THERMOANALYTICAL EVENTS AND ENTHALPIES OF SELECTED PHASES AND SYSTEMS OF THE CHEMISTRY AND TECHNOLOGY OF CONCRETE PART I. CALCIUM-SILICATE-ALUMINATE-SULFATE HYDRATES

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Essential focus of the study has been to acquire thermoanalytical events, incl. enthalpies of decompositions - ΔH, of natural minerals of calcium-silicate-sulfate-aluminate hydrates. The thermoanalytical curves of thaumasite and ettringite are fully in line with that reported in reference sources. The values of ΔH calculated from DSC curves in the intervals of key decomposition steps ranging from 50 to 250 °C, achieve (1215 ± 60) J g^{-1} for thaumasite and (930 ± 40) J g^{-1} for ettringite. The differing values of decomposition enthalpies ΔH, as presented by various research groups, are indicated and critically discussed in the paper.

INTRODUCTION

Cementitious (clinker) minerals, constituents of Portland cement, are used in construction industry as the important hydraulically active components of concrete. These minerals react with water forming hydrates, from which the Calcium-Silicate-Hydrate (*C–S–H*) phases are the most important for the progress of the development of mechanical properties of concrete. Mechanisms and kinetics of transformations of clinker minerals towards the hydrated either poorly crystalline or microstructural crystalline regions exert a key contribution to the progress of the development of mechanical properties of concrete. Current models suppose that the microstructural crystalline regions in concrete contain disordered layer structures typical of hydrated calcium-silicate-aluminate-sulfate minerals, especially tobermorite, jennite and ettringite [1, 2]. Owing to the specific importance of individual concerned phases/minerals these are intensively studied by various experimental methods in order to characterise their composition, structure, various physical-chemical and mechanical properties [3, 4]. 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 ºC, the data on decomposition enthalpy ΔH range from 600 J/g to 750 J/g [7, 10, 13]. Thus, characteristics of *C–S–H* phases are extensively described, while that of sulphate-bearing phases (ettringite and others) are known to a lesser scope.

Another important issue in concrete chemistry is a weathering of cement-based building materials what 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 [5, 6]. Thus, characterization of these minerals has relevance for an explanation of the weathering process. Experimental methods, like X-ray phase analysis, thermal analysis, spectroscopies (IR, Raman) and microscopies [3, 4, 6, 7], can characterize a progress of the changes of phase composition, but also flexural strength development and length changes. In recent years molecular simulations

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Short-hand cement chemistry notation: C = CaO, S = SiO$_2$, Ŝ = SO$_3$, A = Al$_2$O$_3$, c = CO$_2$, H = H$_2$O.

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 calculation [6].

In studying the chemical changes during these very complicated processes of the transformation of cement to concrete various experimental and modelling methods are used; among the experimental ones – 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 well known data about pure minerals are a key reference source of the entire studies in this field. Quoted below are the basic reference thermoanalytical data on minerals of the interest of the present paper, these comprise ettringite and thaumasite. Ettringite; its crystal structure has been reported in [8, 9]. Due to the presence of 46 mass % of water in the structure this phase specifically decomposes between 80-250 °C, the decomposition enthalpy ΔH achieves 500 J/g [7, 10]. Crystal structure of thaumasite has been originally reported in [11] and refined by [12]. Due to the presence of 41 mass % of water in the structure this phase specifically decomposes between 80-250 °C, the decomposition enthalpy ΔH achieves 1030 J/g [5, 6, 7, 13].

The aim of present study has been to acquire thermoanalytical data of specific decompositions of ettringite and thaumasite between 80-250 °C and from these data to calculate the decomposition enthalpies ΔH per entire mass units of both minerals in the above temperature interval. Our study has been inspired by the fact that it is not clear if the decomposition enthalpies of ettringite and thaumasite reported in the original papers [5, 6, 7, 10, 13] relate to the total mass unit of relevant minerals or to the mass units specified by the other mode (i. e. the mass corrected by mass evolved during the decomposition).

EXPERIMENTAL

A natural, transparent crystal sample of thaumasite (ideal formula $Ca_3Si(OH)_6(CO_3)(SO_4)\cdot12H_2O$, $C_3S\ \hat{S}cH_{15}$ in short hand cement chemistry notation) coming from N'Chwaning II mine, South Africa, and the specimen of the rare mineral ettringite (ideal formula $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O$, $C_6A\ \hat{S}H_{32}$ in short hand cement chemistry notation) from Wessels Mine, Northern Cape Province, South Africa were obtained from Thames Valley Minerals company, which sells mineral specimens from the UK and around the world. The basic characteristics of these minerals are well known, incl. the characteristics of thermal decompositions and crystal structures [8-13]. Both minerals have a hexagonal structure in $P\ 6_3$ (thaumasite) [11, 12] and $P\ 31c$ (ettringite) groups of symmetry [8, 9]. The execution of AFM screening of topical probes of minerals enlarged the knowledge on microstructural parameters of both. In particular; the estimated interval of the values of RMS (root mean square) ranging from 107 to 422 nm corresponds well with the interpretations of layered structures of these minerals [8, 9, 11, 12]. Thermal analysis of samples of thaumasite and ettringite minerals carried in this study has been focused towards the acquisition of data on decomposition enthalpies ΔH.

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 N_2, 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 DISCUSION

Our study showed that there are significant features of TG and DSC curves in the temperature region 80-250 °C, cf. reported and discussed below. These features represent finger-prints useful to estimate the presence of both minerals in a variety of compositions, especially in the studies of technological materials based on cementitious components.

The thermogravimetric curves of mineral samples of thaumasite and ettringite (Figs. 1a, 2a) exhibit the sequences of events on thermal decomposition fully identical with that reported in the reference sources [5-7, 10, 13-15]. The mass losses detected on TG curves

in the temperature region 80-250 ºC achieve 33,60% and 33,25 % for thaumasite and ettringite resp. These indicate dehydration, and the reported values stoichiometrically represent 13 and 26 molecules of H_2O volatilized upto 250 ºC from thaumasite and ettringite resp. The high values of mass losses in the above temperature region are of advantage in the analytical use; relative contents of these minerals in various compositions can be estimated with high sensitivity from the data of thermal analysis. The method of estimation of the value of x_{th} was proposed and successfully tested earlier [6, 16]. The method is based on the routine thermogravimetric data and uses simple equation (eq. 1) interrelating the TG mass losses in the analyzed composition – Δm(exp) and that stoichiometrically equal to 13 moles of H_2O volatilized in given temperature region from the pure mineral – Δm(st) = 33.70 %). The content of thaumasite as low as 1 % (x_{th} = 0,01) of the total mass of analyzed composition can be identified.

$$x_{th} = \Delta m(exp)/\Delta m(st) = \Delta m(exp)/33,70 \qquad (1)$$

The values of ΔH of the processes of decomposition of thaumasite and ettringite due to the dehydration in intervals of key decomposition steps (50-250 ºC) were calculated from the DSC curves (Figs. 1b, 2b).

The software package NETZSCH Proteus enables to account besides the exact data on decomposition and stoichiometry also the optimized background levels in the analysed temperature region. The values of ΔH calculated by the software package per total mass unit of the probe achieve 1215 ± 60 J g^{-1} for thaumasite and 930 ± 40 J g^{-1} for ettringite, cf. also in Table 1. The papers [14, 15] present values of ΔH which are lower (by factor 1,2 in the case of thaumasite, but by factor of 1,45 in the case of ettringite) relative to the reported values. The issues of mass of probes per which the calculations are performed but also of background level were not tackled uniformly by different authors, and it results in a presentation of differing values of decomposition enthalpies ΔH. As the example; the factors of difference of selected reference data on ΔH in [7, 14, 15] range between 1,25 and 1,3. Thus, the factors of difference 1,2 and 1,45 shown for the data on ΔH of thaumasite and ettringite reported in this paper vs. that in literature sources are sensible and far not extreme. The data presented in this work (1215 ± 60 J g^{-1} and 930 ± 40 J g^{-1}) are the values of decomposition enthalpies of key decomposition steps ranging from 80 to 250 ºC, where the calculation is performed per entire mass units of thaumasite and ettringite.
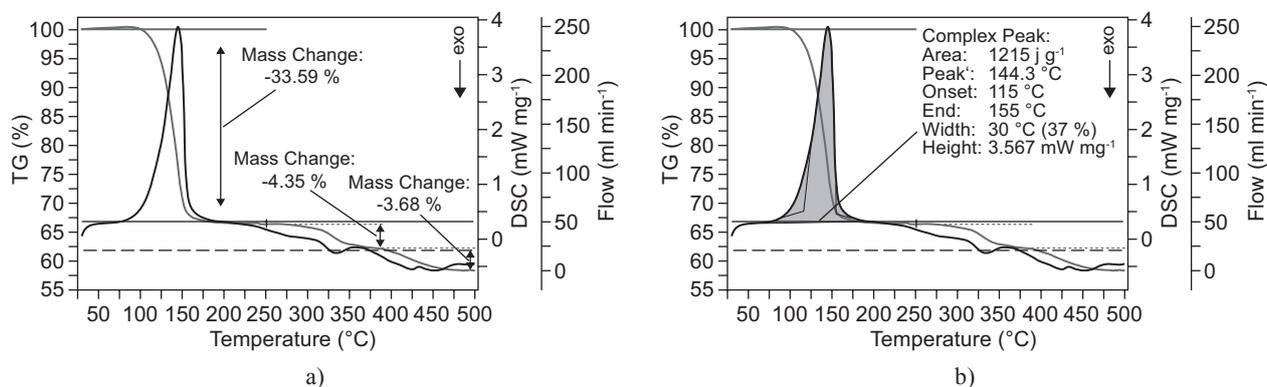
Figure 1. The thermoanalytical curves of thaumasite; a) eva-luation of mass losses (Δm in %) on TG curve, b) evaluation of the decomposition enthalpy (ΔH in J g^{-1}) on DSC curve in the key decomposition step of 50-250°C.
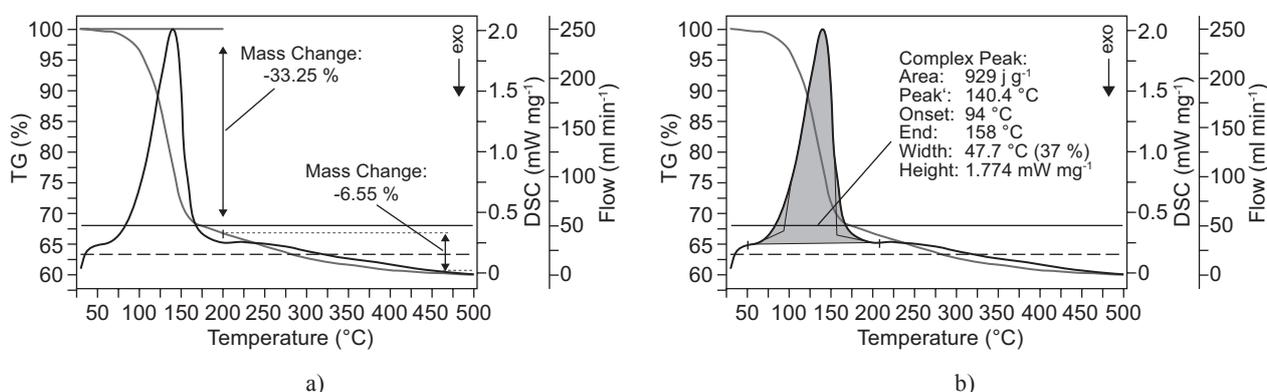
Figure 2. The thermoanalytical curves of ettringite; a) evaluation of mass losses (Δm in %) on TG curve, b) evaluation of the decomposition enthalpy (ΔH in J g^{-1}) on DSC curve in the key decomposition step of 50-250°C.

Table 1. Comparison of the values of decompostion enthalpies (ΔH in J g^{-1}) of mineral probes of thaumasite and ettringite.

Composition / / Mineral	ΔH (J g^{-1}) *(this work)*	ΔH (J g^{-1}) *(based on reference data)*
Thaumasite	1215 ± 60	≈ 1030 [7, 10, 14]
Ettringite	930 ± 40	≈ 500 [7, 14] 640 [15]

The presented and discussed characteristics and parameters update the knowledge on thaumasite and ettringite, especially display the significance of thermal decomposition of these minerals in the temperature region 80-250 ºC. The achieved data may, in addition to [6, 16], serve as finger prints of thaumasite and ettringite. The values of ΔH reported in this study are of prominent use when evaluating thermoanalytical data of decomposition processes of cement-based hydraulic systems [cf. Part II of this series]. These and similar systems, being a specifically important example of technological mineral-like materials, arise when various types of cements are treated with water in accord with the technological rules of cement and construction industry to form multiphase compositions of *C–A–S–Ŝ–H* hydraulic phases, portlandit and cement. The thermoanalytical studies, if done in the same temperature regions and the same software package used, will result in a focused comparison of values of ΔH of a variety of cement-based hydraulic probes with these values of minerals and would contribute also to the interpretation of simultaneously acquired thermogravimetric data of such cement-based hydraulic probes.

CONCLUSIONS

The thermogravimetric curves of mineral samples of thaumasite and ettringite exhibit the sequences of events on thermal decomposition fully identical with that reported in the reference sources.

The significance of thermal decomposition in the temperature region 80-250 ºC is due to indicated dehydration stoichiometrically represented by 13 and 26 H_2O molecules volatilized upto 250 ºC from thaumasite and ettringite resp. The values of ΔH calculated from the DSC curves in this key decomposition interval (50-250 ºC) achieve 1215 ± 60 J g^{-1} for thaumasite and 930 ± 40 J g^{-1} for ettringite.

The values of thermoanalytical events, incl. ΔH of a choice of minerals of calcium-silicate-sulfate-aluminate hydrates, form a valued input for the assessment of phases present and phase changes due to the hydraulic processes of cement-based hydraulic materials (cf. Part II of this series).

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