МІНЕРАЛОГІЧНИЙ ЖУРНАЛ
MINERALOGICAL JOURNAL
(UKRAINE)

UDK 546.11.027:552.52:535.34

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Hydrogen Isotope Exchange in the "$Ca(OD)_2$ — H_2O" System under Normal Conditions

The hydrogen isotope exchange in the "$Ca(OD)_2$ — H_2O" system (with the 1 : 25 mass ratio) under normal conditions was studied by PMR, Mn^{2+} EPR and IR-spectroscopy methods. The solid phase composition in this system has been found to change to $Ca(OD_{1-x}H_x)_2$ at first. Fifty days later there also appeared the phase $Ca(OH)_2$ (~ 5 %), that was explained by the protium diffusion through the lateral surface into the solid structure. Then the exchange was slowed down, and 290 days later the amount of $Ca(OH)_2$ phase was about 6 %. The Mn^{2+} ions in the hydroxide phase have been established to oxidize to Mn^{3+} at that time ($Ca(OD)_2$ and $Ca(OH)_2$ phases therewith are undistinguished). Simultaneously there was formed a carbonate phase. The isotope exchange slowing down with time was explained by the carbonate phase formation directly on the solid surface, in addition to the precipitated $CaCO_3$ phase. The scheme of possible processes in the considered system has been developed. Experimental data have been fitted by equations obtained within this scheme framework. The rate constants of the isotope exchange in superficial structural OD-groups are $6.06 \cdot 10^{-4}/1.42 \cdot 10^{-2}$ $(mol \cdot m^{-2} \cdot c)^{-1}$ on the basal/lateral surfaces, respectively. It was supposed that the carbonate phase on the surface formed in the following way: the $HCO_3^- \rightarrow$ OD(OH)-group ligand exchange reactions (with $k \sim 0.61/1.33$ $M^{-1} \cdot c^{-1}$ at pH ~ 11.5) produce the inner-sphere monodentate complexed CO_3^{2-}-surface species, which then interact with the nearest OD(OH)-groups (with $k_2 \sim 3.2 \cdot 10^{-8}/2.2 \cdot 10^{-8}$ c^{-1}) with the formation of the inner-sphere bidentate complexed CO_3^{2-}-surface species. Mn^{2+} ions in the hydroxide structure oxidize with $k_0 \sim 2.24 \cdot 10^{-7}$ c^{-1}. Deuterium ions diffuse along the interlayer space plane in the $Ca(OD)_2$ structure with $D_0 \sim 4 \cdot 10^{-23}$ $m^2 \cdot c^{-1}$.

Introduction. The clear knowledge of process mechanisms, occurring in systems, containing $Ca(OD)_2$ and water, is of considerable interest for many reasons [7, 8, 12]. First of all, this is due to the broad use of portlandite, $Ca(OH)_2$, in various technological processes of making of new materials or compounds with necessary characteristics — cementing materials, materials with desired pore structures, adsorbents and others, using, in particular, to process and to isolate industrial wastes, including radioactive [5, 14]. The "portlandite — water" system is often considered as a model system to study processes, occurring in more complex water-curing structures, as the $Ca(OH)_2$ structure is similarly or like to layer structures in many layered and band OH-containing minerals with the most varied using (in particular, as engineering barriers against the environment contamination) [4, 11, 13, 15]. The understanding of processes, occurring in this system, is necessary also to study many scientific problems, such as mechanisms of sorption and isotope exchange in like systems, migration of varied ions and molecules, in particular, hydrogen isotopes, in geological formations and crystalline structures and others.

The knowledge of the hydrogen isotope exchange mechanisms in a mineral/water system needs also to solve many practical problems, in particular, to estimate a time period of tritium retention during various minerals contacting with tritiated water, that is required to construct engineering barriers against tritium contamination of the environment on a basis of mineral components [9]. Hydrologic processes are supposed to govern, in general, hydrogen isotope migration in many "geological formation — water" systems [4, 9]. However, it had been found, that heavy hydrogen isotopes can be accumulated (normal conditions) not only in adsorbed water on surfaces of some OH-bearing minerals, but in their structural hydroxyls also [9]. So it seems to be necessary to investigate hydrogen isotope exchange in the relatively simple model system of the "water — layered OH-bearing mineral" at normal conditions.

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The present work aim was to study changes, occurring in the solid phase in the "$Ca(OD)_2$ — H_2O — air" system at normal conditions.

When hydrogen isotopes are transferred in the "water — solid" systems at normal conditions, the quantum nature of occurring processes and, in particular, noticeable isotopic effects are observed [2]. A small amount of heavy hydrogen isotope (D or T) in a large H_2O volume (a mole fraction is less than $1 \cdot 10^{-3}$) does not affect practically on the equilibrium constants of occurring processes [2]. However, kinetic isotopic effects in such systems can be very large as a result of the essential difference of zero energy of an initial bond stretching vibration and the large ratio of hydrogen isotope masses [2]. The rate constants of processes with the O—H bond participation at normal conditions decrease approximately in 15 times as a result of deuterium substitution for protium [2]. The secondary isotopic effects (the isotope substitution affect on nearest bonds) are much less (less than 1.15), and they are often neglected.

The mass ratio of solid/liquid phases was 1 : 25 in the experimental "$Ca(OD)_2$ — H_2O — air" system (see below). Not more than 1.5 % $Ca(OD)_2$ has been dissolved in water as a result of the solution $Ca(OD)_2$-saturating at the experimental conditions (see below). Some peculiarities of the hydrogen isotope migration could be studied in this system — the protium localization (in the adsorbed water only or in the $Ca(OD)_2$ structure also), protium migration ways into the structure (through the lateral and/or the basal crystallite surfaces) and the isotope exchange kinetics on these surfaces.

Except the possible isotope exchange between $Ca(OD)_2$ and H_2O, there could form a some $CaCO_3$ amount in the "$Ca(OD)_2$ — H_2O — air" system due to presence of CO_2 dissolved in water [7, 11]. At approximately equal weights of water and portlandite the $Ca(OH)_2$ dissolution has been shown to slow down noticeably with time as a result of $CaCO_3$ formation on its surface (supposedly, precipitation) [12]. At the same time, it can be presumed, that the other processes can occur on the solid phase surface in the "$Ca(OD)_2$ — H_2O — air" system, in particular, the carbonate ion inner-sphere complexation with the surface, just as in similar (hydro)oxide/water systems [11, 15, 17]. The mechanisms of such processes on II and III valence metal hydroxide surfaces in water are poorly known, though surface complexes of different ions present in solution can noticeably affect on processes in these systems [11, 15, 17].

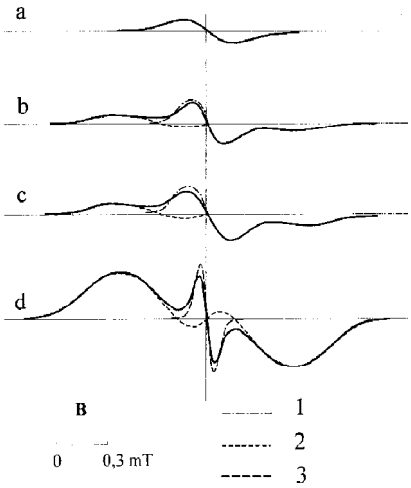
The following methods were used in the present work to detect structural changes in the solid phase in the experimental system: 1) proton magnetic resonance (PMR) — to measure an amount of structural OH-groups in $Ca(OD)_2$ structure and to establish their location peculiarities; 2) infrared spectroscopy (IR-spectroscopy) — to measure an amount of structural OD-groups; 3) electron paramagnetic resonance (EPR) — to measure an amount of Mn^{2+} ions in a carbonate and an hydroxide phases ($Ca(OD)_2$ and $Ca(OH)_2$ phases therewith are undistinguished) [10].

Materials. Calcium deuteride has been synthesized from natural $CaCO_3$ by heating up to 1000 °C and following D_2O-slacking of obtained CaO. By EPR data, natural $CaCO_3$ had about 0.06 % Mn^{2+} impurity ions, which, supposedly, have been included in formed $Ca(OD)_2$ [10]. Synthesized $Ca(OD)_2$ crystallites are thin plates with about 2 μm in diameter and 0.12 μm in thickness. $Ca(OD)_2$ and $Ca(OH)_2$ structures are presumed to be the same (CdI_2 structure), similarly to deutereted analogues of others brucite-like hydroxides. The elementary cell parameters of $Ca(OD)_2$ most probably, are the same as for $Ca(OH)_2$ — $a = 0.3589$ and $c = 0.4911$ nm [5].

Methods and Methodologies. Samples (2 g $Ca(OD)_2$) were curing in 50 ml distilled water in closed glass vessels at room temperature. Within a few weeks a solution was filtered, a solid precipitate was air-dried and its spectra were registered. Changes in the solid phase were studied by PMR, IR- spectroscopy and EPR methods.

The PMR spectra were recorded by РЯ-2301 spectrometer at 16 MHz, IR-spectra — by UR-10 spectrometer (2000–4000 cm^{-1} range) and EPR spectra — by РЭ-1306 spectrometer (3 cm range). All spectra were recorded at room temperature.

It must be noticed that Mn^{2+} EPR spectra ($g \approx 2.0$) are dictated by the structural environment of these ions and are essentially differed for a carbonate and an hydroxide phases $Ca(OD)_2$ and $Ca(OH)_2$ phases therewith are undistinguished) [10]. An amount of Mn^{2+} ions in any phase was evaluated by the peak intensity of the Mn^{2+} EPR band in this phase.



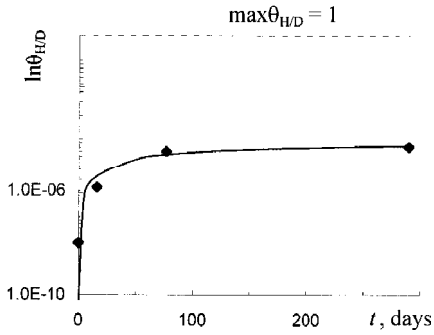


Fig. 1. PMR spectra of solid phase after air-curing of the "$Ca(OD)_2$ — H_2O" system at normal conditions within: *a* — 16, *b* — 77, *c* — 290 days; *d* — the PMR spectrum of $Ca(OH)_2$. There is shown the signal decomposition into the signal of insulated protons (the dashed curve), the signal of adsorbed water molecules (the hatching curve) and the doublet line (the dotted curve). In Fig. 1, *b*, *c* the signal decompositions for the left-hand signal sides are shown, for the right-hand — they are similar (see *d*). *1* — isolated OH_{str}; *2* — $(OH)_2$-structure, *3* — adsorbed H_2O

Fig. 2. The isotope exchange degree $\Theta_{H/D}$ in the solid phase in the "$Ca(OD)_2$ — H_2O — air" system at normal conditions versus the time (rhombs). The curve is plotted by equation (1), in which the *N* values had been calculated by equation (16)

Experimental results. *PMR data*. Relatively isolated protons are responsible for the narrow line with $\Delta B \approx 0.27$ mT wide in the PMR spectrum of the initial $Ca(OD)_2$ phase [28] (Fig. 1, *a*). This fact shows that there was a small amount of light hydrogen isotope in the initial structure which could be represent as $Ca(OD_{1-x}H_x)_2$. The same spectrum was observed during the 16 days contact of $Ca(OD)_2$ with H_2O (Fig. 1, *a*). After more long contact there appeared another, more wide, component with $\Delta B = 1$ mT wide in the PMR spectrum of the solid phase (Fig. 1, *b*, *c*). The form and the wide of component (Fig. 1, *b*, *c*) were practically the same as for the $Ca(OH)_2$ reference (Fig. 1, *d*).

PMR spectra of simple hydroxides, including $Ca(OH)_2$ are like in many respects that is due to their similar structures [1]. The PMR spectrum of $Ca(OH)_2$ demonstrates the wide doublet line with $\Delta B = 1$ mT wide caused by interdependence of protons of OH-groups of neighbouring layers located closely to one another, and the relatively narrow line with $\Delta B \approx 0.11$ mT wide, caused by a small amount of adsorbed water (Fig. 1, *d*) [1]. Correspondingly, the doublet lines appeared in the PMR spectrum of the solid phase in the studied system (Fig. 1, *b*, *c*) are indicative of the bulk $Ca(OH)_2$ phase presence in $Ca(OD)_2$.

IR-spectroscopy data. The stretching O-D-vibration band (2695 cm^{-1}) intensities in the solid phase IR spectra have decreased according to the amount of appeared structural OH-groups (by PMR spectra).

Thereby, it follows from obtained PMR and IR-spectroscopy data that during long air-curing of the experimental system the partial isotopic exchange takes place in the solid phase. By PMR data there were approximately 93 % $Ca(OD)_2$, 6 — $Ca(OH)_2$ and 0.7 Ca(OD)(OH) in the solid phase after 290 days air-curing of the "$Ca(OD)_2$ — H_2O" system.

The isotope exchange kinetics in the "$Ca(OD)_2$ — H_2O" system was studied by changes of the PMR band integral intensities due to relatively isolated OH-groups and the bulk $Ca(OH)_2$ phase. Fig. 2 shows the isotopic exchange degree in the solid phase as a function of the time period of the experimental system air-curing

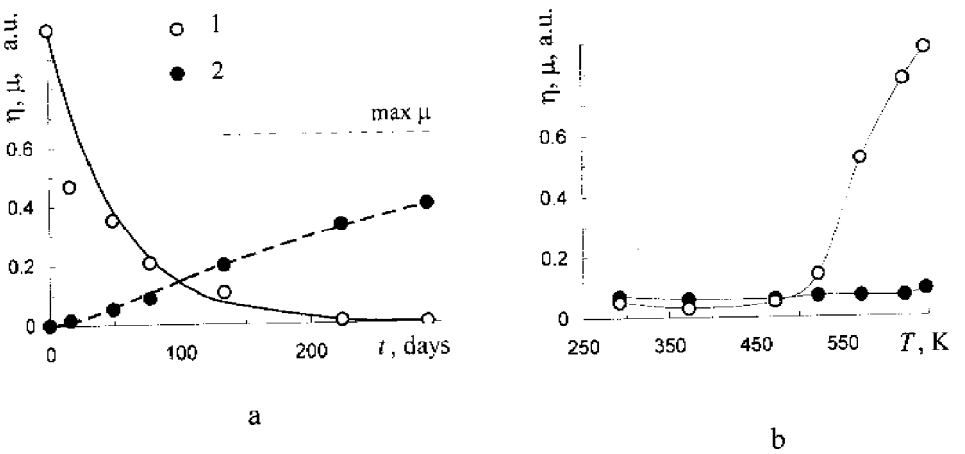


Fig. 3. The relative part of Mn^{2+} ions in the hydroxide (open circles) and the carbonate (closed circles) phases by EPR data: *a* — versus the time of $Ca(OD)_2$ contacting with H_2O at normal conditions, *b* — versus the temperature of 15 minute annealing of the solid phase after 77 days air-curing of the experimental system. The solid curve is plotted by equation (3), the hatching curve — by equation (10) in Fig. 3, *a*. *1* —η – Mn^{2+} in $Ca(OH)_2$, *2* —μ – Mn^{2+} in $CaCO_3$

$$\theta_{H/D} = \frac{\varphi_{H/D}}{\varphi^0_{H/D}} = \frac{(X_H/X_D)^{str}}{(X_H/X_D)^{sol}} \cdot \frac{1}{\varphi^0_{H/D}} = \frac{N/(N^1_D - N)}{(N^0_H - N)/(N^0_D + N)} \cdot \frac{1}{\varphi^0_{H/D}} \quad (1)$$

where $\varphi_{H/D}$ is the partition coefficient, X — the relative part of protium (H) or deuterium (D) atoms in the total amount of hydrogen isotopes, the superscripts designates: "str" — the solid and "sol" — the solution, N is the amount of structural OH-groups in the solid phase, $N_D^1 = N_D^{str}(t = 0)$ — the amount of structural OD-groups in the solid phase remained after solution $Ca(OD)_2$-saturating, N_H^0 — the amount of H atoms in the initial water, N_D^0 — the amount of D atoms came into the water during solution $Ca(OD)_2$-saturating, $\varphi_{H/D}^0 = \varphi_{H/D}(t = \infty)$ — the distribution coefficient. The distribution coefficient was evaluated as $\varphi_{H/D}^0 = (\varphi_{D/H}^0)^{-1}$, where $\varphi_{D/H}^0 = 0.94$ is the distribution coefficient for the "kaolinite — water" system [13].

EPR data. The EPR signal caused by Mn^{2+} ions in a carbonate phase [10] was appeared in the solid phase EPR spectrum after the experimental system air-curing. This band intensity has increased, in the same time the intensity of the band caused by Mn^{2+} ions in the hydroxide phase has fallen practically to zero during long air-curing of the studied system (Fig. 3, *a*). The solid phase air-heating to 375 °C resulted to restore to the initial value of the intensity of the EPR band caused by Mn^{2+} ions in a hydroxide phase, in the same time the intensity of the EPR band caused by Mn^{2+} ions in a carbonate phase did not change (Fig. 3, *b*).

As it was mentioned above, the hydroxide structure amount was not less 99 % of the solid phase mass even after the 290 days experiment. So, decreasing of the intensity of the EPR band due to Mn^{2+} ions in a hydroxide phase can be explained by oxidizing of Mn^{2+} ions, since Mn^{3+} ions do not show themselves in an EPR spectrum [10].

Thereby, during long air-curing of the "$Ca(OD)_2$ — H_2O" system at normal conditions there occurs simultaneously some processes in the solid phase: the H → D isotope exchange with structural OD-groups, formation of a some quantity of carbonate phase and oxidation of Mn^{2+} to Mn^{3+} ions in the hydroxide phase.

Discussion. The following processes can be supposed to take place in different parts of the experimental system.

Solution. 0.0299 g from 2 g $Ca(OD)_2$ has been dissolved in 50 ml water to form the $Ca(OD)_2$-saturated solution (presuming, that $Ca(OH)_2$ and $Ca(OD)_2$ solubilities are the same [2] and equal $pK_{sb} = 5.19$). Thus, the mole part of D atoms came into the solution is equal $\approx 3.1 \cdot 10^{-4}$, and the affect of such isotope amount on rate processes in the solution [2] and a difference of evaluation of molality and a molarity can be neglected.

The experimental system was contacted with the atmosphere and, as a result of CO_2 presence in it, the solution pH was slightly less, than calculated from the pK_{sb} value (pH ~ 12.44 if $Ca(OD)_2$ would be dissolved in deionized water in a closed vessel, taking into account the ionic strength and relevant Ca^{2+}- and OH^--ion activities in the solution) [12]. Thus, there can precipitate $CaCO_3$ (pK_{sb} = 8.34 [12]) in this solution during long air-curing of the experimental system.

Solid phase. The all sp^3-hybrid orbitals of O^{2-} ions in brucite-like hydroxides form bonds. Therefore, at room temperatures hydrogen isotopes move in such structures, including the $Ca(OD)_2$ structure in the experimental system, most probably, by the mechanism of "slow proton" transfer (an O^{2-} state displacement through a crystal): an O^{2-} ion located in an OD(OH)-group site takes an $D^+(H^+)$ ion from the nearest OD(OH)-group, this process activation energy is about 0.65 eV for proton transfer in $Ca(OH)_2$ structure [16].

Mn^{2+} ions can be oxidized when D^+ ions diffuse from the solid into the solution

$$Mn^{2+} + D^+ \underset{25\,^\circ C,\, H_2O}{\overset{k_0}{\rightarrow}} Mn^{3+} + D^0 \uparrow . \tag{2}$$

It follows from this scheme, that the amount of Mn^{2+} ions in a hydroxide phase, taking into account theirs disappearances as a result of oxidation, can be found as (Fig. 3, *a*, the solid curve)

$$\eta = \eta^0 e^{-k_0 t} , \tag{3}$$

where $\eta = M/M_{max}$, M — the amount of Mn^{2+} ions in the hydroxide phase, M_{max} = max M — the total amount of Mn atoms in the hydroxide phase ($M_{max} \approx$ const, since the hydroxide phase amount has not been less 99 % after the 290 days experiment), $\eta^0 = \eta\ (t = 0) \approx 1$, k_0 is the oxidation rate.

Heating to dehydroxylation beginning temperatures results to the reverse process of reduction of Mn^{3+} ions in the hydroxide phase (Fig. 3, *b*). A small quantity of H atoms had been found to appear when structural OH-groups had been destroyed in hydroxides [3]. Most likely, the similar processes took place when the solid phase from the experimental system was heating, that can explain disappearance of Mn^{3+} ions in the hydroxide phase

$$Mn^{3+} + D^0(H^0) \overset{375\,^\circ C}{\rightarrow} Mn^{2+} + D^+(H^+) . \tag{4}$$

Solid phase surface. Considering processes on surfaces, the solution volume was supposed to be large, as the amount of D atoms in 2 g $Ca(OD)_2$ ($\approx 5.26 \cdot 10^{-2}$ mole) was many fewer than the amount of H atoms in 50 ml water ($\approx$ 5.56 mole).

Structures of an adsorbed water layer and a superficial structural layer differs on basal and lateral surfaces of structures, similar to $Ca(OH)_2$ [11, 15]. Correspondingly, processes, occurring on these surfaces in water, are most probably to have specific peculiarities. Thereby, considering possible processes on the solid phase surface in the experimental system, all variables and constants (except *m* — the solid mass) were believed to be different for lateral or basal surfaces.

The light hydrogen isotope accumulation in the solid phase has been established to very slow down with time, not peaked (Fig. 2). This was surmised to be caused by decrease of an amount of structural OD-groups on the surface as a result of the carbonate phase formation and poor permeability of such structure for $D^+(H^+)$ ions.

The carbonate phase formation. As it was mentioned, carbonate can forms inner-sphere complexes with solid phase surface in water solution in some "(hydro)oxide — water — air" systems [11, 17]. In particular, ATR-FTIR study *in situ* has shown that inner-sphere monodentate complexed CO_3^{2-}-surface species only are present on the Al-OH-surface in water solution at pH $\leq$ pH_{pzc} (the zero charge point), and the carbonate speciation and

coordination do not change as a result of air-drying of the sample by DRIFT spectra [17][1].

The pH_{pzc} value equals to the pH of a hydroxide-saturated solution in deionized water [11]. The pH value of such solution is somewhat less, when atmospheric CO_2 is present [12]. Thereby, as $pH \leq pH_{pzc}$ in the "$Ca(OD)_2$ — H_2O" system at normal conditions, than hydroxyls on the solid phase surface in this system will be basic [11, 15, 17]. In this case CO_3^{2-} anions could bind with the solid phase surface immediately in water in the experimental system.

The obtained EPR data on Mn^{2+} ions appeared in $CaCO_3$ structure in the solid phase in the experimental system (Fig. 3, *a*) confirm this. As it is known, oxygen molecules dissolved in water quickly oxidize Mn^{2+} to Mn^{3+} ions [11], which are not detected in EPR spectra [10]. Hence, Mn^{2+} ions in $CaCO_3$ structure formed directly on the surface only and not precipitated can be responsible for this EPR spectrum. Besides, the $H \rightarrow D$ isotope exchange in the solid phase was substantially slowed down with a time (Fig. 2). So, taking into account mentioned data [17], it seemed more probable that inner-sphere bidentate complexed CO_3^{2-}-surface species forms (do not precipitate) immediately in water, though EPR spectra were recorded after a sample air-drying.

Thereby, by EPR data obtained in the present work, $CaCO_3$ structure forms on the solid phase surface in the experimental system, most probably, immediately in water.

It must be noted that, the $CaCO_3$ structure on Ca-OD(OH)-surface is, at least, the continuous layer of the inner-sphere complexed CO_3^{2-}-anions bound to two Ca^{2+} cations, unlike the Al-OH surface [17]. This can be explained by differences in $Al(OH)_3$ and $Ca(OH)_2$ structures, and, accordingly, in process mechanisms on these surfaces. An OH-group oxygen ion on the Al-OH surface has one vacant sp^3-hybrid orbital, what explains occurring of typical chemical reactions on this surface in water solution — in particular, the CO_3^{2-}-ion monodentante complex formation on the surface and the protonization of the OH-group nearest to such complex [17]. Unlike $Al(OH)_3$-surface, all sp^3-hybrid orbitals of an OH-group oxygen ion on the basal $Ca(OH)_2$-surface form structural bonds, what affects essentially on this surface reaction ability [11, 15]. There appear vacant sp^3-hybrid orbitals of OH-group oxygen ions on the lateral $Ca(OH)_2$-surface as a result of break-up of structural bonds, what essentially improves this surface reaction ability [11, 15]. Thereby, as it was mentioned above, the processes on the basal and the lateral surfaces of $Ca(OH)_2$ occurring in water, are most probably to have specific peculiarities and to differ from the Al-OH-surface. The further researches need to establish the mechanism of carbonate phase formation on the solid surface in the experimental system.

At the same time, not making clear each stage mechanism details and supposing, that HCO_3^--anions migrate enough quickly in the adsorbed water layer [17] and do not affect on the of carbonate complex forming rate on the surface, this process can be present by the following scheme

$$\left|\begin{matrix} -\,O^iH \\ -\,O^iH \end{matrix}\right. + {}^iHCO_3^- \ (N_1) \xrightarrow{k_1} \left|\begin{matrix} -\,O^iH \\ -\,O\text{-}\ CO\text{-}\ O^- \end{matrix}\right. + O^iH^- + {}^iH^+ \ (N_2) \xrightarrow{k_2} \left|\begin{matrix} -\,O \diagdown \\ -\,O \diagup \end{matrix}\right. CO + O^iH^- \quad (N_3) \qquad (5)$$

where ${}^iH$ designates any hydrogen isotope — ${}^1H$ and ${}^2H$, k_1 and k_2 are the rate constants of the first and the second stages, respectively (c^{-1}), $k_1 = k \bullet [HCO_3^-]$, the first stage mechanism dictates the k constant value ($M^{-1} \bullet c^{-1}$), $[HCO_3^-] \approx$ const is the HCO_3^- concentration in bulk water, this value is depend on the solution pH (pH $\approx$ const) and the concentration of CO_2 dissolved in water when the CO_2 content in the air is constant (0.03 %) [12].

It follows from the scheme (5), neglecting the inverse reactions and inferring, that processes on the neighboring elementary surface segments are independent, the carbonate phase formed on the *j*-th (lateral or basal) Ca-O^iH-surfaces can be found from the following system of equations

$$\begin{cases} dx/dt = -k_1 \cdot x, \\ dy/dt = k_1 \cdot x - k_2 \cdot y, \\ dz/dt = -k_2 \cdot y, \end{cases} \qquad (6)$$

[1]The γ-Al_2O_3 surface layer transforms in water to $Al(OH)_3$ phase like to the bayerite (with the brucite-like package of elementary layers) [17].

where $x = N_1/(Smn)$, $y = N_2/(Smn)$ and $z = N_3/(Smn)$ are relative parts of N_1, N_2 and N_3 segments on the j-th surface, respectively, N_1 is the amount of the binding centres (^{i}HO — Ca^{2+} — O^{i}H elementary segments), N_2 — the amount of the elementary segments with the immediate structure, N_3 — the amount of the elementary segments with inner-sphere bidentate complexed CO_3^{2-}-surface species ($CaCO_3$ structure), n — the surface concentration of the elementary segments (containing one Ca^{2+} (Mn^{2+}) cation), S — the j-surface specific area, j = lateral or basal, m — the solid phase mass.

Solving this system at $y^0 = 0$ and $z^0 = 0$ the relative part of the elementary surface segments occupied by the carbonate phase on the j-th surface can be found

$$z = x^0 + \frac{x^0}{k_1 - k_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right), \tag{7}$$

where $x^0 = x\ (t = 0)$, $y^0 = y\ (t = 0) = 0$, $z^0 = z\ (t = 0) = 0$.

In this case the j-th surface area, where the isotope exchange occurs, can be found as follows, taking into account its decrease with a time as a result of the carbonate phase formation

$$S = S^0(1 - z), \tag{8}$$

where S^0 is the j-th surface initial specific area, j = lateral or basal.

As it was mentioned, only Mn^{2+} ions located in the carbonate phase, formed immediately on the surface, most probably, in water during the experimental system air-curing, could be responsible for the signals in EPR spectra. So, it can be supposed that obtained data on Mn^{2+} ion appearance in the carbonate phase are represented of the kinetics of this phase formation on the surface, at least, during the initial stage (Fig. 3, *a*). During longer air-curing of the experimental system (more than 150 days) the intensity growth of the EPR signal of Mn^{2+} ions in the carbonate phase decelerates (Fig. 3, *a*). This is, most probably, caused by decrease of an amount of Mn^{2+} ions in the superficial structural layer of the hydroxide phase due to oxidation.

It was supposed, that this oxidation occurs by the scheme (2), similar to the bulk structure, but with the k_0^s rate, and, at the same time, Mn^{2+} ions in the elementary segments with the intermediate structure do not oxidize (see the scheme (5)). Then the appearance of Mn^{2+} ions in the carbonate phase on the j-th surface can be described by the system of equations (6), in which variables of x, y and z are changed to ξ, χ and ζ, respectively[2], and the term of "$-k_0^s\xi$" is added in the first equation to take into account of Mn^{2+} ions disappeared as a result of oxidation. Such system can be solved similarly to the system (6), then the relative part of Mn^{2+} ions in the carbonate phase on the j-th surface will be equal to

$$\zeta = \xi^0 k_1 + \frac{\xi^0 k_1}{q - k_2}\left(k_2 e^{-qt} - q e^{-k_2 t}\right), \tag{9}$$

where $\xi^0 = \xi\ (t = 0)$ is the relative part of Mn^{2+} ions in the hydroxide phase on the j-th surface at $t = 0$, $\xi^0 \cong x^0$, $q = k_1 + k_0^s$, j = lateral or basal.

Thus, the accumulation of Mn^{2+} ions in the carbonate phase on the j-th surface of the solid phase in the experimental system can be found as

$$\mu = \frac{M_c}{M^{surf}} = \frac{\sum_j M_c^j}{M^{surf}} = \sum_j \frac{M^j}{M^{surf}}\zeta^j = \sum_j \mu^j \zeta^j, \tag{10}$$

where M_c is the amount of Mn^{2+} ions in the carbonate phase on the j-th surface, M^{surf} — the total amount of Mn atoms in the superficial structural layer, $\mu^j = M^j/M^{surf}$ — the relative part of Mn atoms in the superficial structural layer on the j-th surface, ζ^j is determined by equation (9)

[2] ξ— the relative part of the binding centres (the elementary segments ^{i}HO — Mn^{2+} — O^{i}H) on the j-th surface, χ — the relative part of the elementary segments with the intermediate structure on the j-th surface, ζ — the relative part of the elementary segments with $MnCO_3$ structure on the j-th surface, n_{Mn} — the surface concentration of the elementary segments, containing one Mn^{2+} cation, on the j-th surface, S and m — as for the system (6).

with the relevant constants for the j-th surface, j = lateral or basal.

The constants of k_0^s, k_1 and k_2 (Table) for the basal and the lateral Ca-O^{i}H-surfaces have been determined by experimental data fitting by this equation (Fig. 3, *b*, the hatching curve).

T h e i s o t o p e e x c h a n g e. Structural OD-groups located on crystallite surfaces, first of all, will be participate in the H → D isotope exchange between the solution and the solid phase (Figs. 1, 2). This isotope exchange on the j-th Ca-OD-surface in the experimental system can be present schematically as follows, taking into account that H_2O molecules were in a large excess in the bulk water and in the water layer adsorbed on the surface

$$|\text{-OD}_{str} + \text{H}_2\text{O}_{ads} \xrightarrow{h} |\text{-OH}_{str} + \text{HDO}_{ads}, \tag{11}$$

where $h = k_i n_s S m$, k_i is the isotope exchange rate constant, n_s — the surface concentration of OD_{str}-groups, j = lateral, basal.

It follows from this scheme that the isotope H accumulation in structural OD-groups on the j-th surface during a short air-curing of the experimental system can be approximately described as

$$\frac{d\rho}{dt} = h(1-\rho) \tag{12}$$

whence

$$\rho = 1 - \left(1 - \rho^0\right) e^{-ht}, \tag{13}$$

where $\rho = N/(Smn_0)$, N is the amount of H atoms substituted for D atoms in structural OD-groups on the j-th surface, $n_0 = 2n$ — the surface concentration of structural O^{i}H-groups on the j-th surface (one elementary surface segment contains two structural O^{i}H-groups), j = lateral or basal.

For a long air-curing of the experimental system it needs to take into account the disappearance of structural OD-groups on the solid surface as a result of the carbonate phase formation. Then the H isotope amount in the superficial structural hydroxyl groups on the j-th surface can be found as

$$N = \rho S n_0 m, \tag{14}$$

where S is determined by equation (8), j = lateral or basal.

As it was mentioned, the three-dimensional $Ca(OH)_2$ phase formation in the solid phase (Fig. 1) can be explained by the H isotope diffusion into the $Ca(OD)_2$ structure. Hydrogen isotopes can be supposed to diffuse along the plane of elementary layer surfaces in $Ca(O^iH)_2$ much more rapidly, than in the perpendicular direction, like that, as in brucite [13]. In this case the hydrogen isotope flows through the lateral surfaces only should be considered. Then, taking into accoun the decrease of the lateral surface area, through which H^+ ions diffuse into the

The constants, characterizing processes on the surface and in the bulk of the solid phase in the "$Ca(OD)_2$ — H_2O" system at normal conditions

Constants		Surface		Scheme	Equation	Note
		Basal	Lateral			
k_0^s	c^{-1}	$1.18\cdot10^{-7}$	$1.39\cdot10^{-7}$	(2)	(10)	
k_1	c^{-1}	$4.12\cdot10^{-7}$	$8.981\cdot10^{-7}$	(5)	(10)	
k	$M^{-1}\cdot c^{-1}$	0.609	1.33	(5)	(10)	$[HCO_3^-] = 6.76\cdot10^{-7}$ M pH ~ 11.5
k_2	c^{-1}	$3.13\cdot10^{-8}$	$2.22\cdot10^{-8}$	(5)	(10)	
h	c^{-1}	$3.17\cdot10^{-7}$	$4.64\cdot10^{-7}$	(11)	(13)	
k_i	$(mol\cdot m^{-2}\cdot c)^{-1}$	$6.06\cdot10^{-4}$	$1.42\cdot10^{-2}$	(11)	(13)	
n_s	$mol\cdot m^{-2}$	$2.99\cdot10^{-5}$	$3.79\cdot10^{-5}$			[17]
ρ^0		$1\cdot10^{-5}$	$1\cdot10^{-5}$	(11)	(13)	
		Bulk structure				
k_0	c^{-1}	$2.24\cdot10^{-7}$		(2)	(3)	
D_0	$m^2\cdot c^{-1}$	$4.05\cdot10^{-23}$			(15)	

$Ca(OD)_2$ structure, the H isotope accumulation in the bulk solid phase can be approximately described as [6]

$$N^{volume} = \int_0^t JmS^j d\tau \approx \frac{\rho n_0}{\delta}\left(\frac{D_0}{\pi}\right)^{1/2} mS_0^j \int_0^t \frac{1 - z^j(\tau)}{\tau^{1/2}} d\tau \approx \frac{\rho n_0}{\delta}\left(\frac{D_0}{\pi}\right)^{1/2} mS_0^j f(t), \qquad (15)$$

where j = lateral, $J \approx [OH]^j(D_0/\pi t)^{1/2} = (\rho n_0/\delta)^j(D_0/\pi t)^{1/2}$ is the H isotope flow through the lateral crystallite surface, [OH] — the surface concentration of H atoms in the superficial structural layer, δ — this layer thickness, D_0 — the isotope H diffusion coefficient into the solid phase, $S^{lateral}$ is determined by equation (8).

The total amount of H isotope in the solid phase will be equal

$$N = N^{volume} + N^{lateral} + N^{basal} = N^{volume} + m\sum_j \rho^j S^j n_0^j, \qquad (16)$$

where N^{volume} is determined by equation (15), N^{basal} and $N^{lateral}$ — by equation (14) with the relevant constants for the j-th surface, j = lateral or basal.

To calculate the integral in equation (15), the $z^{lateral}(\tau)$ function has been fitted by the 3rd degree polynom (with validity 0.9999), using obtained above rate constants of the carbonate phase formation on the lateral surface (Table).

The experimental data were fitted by equation (1), in which the N value was calculated by equation (16) (Fig. 2, the solid curve). The values of ρ^0, h and D_0 (Table) were used as fitting parameters.

Thus, using described above the scheme of processes in the experimental system, the rate constants of the H → D isotope exchange and the carbonate phase formation on the basal and the lateral surfaces of crystallites and the rate constants of Mn^{2+} ion oxidation on the surface and in the bulk structure of $Ca(OD)_2$ were calculated (Table).

It should be noted, that obtained values of the rate constants of the isotope exchange and the first stage of the carbonate phase formation on the lateral $Ca(O^iH)_2$-surface are much more, than on the basal surface (Table). This is indicated, that the reaction ability of O^iH-groups on the lateral $Ca(O^iH)_2$-surface, as it would be expected [15], was much higher, as on the basal surface. However, the rate constant of the second stage of the carbonate phase formation is several more on the basal surface (Table), that can be explained by the larger concentration of O^iH-groups here and, consequently, higher probability of the second stage happening (the scheme (5)).

It should be mentioned that the rate constant of the H → D isotope exchange even on the lateral Ca-OD-surface (where O^{2-} ions have vacant orbitals) are essentially lower (Table), than obtained earlier data on the T → H isotope exchange on Al-OH-surface of kaolinite — $k_i = 6.54 \cdot 10^4$ (mol•c)$^{-1}$ (taking into account the total surface area of investigated sample and the ratio of $\varphi^0_{D/H} \cdot [T]/[H] = 1.33 \cdot 10^{-11}$ in solution) [9]. It can be due to acceleration of isotope exchange in similar system under weak β-irradiation (caused by radioactive tritium decay), similar to γ-irradiation [9]. Beside that, the more stronger binding of a D^+ ion in a D-O-Ca-group can be signify (the Al electronegativity is about in 1.5 time higher than Ca that results to the larger displacement of an electron density to an Al ion in a Al-O-H-group and, consequently, to O-H-bond weakening).

The activation energy of proton moving in $Ca(OD)_2$ structure calculated by the D_0 value (Table), U_a = 0.97 eV, is the same order, as the slow proton transfer activation energy in the $Ca(OH)_2$ structure, U_a = 0.65 eV [16]. The value of U_a obtained in the present work has been determined for deutereted portlandite analogue, $Ca(OD)_2$, that can explain its somewhat higher value.

At the same time this U_a value is slightly lower, than the activation energy of proton diffusion along elementary layer surfaces in kaolinite structure at normal conditions, 1.2 eV [9]. This can be caused the faster diffusion of hydrogen isotopes along the elementary layer surfaces in structures

of $Ca(OH)_2$ and $Ca(OD)_2$, than in kaolinite structure, in so far as the concentration of OH-groups in the kaolinite interlayer space is less.

The activation energy of proton diffusion along the elementary layer surfaces in $Mg(OH)_2$ structure at 500 °C is somewhat higher — U_a = 1.5 eV [9]. But a proton may move in hydroxide structure at such temperature by the other mechanism — there can appear fast protons split out from OH-groups, the activation energy is $U_a \approx$ 2 eV for $Mg(OH)_2$ structure [16].

Conclusions. 1. It has been established, that the intermediate Ca(OH)(OD) phase formed at first and the three-dimensional $Ca(OH)_2$ phase (about 5 %) appeared in the solid phase after 50 days air-curing of the "$Ca(OD)_2$ — H_2O" system at normal conditions.

2. It was shown, that the essential deceleration of the isotope exchange in the "$Ca(OD)_2$ — H_2O" system at normal conditions with time can be explained by the carbonate phase formation on the solid phase surface.

3. The scheme of possible processes has been considered. The isotope exchange rate constants in the superficial structural OD-groups and the carbonate phase formation on the solid phase surface in the "$Ca(OD)_2$ — H_2O" system at normal conditions have been evaluated.

Acknowledgements

This study was supported by the INTAS-01-2166 Project.

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Received 10.11.2003

РЕЗЮМЕ. Методами ПМР, ИКС и ЭПР исследован обмен изотопов водорода при нормальных условиях в системе "$Ca(OD)_2$ – H_2O" с отношением компонентов 1 : 25. Установлено, что в такой системе состав твердой фазы сначала изменяется до $Ca(OD_{1-x}H_x)_2$. Через 50 суток появляется объемная фаза $Ca(OH)_2$ (~ 5 %), что объясняется диффузией протия вглубь структуры твердой фазы через боковую поверхность. В дальнейшем обмен замедляется, и через 290 суток количество фазы $Ca(OH)_2$ составляет около 6 %. Установлено, что при этом происходит окисление ионов Mn^{2+} в гидроксидной фазе до Mn^{3+} (фазы $Ca(OD)_2$ и $Ca(OH)_2$ при этом неразличимы). Замедление изотопного обмена со временем объясняется образованием карбонатной фазы непосредственно на поверхности твердого вещества помимо осаждения $CaCO_3$. Рассмотрена схема возможных процессов в исследованной системе. Экспериментальные данные были аппроксимированы уравнениями, полученными в рамках этой схемы. По полученным данным, значения константы скорости изотопного обмена в поверхностных структурных OD-группах составляют $6{,}06 \cdot 10^{-4}/1{,}42 \cdot 10^{-2}$ (моль•м$^{-2}$•с)$^{-1}$ на базальной/боковой поверхности соответственно. Предположено, что карбонатная фаза на поверхности формируется так: образование прикрепленных к поверхности монодентантных карбонатных комплексов (в результате реакции обмена лигандов $HCO_3^- \rightarrow$ OD(OH)-группы на поверхности с $k \sim 0{,}61/1{,}33$ М$^{-1}$•с$^{-1}$ при pH ~ 11,5), которые затем взаимодействуют с ближайшими поверхностными структурными OD(OH)-группами (с $k_2 \sim$ $\sim 3{,}2 \cdot 10^{-8}/2{,}2 \cdot 10^{-8}$• с$^{-1}$), в результате чего формируются бидентантные карбонатные комплексы. Ионы Mn^{2+} в гидроксидной структуре окисляются с $k_0 \sim 2{,}24 \cdot 10^{-7}$• с$^{-1}$. Диффузия ионов дейтерия вдоль межслоевого пространства в структуре $Ca(OD)_2$ происходит с $D_0 \sim 4 \cdot 10^{-23}$ м^2•с$^{-1}$.

РЕЗЮМЕ. Методами ПМР, ІЧС і ЕПР було досліджено обмін ізотопів водню за нормальних умов у системі "$Ca(OD)_2$ — H_2O" зі співвідношенням компонентів 1 : 25. Встановлено, що спочатку утворюється фаза $Ca(OD_{1-x}H_x)_2$, а через 50 діб з'являється і об'ємна фаза $Ca(OH)_2$ (~ 5 %), що пов'язується з дифузією протію вглиб структури $Ca(OD)_2$ через бокову поверхню. Пізніше обмін уповільнюється, і через 290 діб кількість фази $Ca(OH)_2$ становить близько 6 %. Встановлено, що при цьому відбувається окислення іонів Mn^{2+} у гідроксидній фазі до Mn^{3+} (фази $Ca(OD)_2$ и $Ca(OH)_2$ при цьому не розрізняються). Одночасно утворюється карбонатна фаза. Уповільнення ізотопного обміну з часом пояснюється утворенням карбонатної фази на поверхні твердої фази окрім випадіння осадку $CaCO_3$. Розглянуто можливу схему процесів, що відбувались у дослідженій системі. Експериментальні дані були апроксимовані рівняннями, одержаними в рамках цієї схеми. За отриманих даних значення константи швидкості ізотопного обміну в поверхневих структурних OD-групах складають $6{,}06 \cdot 10^{-4}/1{,}42 \cdot 10^{-2}$ (моль•м$^{-2}$•с)$^{-1}$ на базальній/боковій поверхні відповідно. Припущено, що карбонатна фаза на поверхні формується наступним чином: утворення прикріплених до поверхні монодентантних карбонатних комплексів (в результаті реакції обміну лігандів $HCO_3^- \rightarrow$ OD(OH)-групи на поверхні з $k \sim 0{,}61/1{,}33$ М$^{-1}$•с$^{-1}$ при pH ~ 11,5), які потім взаємодіють з найближчими поверхневими структурними OD(OH)-групами (з $k_2 \sim 3{,}2 \cdot 10^{-8}/2{,}2 \cdot 10^{-8}$•с$^{-1}$), внаслідок чого формуються бідентантні карбонатні комплекси. Іони Mn^{2+} в гідроксидній структурі окислюються з $k_0 \sim 2{,}24 \cdot 10^{-7}$• с$^{-1}$. Дифузія іонів дейтерію вздовж міжшарового простору в структурі $Ca(OD)_2$ відбувається з $D_0 \sim 4 \cdot 10^{-23}$ м^2•с$^{-1}$.