard humidity (dry storage) [1, 3, 5]. The increase of ΔH ($4 - 69 \text{ J}\cdot\text{g}^{-1}$ vs. $5 - 139 \text{ J}\cdot\text{g}^{-1}$) and also the increase of Δm ($0.32 - 1.85 \%$ vs. $0.40 - 3.67 \%$) was observed in the series of samples treated for 90

Table 1. Characteristic thermoanalytical values in the temperature interval $80 - 300^\circ\text{C}$, as acquired for the studied range of cement composition, conditions and duration of hydraulic reactions. Decomposition enthalpies are expressed as the value ΔH (mean)/ $\text{J}\cdot\text{g}^{-1}$ of sets of data for each duration of given environmental treatment, the difference of those values acquired in probes treated for 365 days vs. 90 days is presented also, cf. rows ΔH (365 – 90)/ $\text{J}\cdot\text{g}^{-1}$.

Composition and conditions of treatment	Estimated parameter	90 days	365 days
CEM I standard R.H.	ΔH (mean)	253 ± 25	166 ± 20
	ΔH (365 – 90)		-87
CEM I R.H. = 100 %	ΔH (mean)	279 ± 30	293 ± 35
	ΔH (365 – 90)		14
CEM V (probe 1) standard R.H.	ΔH (mean)	325 ± 30	175 ± 20
	ΔH (365 – 90)		-150
CEM V (probe 1) R.H. = 100 %	ΔH (mean)	304 ± 30	288 ± 30
	ΔH (365 – 90)		16
CEM V (probe 2) standard R.H.	ΔH (mean)	226 ± 25	186 ± 20
	ΔH (365 – 90)		-40
CEM V (probe 2) R.H. = 100 %	ΔH (mean)	337 ± 35	363 ± 35
	ΔH (365 – 90)		26

vs. 365 days at the humidity of 100 %. These data unanimously depict that, due to the access of water, the amount of CH increases and the period of existence of CH is prolonged under these conditions in studied technological mineral-like hydraulic materials. Humid conditions in general [1, 6, 7, 13, 25] postpone those hydraulic reactions in which C–A–S–H phases form on account of CH, but may contribute to the weathering process, where the phase changes resulting in the occurrence thaumasite are also obvious [13].

Table 2. Characteristic thermoanalytical values as extracted from TG and DSC curves in the temperature interval 400–500°C for the studied range of cement composition, conditions and duration of hydraulic reactions. Mass changes ($\Delta m / \%$) and changes of enthalpies expressed as $\Delta H / \text{J}\cdot\text{g}^{-1}$ and $\Delta H (365 - 90) / \text{J}\cdot\text{g}^{-1}$ are given.

Composition and conditions of treatment	Estimated parameter	90 days	365 days
CEM I standard R.H.	$\Delta m / \%$	0.82	0.54
	$\Delta H / \text{J}\cdot\text{g}^{-1}$	17	9
	$\Delta H (365 - 90) / \text{J}\cdot\text{g}^{-1}$	–	- 8
CEM I R.H.=100%	$\Delta m / \%$	1.85	3.67
	$\Delta H / \text{J}\cdot\text{g}^{-1}$	69	139
	$\Delta H (365 - 90) / \text{J}\cdot\text{g}^{-1}$	–	70
CEM V (probe 1) standard R.H.	$\Delta m / \%$	0.53	0.49
	$\Delta H / \text{J}\cdot\text{g}^{-1}$	9	3
	$\Delta H (365 - 90) / \text{J}\cdot\text{g}^{-1}$	–	- 6
CEM V (probe 1) R.H.=100%	$\Delta m / \%$	0.32	0.40
	$\Delta H / \text{J}\cdot\text{g}^{-1}$	4	5
	$\Delta H (365 - 90) / \text{J}\cdot\text{g}^{-1}$	–	1
CEM V (probe 2) standard R.H.	$\Delta m / \%$	0.57	0.43
	$\Delta H / \text{J}\cdot\text{g}^{-1}$	17	2
	$\Delta H (365 - 90) / \text{J}\cdot\text{g}^{-1}$	–	- 15
CEM V (probe 2) R.H.=100%	$\Delta m / \%$	0.67	1.06
	$\Delta H / \text{J}\cdot\text{g}^{-1}$	19	26
	$\Delta H (365 - 90) / \text{J}\cdot\text{g}^{-1}$	–	7

The comparison of values of ΔH exerted by studied technological hydraulic materials in the first temperature region and that of pure minerals is given in Table 3. It provides an inevitable input towards discussion of focused indications on phase composition and phase changes, including the account of the presence of unhydrated cement residues.

The interval of values 166 – 363 $\text{J}\cdot\text{g}^{-1}$ achieved by technological compositions as calculated in present study is larger but correlates with the reference data [22] of relevant (similar) compositions (165 – 223 $\text{J}\cdot\text{g}^{-1}$). Lower values of ΔH reported for this system of technological materials in [22] are most probably due to the different account of the decomposition stoichiometries. Both sets are far less than these values of tobermorite, ettringite and thaumasite (600 – 750 $\text{J}\cdot\text{g}^{-1}$, 500 – 930 $\text{J}\cdot\text{g}^{-1}$ and 1030–1215 $\text{J}\cdot\text{g}^{-1}$ resp.), cf. in Table 3. The calculated decomposition enthalpies are, as the rule, expressed

per total mass unit of probes. This and account of the presence of residues of cement in probes rationalizes the postulation of “a diluting” effect of unhydrated cement residues. Accordingly, cement residues cause a decrease of ΔH parameter and affect also the data on relative content of C–A–S–H hydrates, if the evaluation of mass unit of hydraulic materials is attempted from points of view of both the value of ΔH parameter and the amount of C–A–S–H hydrates. Due to complexity of that effect it is not possible to make use of the present data on ΔH for a quantitative assessment. However, the evidence of cement residues alongside CASH hydrates during the tested period of treatment is a qualitative output in addition to the differentiation of phase compositions of cements CEM I and CEM V treated with water under both wet and dry conditions in accord with the technological rules of cement and construction industry.

Table 3. Comparison of the values of changes of enthalpies ($\Delta H / \text{J}\cdot\text{g}^{-1}$) of technological mineral-like hydraulic materials and various minerals, this study and the reference data.

Composition / Mineral	$\Delta H / \text{J}\cdot\text{g}^{-1}$ (this work, reference data)
Technological compositions, 90 days of treatment	226 – 337 165 – 223 [22]
Technological compositions, 365 days of treatment	166 – 363
Ettringite	500 – 930 [1, 18, 23, 24]
Thaumasite	1030 – 1215 [1, 17, 23, 18]
Tobermorite	600 – 750 [1, 21]

CONCLUSIONS

1. Evaluation of ΔH (and also Δm) from the thermoanalytical data / curves is a handy tool for investigating a choice of specific details of hydraulic systems and phase compositions, mutually based on both C–A–S–H and CH thermal decompositions.
2. The values of ΔH reported in this paper are the relative data and reflect the effects of treatment, composition & measuring conditions, anyway, the information on ‘tendencies’ is a valued one. Comparison of values of ΔH of probes of cements CEM I and CEM V treated in accord with the technological rules of cement and construction industry with these values of minerals shows that technological mineral-like materials are multiphase compositions of C–A–S–H hydraulic phases, CH and cement.
3. The results achieved in probes of cements CEM I and CEM V treated with water suggest the effects of both cement type and conditions of treatment upon the achievable level / degree of the topical hydraulic processes.

4. The results of presented study indicate mainly the effects of „standard humidity“ or „wet storage“ of the entire hydration/hydraulic treatment, but also the presence (and effects) of cement residues besides C–A–S–H hydrates (during the tested period of treatment). The later, being “a diluting” effect of cement residues upon the amount of C–A–S–H hydrates in the entire compositions, is obviously reflected by the values of enthalpies of decompositions in the studied multiphase system.

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