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Physically and chemically bound H_2O in the gyrolite structure

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Synthetic pure gyrolite prepared under hydrothermal conditions (32 h, 200 °C) from a stoichiometric composition ($CaO/SiO_2 = 0.66$) of calcium oxide and a fine-grained $SiO_2 \cdot nH_2O$ mixture can easily adsorb water vapour. The equilibrium quantity of adsorbed water vapour was estimated from desorption thermograms. It was determined that the thermal effect of desorption is close to the steam-heat of water vapour at temperatures up to 175 °C. This part of water vapour adsorption can be described by a physical adsorption model, only a small quantity of water vapour being chemisorbed. The crystal structure of gyrolite under a pressure of water vapour and at low temperatures (–197 °C) was stable.

Key words: *gyrolite; adsorption; thermal analysis; calcium silicate hydrate; X-ray diffraction*

1. Introduction

Calcium silicate hydrates, occurring in nature as hydrothermal alteration products of calcium carbonate rocks and as vesicle fillings in basalts, include many chemically and structurally distinct phases [1]. Many calcium silicate hydrates are structurally very similar, consisting of similar arrangements and modifications of the same types of structural units, i.e. dreierketten chains. Intrinsic disorder within the crystal structure of even the most crystalline natural C–S–H mineral samples can affect the crystallographic and physical characteristics of these phases [2, 3]. Moreover, the hydrothermal formation of these phases is complicated, and crystallization usually occurs via a semi-crystalline precursor and intermediate phases [4–13]. These phases can be very stable, and a long synthesis (months) may be required before the system reaches an equilibrium. This makes the exact crystallization mechanism and kinetics difficult to determine. The dehydration and recrystallization processes of these phases are also complex and vary from phase to phase, due to the different structures and varying

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*Corresponding author, e-mail: kestutis.baltakys@ktu.lt amounts of OH and/or H_2O. A few of these compounds contain molecular water, some hydroxyl, and others contain both hydrous species.

Recently, Allen et al. presented an obvious schematic diagram of the nanoscale C–S–H particles containing liquid H_2O in nanopores, adsorbed H_2O, interlayer space with physically bound H_2O and calcium silicate sheets with OH^- groups [14].

However, some properties, e.g. sorption capacity, depend not only on the crystal lattice of a porous body but also on the surface microstructure and specific surface area, as well as on the dominant pore size and their differential distribution in the compound relative to the radius. In the case of gyrolite crystal lattice, these properties usually depend on the proportion of crystalline (SiO_4 tetrahedral and CoO_6 octahedral sheets) and amorphous parts. However, no data was found on the influence of partial pressure of water vapour on the gyrolite crystal lattice.

Recently, the interest in gyrolite has increased because new possibilities of its application have been found; it may be used to educe heavy metal ions and remove them from wastewaters [15, 16]. Of specific interest is the purported ability of gyrolite to separate supercoiled plasmid, opencircular plasmid, and genomic DNA [17].

The aim of the present work was to elucidate the influence of partial pressure of water vapour on the gyrolite crystal lattice. Based on experimental measurements, the form of adsorbed water in the gyrolite structure was highlighted.

2. Experimental

In this work, the following reagents were used as starting materials: fine-grained $SiO_2 \cdot nH_2O$ (Reachim, Russia, ignition losses 21.43 %, specific surface area $S_a = 1560$ m²/kg by Blaine's) and CaO (99.6 % Reachim, Russia) additionally burned at 1000 °C for 0.5 h.

Pure gyrolite was synthesized after 32 h at 200 °C from a stoichiometric composition of calcium oxide and $SiO_2 \cdot nH_2O$ mixture ($CaO/SiO_2 = 0.66$). The dry primary mixture was mixed with water in stainless steel vessels (water/solid ratio of the suspension W/S = 10.0). The product was filtered, dried at 50 ± 5 °C and sieved through a sieve with the mesh size of 80 μm. These synthesis conditions were chosen based on previously published data [12, 13].

Experiments of adsorption of water vapour by gyrolite were carried out at room temperature. Samples of gyrolite were kept in desiccators with sulfuric acid for 60 h. Variation of sulfuric acid solution concentrations made it possible to achieve a desired relative pressure of water vapour p/p_0 (p – partial pressure of adsorbate, p_0 – saturated vapour pressure of adsorbate) (Table 1). The quantity of adsorbed water vapour was determined from data of a simultaneous thermal analysis.

In order to evaluate the stability of gyrolite structure at low temperatures and to estimate the influence of the adsorbed water vapour (adsorbate) on the structure of its crystal lattice, gyrolite samples were first saturated with water vapour, i.e. kept in a desiccator for 60 h at various relative pressures p/p_0 (1, 0.877, 0.753, 0.56, 0.355).

Later, these samples were cooled in liquid nitrogen (–197 °C) for 15 min each and heated to room temperature (20 °C). The stability of gyrolite structure was estimated from X-ray powder diffraction data.

Table 1. Partial pressures of H_2O vapour in the air above H_2SO_4 solutions at 25 °C

No.	Relative pressure (p/p_0) of water vapour	Concentration c of H_2SO_4 solutions [%]
1	0.355	50
2	0.56	40
3	0.753	30
4	0.877	20
5	1	0

The X-ray powder diffraction results were collected with a DRON-6 X-ray diffractometer with the Bragg–Brentano geometry using Ni-filtered CuK_α radiation and a graphite monochromator operating at the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2–60° (2θ) in steps of $2\theta = 0.02°$. The computer program X-fit [18] was used for diffraction profile refinement under the pseudoVoid function and for description of the diffractional background under the 3rd degree Tchebyshev polynomial.

Simultaneous thermal analysis (STA, differential scanning calorimetry – DSC and thermogravimetry – TG) was carried out on a Netzsch instrument STA 409 PC at the heating rate of 15 °C/min. The temperature ranged from 30 °C up to 1000 °C in an ambient atmosphere. The ceramic sample handlers and Pt–Rh crucibles were used.

IR spectra were carried out with a Perkin Elmer FT–IR system spectrum X spectrometer. The specimens were prepared by mixing 1 mg of a sample with 200 mg of KBr. Spectral analysis was performed in the range of 4000–400 cm^{-1}, with the spectral resolution of 1 cm^{-1}.

The specific surface area of raw materials was determined by Blaine's method with an air permeability apparatus (Model 7201, Toni Technik Baustoffprufsysteme GmbH).

3. Results and discussions

Water vapour adsorption by gyrolite was studied in function of the partial pressure of water vapour in the air. The latter parameter was controlled by changing the concentration of sulfuric acid in H_2SO_4–H_2O solutions (Table 2). The equilibrium quantity of water vapour ($\Sigma X_p^{H_2O}$) adsorbed on gyrolite was estimated from desorption termograms (Fig. 1). We can see from Fig. 1 that the largest change of mass (Δm) occurs in the temperature range 50–150 °C and is attributed to the desorption of free water.

Table 2. Dependence of adsorbed water vapour quantity on p/p_0 in the temperature range 50–200 °C [mg]

p/p_0	*t* [°C]															
	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200
1.000	0.18	0.27	0.48	0.83	1.45	2.53	4.21	6.22	8.11	9.26	9.57	9.80	10.03	10.19	10.32	10.40
0.877	0.10	0.19	0.37	0.66	1.14	1.81	2.66	3.42	3.75	3.97	4.18	4.40	4.61	4.78	4.91	5.02
0.753	0.10	0.18	0.29	0.44	0.72	1.14	1.58	1.84	2.03	2.23	2.43	2.63	2.80	2.92	2.95	3.04
0.560	0.10	0.15	0.25	0.43	0.80	1.07	1.33	1.51	1.66	1.81	1.96	2.12	2.26	2.37	2.46	2.55
0.355	0.05	0.09	0.16	0.30	0.48	0.67	0.86	1.02	1.18	1.34	1.48	1.65	1.85	1.98	2.11	2.23
0.000	0.11	0.13	0.17	0.23	0.33	0.45	0.63	0.76	0.87	0.98	1.14	1.31	1.50	1.65	1.81	1.96

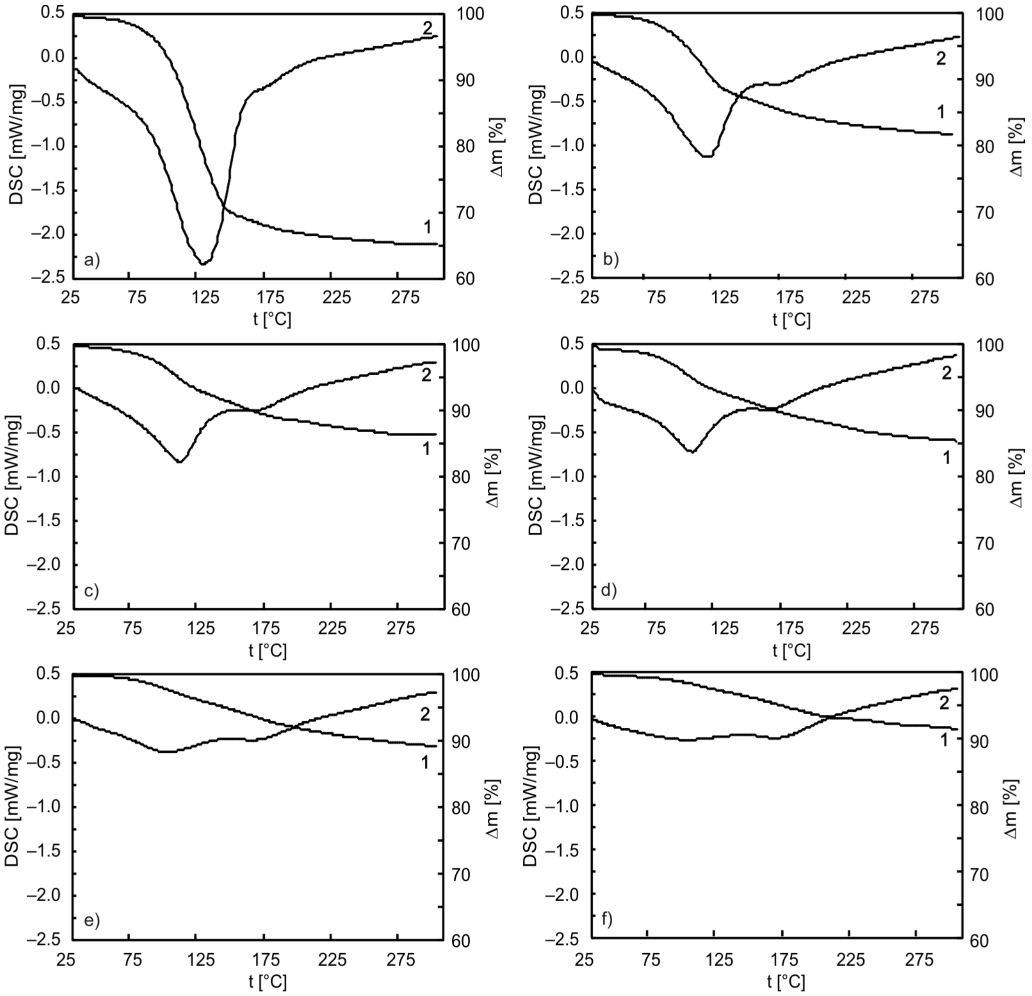

Fig. 1. TG (1) and DSC (2) curves of gyrolite at the p/p_0 ratio:
a) 1, b) 0.877, c) 0.753, d) 0.56, e) 0.355, f) reference sample

It should be emphasized that the value of $\Sigma X_p^{H_2O}$ changes most significantly, i.e. increases from 0.18 to 10.40 mg, when the p/p_0 ratio is equal to 1.0 (saturated water vapour) in the temperature range 50–200 °C (Fig. 2).

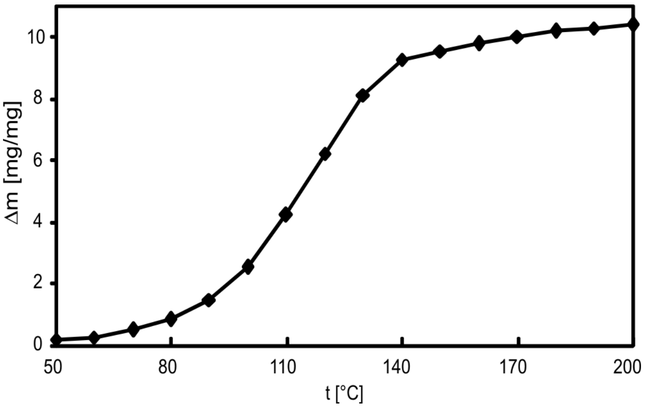

Fig. 2. Increment of the quantity of adsorbed water vapour on gyrolite surface at the p/p_0 ratio equal to 1.0 in the temperature range 50–200 °C

Experimental data and the theoretical hypothesis were also confirmed by thermodynamic calculations. It was determined that the thermal effect of water vapour desorption on gyrolite structure is close to the steam-heat of water vapour at a temperature up to 150 °C (Fig. 3). This part of adsorption of water vapour can be described by a physical adsorption model: no strong bands are formed and the adsorbed water is equilibrated. In this case, the humidity at a certain temperature has no influence on the amount of adsorbed water. However, at a low temperatures the amount of adsorbed water is related to a change of humidity (Fig. 4).

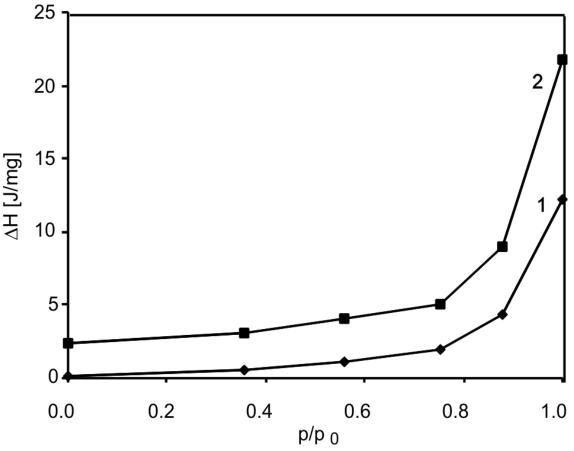

Fig. 3. Calculated isotherm (1) by steam-heat of H_2O vapour and measured isotherm (2) by desorption of H_2O vapour on gyrolite surface in the temperature range 50–150 °C

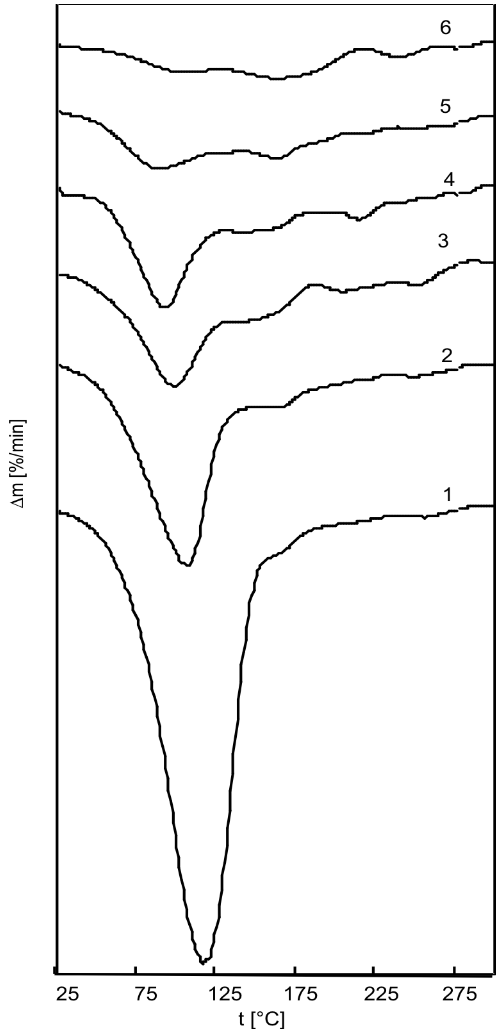

Fig. 4. DTG curves of gyrolite at the p/p_0: 1 – 1, 2 – 0.877, 3 – 0.753, 4 – 0.56, 5 – 0.355, 6 – reference sample

Moreover, a small variation of Δm was determined at 175 °C (Fig. 4). It should be emphasized that this adsorbed water is not balanced with the content of H_2O vapour in the gyrolite environment, and remains almost the same in all ranges of p/p_0. Thus, in this case the influence of the p/p_0 ratio on the adsorption process is negligible (Fig. 4, endothermic peak at 175 °C). This fact means that only a small quantity of adsorbed water is chemisorbed.

FT-IR spectroscopy is very well suited for investigating structural properties of adsorbed or chemisorbed water. Figure 5 presents FT-IR spectra of gyrolite samples, saturated (60 h) with water vapour at different p/p_0 ratios.

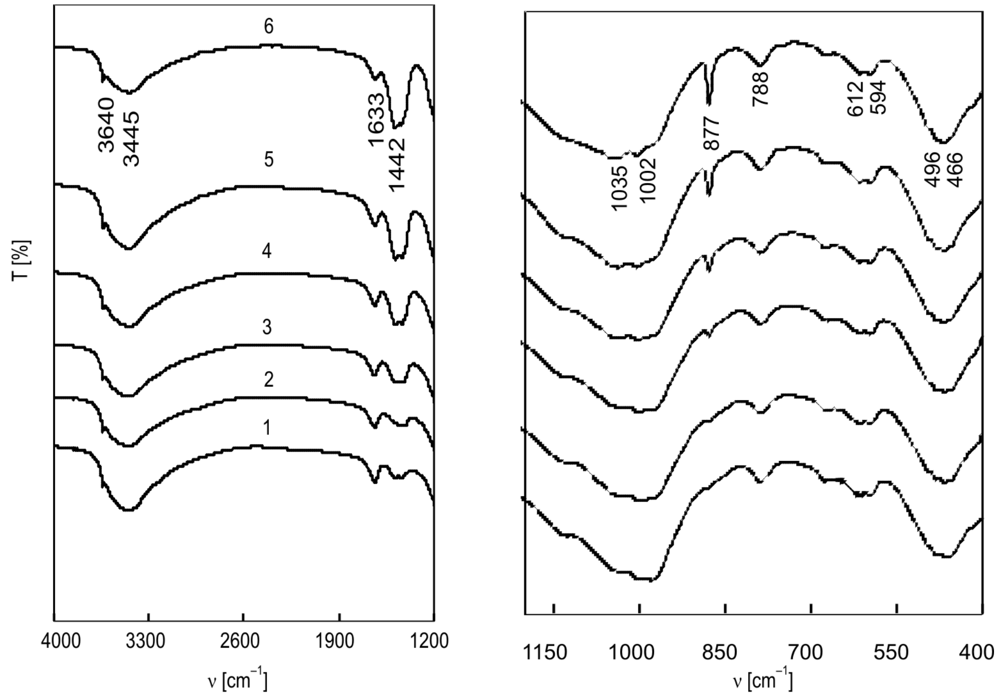

Fig. 5. FT-IR spectra of gyrolite at the p/p_0 ratio:
1 – reference sample, 2 – 0.355, 3 – 0.56, 4 – 0.753, 5 – 0.877, 6 – 1

It should be noted that the intensity of bands near 3637, 3450 and 1634 cm^{-1} does not depend on the p/p_0 ratio. Thus, chemisorption bands may appear only during synthesis at high temperatures. Besides, a sharp band near 3637 cm^{-1} proves that clearly distinguished OH positions exist in the structure of gyrolite, the OH groups being connected only with Ca atoms and not influenced by hydrogen bridge links. A wide band near 3450 cm^{-1} means the opposite – molecular water forms hydrogen bridge links in the interlayers. The bands in the 1634 cm^{-1} frequency range are assigned to $\delta(H_2O)$ vibrations, and confirm this presumption (it can be assigned to chemisorbed water). The intensity of absorption bands near 873 and 1442 cm^{-1} significantly increases during the adsorption process. Thus, analysis of absorption band profiles leaves us to conclude that water vapour was adsorbed close to the physical adsorption model. It should be underlined that chemisorption bands in the gyrolite structure can be created only during synthesis at a high temperature. The obtained experimental data on the stability of gyrolite structure at a low temperature (–197 °C) are summarized in Fig. 6. The results of XRD studies confirmed that adsorbed water has no influence on the structure of gyrolite crystal lattice, because the intensity and profile of the main peak with *d* spacing – 2.2 nm of gyrolite remains essentially unchanged. Moreover, in the X-ray diffraction pattern there were peaks determined having the *d* spacing 1.1262, 0.8371, 0.4197, 0.3732, 0.3511, 0.2803, 0.2141 nm, which are also typical of gyrolite (Fig. 6).

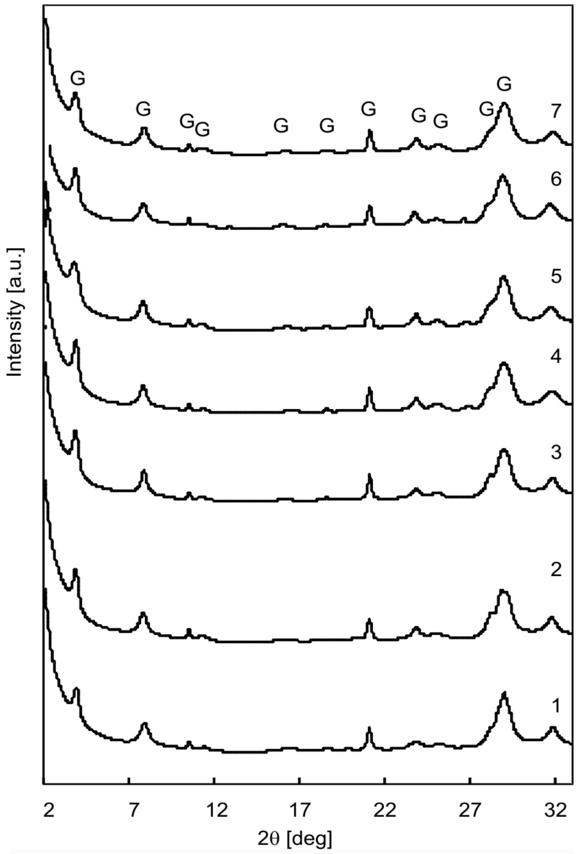

Fig. 6. X-ray diffraction patterns of gyrolite samples saturated (60 h) with water vapour, frozen in liquid nitrogen (–197 °C) for 15 min each and heated to room temperature (20 °C) at p/p_0: 1 – pure sample, 2 – 0.355, 3 – 0.56, 4 – 0.753, 5 – 0.877, 6 – 1, 7 – references sample, G – gyrolite

Thus, our research has shown that gyrolite can easily adsorb water vapour by the physical adsorption. The adsorption has no influence on the structure of gyrolite at liquid nitrogen temperature. It should be emphasized that this part of water is balanced with the content of H_2O vapour in the gyrolite environment, and its variation depends upon the p/p_0 ratio. The obtained data explain why many authors [19] indicate different chemical formulas of gyrolite with an unlimited content of water.

5. Conclusions

The equilibrium quantity of water adsorbed on gyrolite structure increases when the p/p_0 ratio of relative pressure of water vapour varies from 0.355 to 1.0. It was determined that the thermal effect of desorption is close to the steam-heat of water vapour. This part of water vapour adsorption can be described by the physical adsorption model.

It was observed that only a small quantity of water vapour is chemisorbed, and this water is not balanced with the content of H_2O vapour in the gyrolite environment: it remains almost constant throughout the p/p_0 range. Bands due to chemisorbed water in the gyrolite structure can be created only during hydrothermal treatment.

It was found that the crystal structure of gyrolite is stable under conditions of extreme cold (especially if in liquid nitrogen), and its stability does not depend on the quantity of adsorbed water.

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