Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 2, 469–475

COMPUTER SIMULATIONS OF HYDROGEN BONDS FOR BETTER UNDERSTANDING OF THE DATA OF THERMAL ANALYSIS OF THAUMASITE*

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Thermal decomposition of thaumasite is a step-wise process strongly related to the hydrogen bond breaking. Description and classification of hydrogen bonds in this mineral is necessary for better understanding of steps of the decomposition reaction. A computer simulation of a structure is an effective tool for confirming or opposing indicated steps of decomposition reactions. Computer simulations were performed on the crystal structure of the mineral thaumasite. All atomic positions together with unit cell parameters were relaxed. Hydrogen bonds, representing the dominant feature of the structure, were analyzed. Four types of them were found: between *i*) water molecules and carbonate ions, *ii*) water molecules and sulfate ions, *iii*) $Si(OH)_6^{2-}$ and water molecules and *iv*) water molecules themselves. Obtained results contribute to the explanation of some uncertainties of X-ray experiments and of the complexity of the thermochemical process, particularly, of the stepwise thermal decomposition of thaumasite in the low-temperature region 100–300°C. Moreover, TG data of the 1st step sensitively and reliably enough detect thaumasite sulphate-attack and determine the content of thaumasite in attacked building constructions.

Keywords: *computer simulation, hydrogen bonds, thaumasite, thaumasite–sulfate attack on concrete, thermal decomposition, thermogravimetric quantitative identification*

Introduction

Thaumasite is a mineral of approximate composition $3CaO\cdot SiO_2\cdot SO_3\cdot CO_2\cdot 15H_2O$, with usual natural abundances in the wall rocks of sulfide mines, carbonate rocks, more rarely basaltic rocks. The mineral samples can be collected i.e. in mid-European Alps, Sweden, Norway, Latain volcano, Mururoa atoll. Another possible occurrence of thaumasite is in cement based building materials, where the negative technological consequences of thaumasite-sulfate attack are reported [1]. Basic problem represents a fact that thaumasite is a non-binder which is formed from the main cementitious binder hydrates (calcium silicate hydrates and ettringite–CSH and $C_3A\cdot 3C\overline{S}H_{32}$ according to cement chemistry notation).

The crystal structure of thaumasite is hexagonal ($P6_3$ symmetry, a=1.104 nm, c=1.039 nm, Z=2) and has been determined by Edge and Taylor [2] and later refined by Effenberg *et al*. [3]. There are several interesting features in the structure of thaumasite. It is the only silicate substance possessing an octahedral coordination of Si atom at ordinary pressure. Six hydroxyl groups coordinate Si^{4+} cation what forms the $Si(OH)_6^{2-}$ anion. The negative charges of $Si(OH)_6^{2-}$ anions are compensated by Ca^{2+} cations. Both ions are surrounded by water molecules what forms columns of empirical composition $[Ca_3Si(OH)_6\cdot 12H_2O]^{4+}$ (Fig. 1). These columns are parallel to c axis. The complement to the columns in the thaumasite structure consists of CO_3^{2-} and SO_4^{2-} ions, which are alternatively distributed between columns and are involved in the network of hydrogen bonds (HBs) with water molecules (Fig. 2). The negative charges of the CO_3^{2-} and SO_4^{2-} ions are also compensated by Ca^{2+} cations from the columns. The system of hydrogen bonding is unique in a way that all the H atoms of the H_2O molecules take part in the hydrogen bonds. Weak hydrogen bonds are also suggested between water

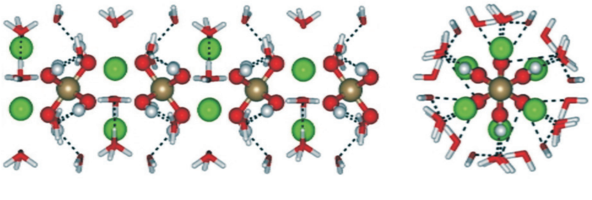

Fig. 1 Two views on the structure of the $[Ca_3Si(OH)_6\cdot 12H_2O]^{4+}$ columns in thaumasite

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* Paper is dedicated to the memory of the late Prof. I. Odler (passed away on August 16, 2005) one of the worldwide leading specialists in the chemistry of cement and builidng materials.

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1388–6150/$20.00

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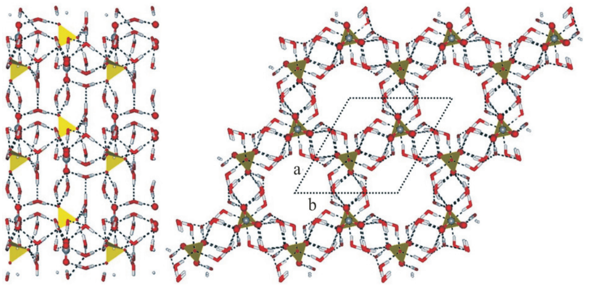

Fig. 2 Two views on the network of hydrogen bonds (dashed lines). Water molecules are displayed as stick, CO_3^{2-} as ball-and-stick and SO_4^{2-} as polyhedral models. The unit cell is drawn as a dashed line

molecules and $Si(OH)_6^{2-}$ anions [2, 3]. In this case water molecules act as proton acceptor via oxygen atoms, and hydroxyl groups from the $Si(OH)_6^{2-}$ anions represent proton donors. $Ca_3Si(OH)_6CO_3SO_4{\cdot}12H_2O$ or $[Ca_3Si(OH)_6{\cdot}12H_2O](CO_3)(SO_4)$ are alternative formulae of thaumasite resembling the introduced features of the crystal structure.

Thaumasite undergoes dehydration and decomposition during a heating. The kinetics of the isothermal heating as well as DSC, DTA and TG results, together with the usefulness of these data in the cement chemistry, have been reported [4–7]. Possible effects of the system of HBs upon a mechanism of releasing of H_2O molecules, CO_3^{2-} and SO_4^{2-} ions from the structure of thaumasite during the thermal decomposition already at low temperatures were proposed [5, 6]. In contrast, the decomposition of $Si(OH)_6$ groups with octahedral coordination of silicon has been suggested to remain nearly free of the effect of HBs [2–4].

The correct description of HBs can help to understand the processes of thermal decomposition of thaumasite. Since the structure of thaumasite is built on the HBs, it is important to know the positions of hydrogen atoms. It is known that conventional X-ray crystal diffraction usually cannot resolve the positions of hydrogen atoms with required accuracy. For example, unusually short O–H bond lengths in thaumasite (0.072–0.088 nm) were estimated from diffraction measurements [3] although typical O–H bond lengths in water are 0.097 nm (this underestimation of O–H bond lengths is well-known for conventional diffraction techniques). The other methods, e.g. infrared spectroscopy, can give only an indirect insight on the structure of HBs. Computer simulations represent a good alternative to experimental methods and can help to explain open structural and physical chemical questions accompanying the experiments.

The presence of thaumasite in the concrete constructions represents the serious problem. There are various proposals for the identification and the (semi)quantitative determination of the content of thaumasite in those constructions [6–9]. The task may be successfully addressed also to the TG/DTA methods. This paper concerns the application of the computer simulation approach to the structure of thaumasite with the aim to refine the positions of hydrogen atoms and to define the possible impact of HBs upon the thermal decomposition of thaumasite. The system of HBs is reliably described and is directly related to the differentiation of two-steps of the thermal decomposition of thaumasite in the temperature region 100–300°C.

Methods and methodologies

Computational details

Ab initio total-energy geometry optimizations were performed using the Vienna ab initio simulation package (VASP) [10, 11] developed for periodical systems. The localized density approximation (LDA) [12] corrected with the generalized gradient approximation (GGA) [13] was used for the expression of the exchange-correlation functional of the density functional theory (DFT). The calculations were performed in a plane-wave basis set using the projector-augmented wave (PAW) method [14, 15] and ultrasoft pseudo-potentials [16, 17]. The energy cutoff of 400 eV was used for the plane wave expansion allowing for an extended basis set and high-precision calculations. Since the computational unit cell is sufficiently large, the Brillouin-zone sampling was restricted to the Γ point, using modest smearing of the eigenvalues to improve total energy convergence.

The structure of thaumasite was taken from the work of Edge and Taylor [2]. Some of important experimental structural data are given in Table 1. During the geometry optimization no symmetry constrains on the atomic positions were applied. The geometry optimizations were performed in two steps. Firstly, the experimental unit cell parameters (fixed shape and volume of the unit cell) were kept constant and all atoms were allowed to relax. After that the unit cell parameters together with atomic positions were optimized (fixed shape and optimized volume of the unit cell). The optimization of atomic positions was performed using a

Table 1 Experimental and calculated structural parameters of thaumasite

Parameter	Experimental^a	Calculated
a/nm	1.104(2)	1.089
c/nm	1.039(2)	1.025
V/nm^3	1.097(2)	1.053
$\bar{r}$(Si–O)^b	0.178(7)	0.177
$\bar{r}$(S–O)^b	0.147(2)	0.148
$\bar{r}$(C–O)^b	0.129(1)	0.128
$\bar{r}$(Ca–O)^c	0.245(1)	0.243

^{a}[2], ^{b}Averaged bond lengths in $Si(OH)_6^{2-}$, SO_4^{2-} and CO_3^{2-} anions, ^{c}Averaged interatomic distances for the Ca^{2+} cation coordinated by 8 oxygen atoms conjugate-gradient algorithm with a stopping criterion of 10^{-5} eV for the total energy and with a tolerance of 0.001 Å for the atomic displacement.

Thermal analysis (decomposition)

Simultaneous TG/DTA curves have been acquired on *i*) T. A. I. SDT 2960 and *ii*) Derivatograph Q 1500 devices. Using the derivatograph device the data were acquired with routine measuring conditions (sample mass 100 mg, heating rate 10°C min^{-1}, heating from ambient temperature to 1000°C in the atmosphere of static air). In contrast, various combinations of data acquisition have been used with the T. A. I. SDT 2960 device. Multi-step measuring of 20 mg samples combined dynamic and isothermal heating from the ambient temperature to the maximum of 1000°C in atmospheres of air or $N_2(g)$. The temperature profiles (heating rates, temperatures and duration of isothermal sequences and also terminating temperatures) have been modulated in large scales.

Besides the mineral sample of thaumasite from mid-European Alps (mineralogical collections of the Faculty of Natural Sciences, Comenius University, Bratislava), the probes of additional interest have been *i*) thaumasite-bearing samples synthesized in the laboratory under conditions simulating the reactions of the thaumasite-sulfate attack (basically mixtures of Portland cement with the limestone mineral in the mass ratio 85:15, kept in the wet and sulfates containing environment at temperatures about 10°C for periods of 3×84 days) and *ii*) series of cementitious samples, in which the technological consequences of thaumasite- sulfate attack (TSA) have been reported or where the environmental conditions make the occurrence of this phenomenon probable. Both SDT 2960 and Derivatograph Q1500 equipments were used, with the purpose to compare the sensitivity of two different thermoanalytical devices.

Results and discussion

The optimization of atomic positions together with the unit cell volume resulted in the new unit cell parameters of 1.089 nm (a) and 1.025 nm (c) what means only 4% reduction of the unit cell volume in comparison to the experimental one. This small reduction reflects the fact that used DFT method slightly overestimates the strength of HBs [18]. Calculated unit cell parameters and the unit cell volume together with calculated averaged interatomic distances in the basic structural units ($Si(OH)_6^{2-}$, SO_4^{2-}, CO_3^{2-}) are collected in Table 1. In the structure of thaumasite the eight-fold coordination of the Ca^{2+} cation is interesting and in Table 1 the averaged Ca^{2+}–O distance is given. Six oxygen atoms in the Ca^{2+} coordination come from the structural water molecules while two rest oxygen atoms are from the $Si(OH)_6^{2-}$ anion. Comparing calculated and experimental values in Table 1 one can see that differences are minimal. The much more significant changes have been expected in the positions of hydrogen atoms and, consequently, in the formation of HBs.

Performed analysis of HBs in thaumasite showed following types: those formed between *i*) water molecules and carbonate anions, *ii*) water molecules and sulfate anions, *iii*) water molecules and $Si(OH)_6^{2-}$ anions and *iv*) water molecules themselves. HBs formed between water molecules and carbonate and/or sulfate anions, respectively, are very similar. All the oxygen atoms of both anions are acceptors in three HBs. The only difference between both types of HBs is in their average values and distributions. Figure 3 shows the distribution of calculated lengths of all HBs in thaumasite. Although in the experimental work [2] are given only estimations of the hydrogen positions we performed the same separation of the experimentally determined HBs as in the case of calculated values. This distribution is also given in Fig. 3. In spite the fact that the experimental HBs are only estimated one can see some accordance with the calculated distribution. HBs are separated into three main groups corresponding to intervals 0.160–0.175, 0.175–0.185 and 0.185–0.20 nm in both distributions. Calculated

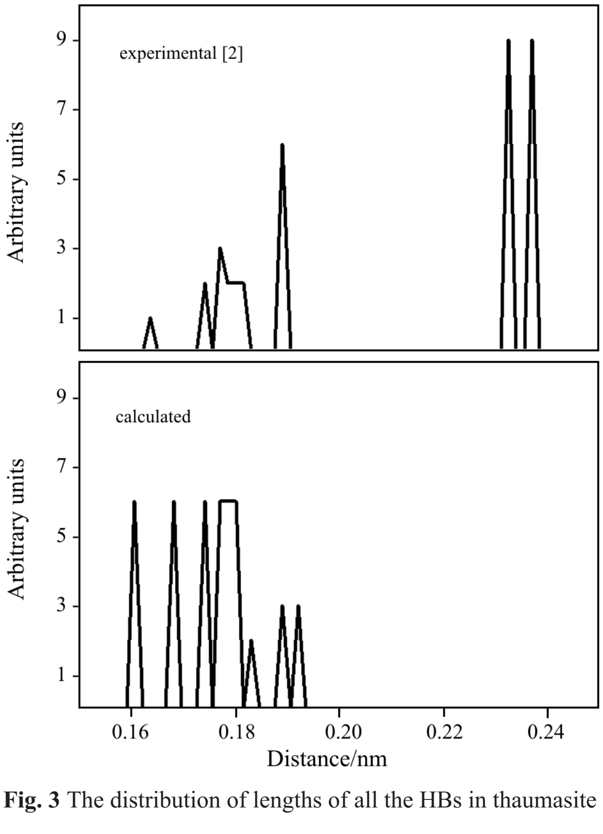

Fig. 3 The distribution of lengths of all the HBs in thaumasite

distributions are better separated than experimental ones. The difference is also observed for distances longer than 0.2 nm. While some O···H distances are observed in the experimental chart (Fig. 3), in the calculations this region is empty. This region represents mainly distances between water molecules and their next neighboring water molecules. In the calculated distributions we have observed a shift of these distances to values larger than 0.24 nm. It means that mainly the positions of water molecules were mostly rearranged to reach the optimized structure in comparison to the experimental determinations.

The analysis showed that the carbonate anions form three hydrogen bonds with water molecules and the lengths of these HBs are in the interval 0.162–0.182 nm. The lengths of HBs corresponding to the sulfate anions are found in the interval 0.177–0.182 nm. The first two peaks (the strongest HBs) in the calculated distribution (Fig. 3) represent O···H distances belonging to the effectively formed HBs between two water molecules and the carbonate anions having O–H···O angles about 173º. The peak belonging to the third hydrogen bond of the CO_3^{2-} anions overlaps with peaks about 0.18 nm and represents less effectively formed HB with the O–H···O angle about 156º. The averaged value of the HBs of the carbonate anions is 0.170 nm while for the sulfate anions it is 0.178 nm. Two different hydrogen bond angles were also found for the sulfate anions. 2/3 of these HBs are effectively formed with the angles about 172º while the rest of them are formed less effectively having the angles about 162º. The middle region of the O···H distances in Fig. 3 covers also HBs formed between water molecules (the averaged value of 0.184 nm and the angle of about 168º). The last group of HBs, lying at about 0.19 nm, are formed between water molecules and the $Si(OH)_6^{2-}$ anions from the structural columns and are weaker than previous ones. The analysis showed two slightly different lengths of these HBs (0.193 and 0.190 nm) what corresponds to two experimentally observed stretching vibrations of the hydroxyl group (3470 and 3500 cm^{-1}) in the infrared spectrum of thaumasite [19]. The angles of these weaker HBs are about 166°, what are not fully effectively created HBs. It is probably due to strong Coulombic effect of calcium cations coordinated the $Si(OH)_6^{2-}$ anions. To complete the picture of HBs in thaumasite, we present in Fig. 4 all O···O distances up to 0.320 nm taken from the experiment [2] and calculated in this work. The agreement between experimental and calculated distributions is better than in case of hydrogen bonds in Fig. 3. The first two (three in the experimental chart) and the last two (also three in the exp. chart) peaks correspond to the O···O distances in the carbonate anions (0.222 nm), sulfate anions (0.240 nm) and/or in the $Si(OH)_6^{2-}$ anions (0.295, 0.297 nm), respectively. Calculated results showed clear separations of the O···O distances from the HBs into three groups, similarly like for the O···H distances (Fig. 3). The first one, about 0.258 nm, corresponds to the shortest HBs of the carbonate anions, the second one, about 0.272 nm, corresponds to the HBs of the sulfate anions and the last one, about 0.288 nm, corresponds to the HBs of the $Si(OH)_6^{2-}$ anions. The O···O distances between water molecules involved in the mutual HBs are lying in the middle region (about 0.272 nm). The calculated interval of the O···O distances (0.25–0.29 nm) is somewhat shifted to the smaller values in comparison with experimentally determined interval of 0.267–0.294 nm [3].

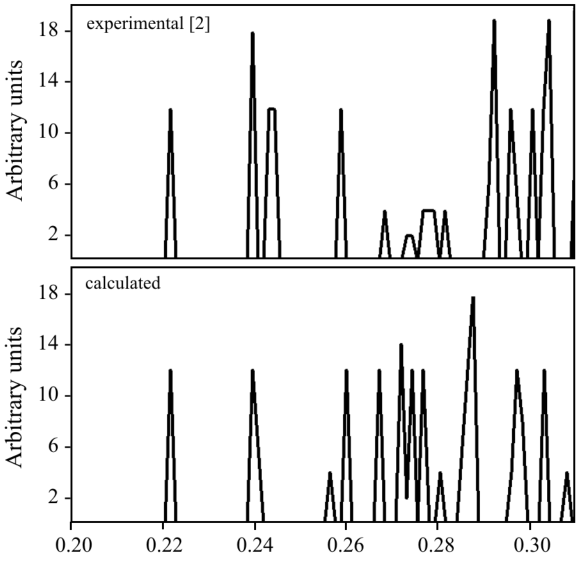

Fig. 4 The distribution of the O···O distances up to 0.320 nm in thaumasite

The data of thermal analysis (TG, DTG and DTA curves) of the pure mineralogical thaumasite sample heated in the temperature interval 65–250°C by the rate of 0.5°C min^{-1} document, as presented in Fig. 5, the steps I and II of the thermal decomposition. The complete thermoanalytical data can be found in [4–7]. The TG mass losses and DTA effects of the mineral occur in the temperature regions 100–130°C (I), 150–250°C (II) and 580–680°C (III) and were observed in patterns acquired on both devices. The values of mass losses, Δm_i(exp), derived from the TG curves –37.37% (I), 4.50% (II) and 6.95% (III), are in a good agreement with Δm_i(st)=37.60% (I), 5.78% (II) and 7.07% (III), as calculated from the stoichiometry of the sequence of chemical Eq. (1):

$$\begin{gathered}
\text{I. } CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O \xrightarrow{100-130℃} \\
CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 2H_2O + 13H_2O \\
\text{II. } CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 2H_2O \xrightarrow{<300℃} \\
CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 + 2H_2O \\
\text{III. } CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \xrightarrow{>600℃} \\
CaSiO_3 \cdot CaO \cdot CaSO_4 + CO_2
\end{gathered} \tag{1}$$

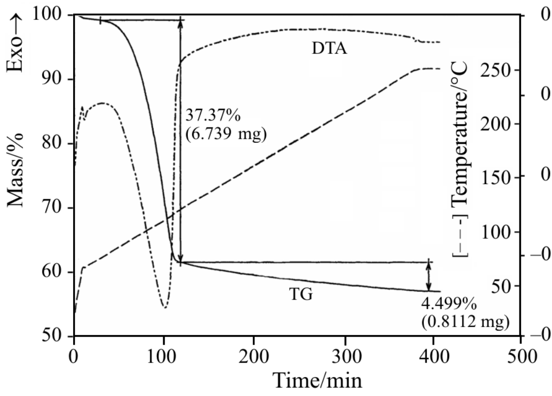

Fig. 5 TG and DTA curves of pure mineralogical thaumasite, heating rate 0.5°C min^{-1} in the temperature interval 65–250°C

The thermal event in the step II of the thermal decomposition of thaumasite (cf. Eqs (1) and (2)), being difficult to follow, has been neglected by some authors [4–6]. Our former study [7] ultimately demonstrates the importance to distinguish this step from step I, especially when the dynamic conditions of thermal analysis are used. Computer simulations performed on the thaumasite structure as reported and discussed in this paper became an effective tool supporting the indicated steps of the decomposition reactions.

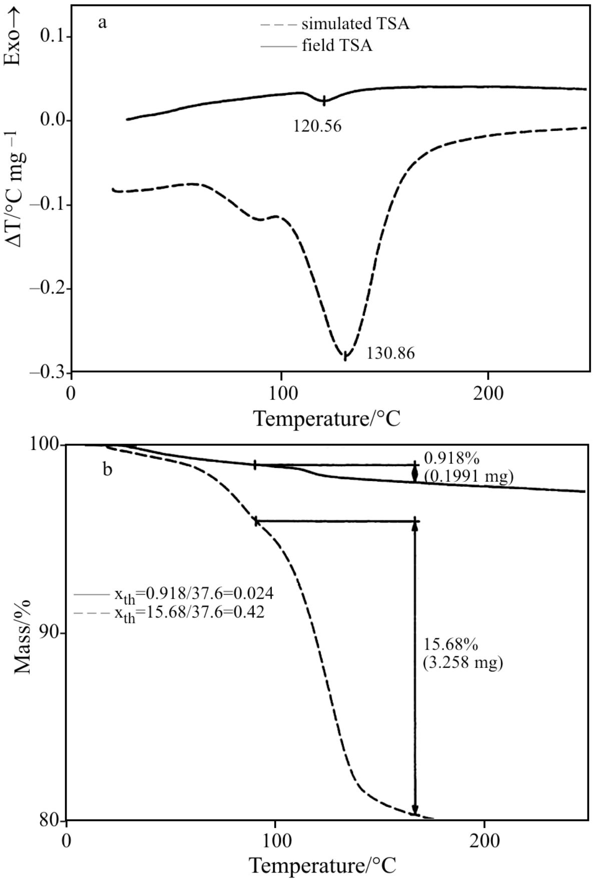

Fig. 6 Exemplified data of thermal analysis of cementitious samples in which the technological consequences of TSA have been reported. a – Qualitative identification of the presence of thaumasite visualized as DTA effect of the step I of decomposition. b – Mole fractions of thaumasite $-x_{\text{th}}$ calculated as the ratio of topical TG mass loss *vs.* stoichiometric mass change of the step I ; x_{th}=0.42 for the probe with simulated TSA, x_{th}=0.024 for the probe of field TSA

Distributions of O···H and O···O distances resulting from the computer simulations correspond to the different energies of HBs between individual counterparts in the structure of thaumasite. This knowledge can support the explanation of the observed thermochemical processes, i.e. the stepwise decomposition on heating (cf. Figs 5 and 6). Analysis of TG curves of mineral sample shows that structural water molecules release the structure in the step I (Δm=37.60%, 100–130°C in Eq. (1)). It means that this decomposition step represents the continual hydrogen bond breaking between the structural water and the CO_3^{2-}, SO_4^{2-} and $Si(OH)_6^{2-}$ anions. The end of this process is accompanied with the collapse of the $Si(OH)_6^{2-}$ anion, which becomes unstable after the water lost. The collapse of the structure after the dehydroxylation of the $Si(OH)_6$ octahedron was reported in experimental works [3, 5]. It is seen also as the DTA effect (cf. Figs 5 and 6a) accompanying the step I of the decomposition. Similar conclusion was also reported on the base of DSC data [6]. Two water molecules formed in course of the collapse of the $Si(OH)_6^{2-}$ anion are probably caught in the strong HBs with the rests representing by SO_4^{2-}, CO_3^{2-}, SiO_3^{2-} and Ca^{2+} ions and, due to structural rearrangement and the Coulombic balance, a relatively stable intermediate is formed after the step I of the decomposition. It means that the final elimination of remaining two H_2O molecules is under the dynamic conditions the separated effect seen as the step II (160–300°C) on TG curves (cf. Fig. 5). Stoichiometry and complete series of the decomposition equations can be found earlier in this paper (Eq. (1)) and also in [7, 20]. The steps I and II of the decomposition are re-drawn (Eq. (2)) to resemble as the features of the crystal structure of thaumasite so the above discussed effects of HBs upon the decomposition under the dynamic heating conditions:

$$\begin{aligned}\text{I. }&[Ca_3Si(OH)_6{\cdot}12H_2O](CO_3)(SO_4)\xrightarrow{100-130℃}\\&[Ca_3SiO_3{\cdot}2H_2O](CO_3)(SO_4)+13H_2O\qquad(2)\\\text{II. }&[Ca_3SiO_3{\cdot}2H_2O](CO_3)(SO_4)\xrightarrow{<300℃}\\&Ca_3SiO_3CO_3SO_4+2H_2O\end{aligned}$$

Thaumasite is far not new mineral phase, however, it is the phase newly recognized in some sulfate-attacked building constructions [1, 20, 23]. Exemplified sets of the thermoanalytical data of the 1st decomposition step and their use for the identification of thaumasite in building constructions attacked by TSA are given in Fig. 6 and Table 2. The tests em-

Table 2 The data of the step I of the thermal decomposition, the series of field TSA is from municipal building constructions tested on the presence of thaumasite

Sample No.	DTA endoeffect/ (109–131°C)	TG mass loss/%	x_{th}
1	+	0.43	0.011
2	–	–	–
3	–	–	–
4	–	–	–
5	+	0.92	0.024
6	+	0.48	0.013
7	+	0.54	0.014
8	+	0.61	0.016
9	+	0.83	0.022
10	+	1.31	0.035

+ – thaumasite present, x_{th}– value of mole fraction of the present thaumasite

ploying TG mass losses may answer the question if thaumasite is present and, on condition that experimental results are compared with appropriate stoichiometry of decomposition, a vital knowledge about a fraction of thaumasite in the inspected sample is achieved. The mass change during the step I is as high as (37.5±0.5)% of the total amount of thaumasite present in the probe. Consequently, a high sensitivity of the quantitative thermogravimetric analysis is achieved, if the data of step I are evaluated.

The quantification of thaumasite in mixes with the other cementitious phases is based on the comparison of mass losses of probes during the step I of the decomposition (cf. Fig. 6b) with the stoichiometric mass change of the step I (37.60 %), giving the mole fraction (x_{th}) of thaumasite in the topical probe. The details of the method have been reported in [7]. This approach has been experimentally tested on a large series of cementitious thaumasite-bearing samples. The mole fractions of thaumasite (x_{th}), as determined in the statistically representative series of probes [20], are given in Table 2. Similar contribution and feedback of novel thermoanalytical methodologies and approaches towards the knowledge of a variety of ceramics and cementitious materials are of the recent interests [21–23].

The results of present study, achieved on both SDT 2960 and Derivatograph Q1500 devices, complete the former ones in a way that: *i*) the values $x_{th} \geq 0.01$ are detectable when evaluating the step I of TG data acquired using SDT 2960, while *ii*) the edge of sensitivity of Derivatograph Q1500 is $x_{th}=0.02$. Thus, the topical thermoanalytical limit of the quantitative identification of thaumasite is close to the level of 1% with highly sensitive and accurate SDT 2960 and 2% for Derivatograph Q1500-device frequently used in control labs in mid-European region. Taking into account the subject matter and sensitivities of the other methods (see below), already the sensitivity achieved by Derivatograph Q1500 is sufficient enough for the check of the presence and amount of thaumasite in sulfate attacked concretes. For purposes of a comparison; IR spectroscopy gives qualitative identification only, quantitative powder X-ray phase analysis is affected by the presence of amorphous components. Thermal analysis and especially TG data generally do not suffer from these drawbacks and results of this paper together with previous ones [7, 20] submit a powerful background and tool for cement chemists when dealing with the problem of reliable identification of thaumasite in sulfate-attacked building constructions.

Conclusions

Computer simulation methods allowed determining the positions of hydrogen atoms in the structure of thaumasite. Hydrogen bonds formed between various structural units were characterized and categorized. This hydrogen bond characterization contributed to the understanding of the thermal decomposition of the thaumasite mineral, especially of the first low temperature phase (step I in Eqs (1) and (2)).

The first step represents the dehydration and dehydroxylation of $[Ca_3Si(OH)_6{\cdot}12H_2O]^{4+}$ groups and structural collapse what results in the formation of the intermediate with two remaining water molecules involved in the hydrogen bonds with the structural residues (SO_4^{2-}, CO_3^{2-}, SiO_3^{2-} and Ca^{2+} ions). The subsequent dehydration of intermediate has been distinguished in the step II (cf. Eqs (1) and (2)).

The TG data of step I are sensitive and reliable enough to detect thaumasite sulphate-attack (TSA) and to determine the content of thaumasite in attacked building constructions independently of the sensitivity and accuracy of thermoanalytical device. The topical quantitative sensitivity is close to the level of 1% (highly sensitive and accurate device) and 2% (the device frequently used in control labs).

Acknowledgements

The research has been conducted under the project No. 2/5011/5 of the Slovak scientific grant agency VEGA. We are grateful for technical support and computer time at the Linux-PC cluster Schrödinger II of the computer center of the University of Vienna.

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Received: July 21, 2005
Accepted: July 27, 2005
OnlineFirst: January 11, 2006

DOI: 10.1007/s10973-005-7236-0