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The Chemistry of the Surfaces of the Acid Forms of Natural Layer Silicates

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Modern ideas about the nature of the exchangeable acidity of a group of layer silicates (clay minerals) are described and the results obtained during the last decade with the aid of physical and physicochemical techniques are surveyed. The dependence of the surface acidity on non-stoichiometric substitutions in the structure of the minerals, the influence of a number of factors on the spontaneous conversion of the H-forms of the silicates into Al-Fe-Mg-forms, the mechanism of this phenomenon, the ion-exchange properties and the thermal stabilities of the H- and Al-Fe-Mg-forms, and other problems are examined.
The bibliography includes 80 references.

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I. INTRODUCTION

Natural silicates (clay minerals) have acquired considerable importance recently in scientific research and in practice[1-11]. The amounts of these minerals available in the USSR are enormous and many of their physicochemical properties permit their successful use as substitutes for expensive and scarce synthetic materials. For a more effective and purposeful utilisation of layer minerals in industry, it is necessary to have at ones disposal reliable information both about the chemistry of their surfaces and about methods for their modification. The present review deals with modern ideas about the nature of the exchangeable acidities† of the acid forms of clay minerals. The solution of this problem opens considerable prospects for the application of the above forms as catalysts, stationary phases in gas-adsorption chromatography, fillers of polymeric media, etc. The elucidation of the nature of the exchangeable acidity of clay minerals is important for geochemistry and soil science, since it promotes a correct understanding of the processes involved in the genesis of minerals and soils and also for the development and justification of practical measures undertaken to improve the fertility of acid soils.

II. NON-STOICHIOMETRIC SUBSTITUTIONS IN THE STRUCTURE AND THE NATURE OF THE EXCHANGEABLE ACIDITY

In the study of the nature of clay minerals and of the chemical stability of their hydrogen-forms, one must take into account the crystal structures of these aluminosilicates and the causes, associated with the latter, which are responsible for the cation exchange in which such substances are involved. For this purpose, it is necessary to develop new, more accurate methods for the determination of the non-stoichiometric isomorphous substitutions or other defects in the lattices of the minerals, which cause them to behave as ion exchangers.

Table 1. The influence of the heat treatment of the Li-forms of layer silicates on their capacity (μequiv.g^{-1}) (duration of heat treatment of specimens 1.5 h).

Mineral	25° C	100° C	200° C	300° C	400° C	500° C	Isomorphism, %	
							in octahedra	in tetrahedra
Pyzhevskii [Pyzhev?] montmorillonite	1130	1050	40	34	10	0	97.0	0.0
Gorbskii [Gorbi?] beidellite	410	410	410	408	400	395	0.0	100.0
Kovdorskii [Kovd?] vermiculite	1420	1420	1420	1420	1420	1420	0.0	100.0
Bug region nontronite	980	965	202	202	202	190	79.0	21.0
Glukhov kaolinite	250	242	34	34	46	48	86.0	12.0
Cherkassy palygorskite	150	150	120	80	208	210	47.0	53.0

A method based on the different types of behaviour of the exchangeable Li^+ ions on heating layer minerals at 200 to 300°C for 1-1.5 h has been proposed[12] (Table 1). It follows from the data in the Table that, when the non-stoichiometric isomorphous substitutions in minerals with a dioctahedral structure are located in the octahedral network, then Li^+ ions migrate under the influence of temperature to the vacant sites of the silicate[13] or into the interstices[14]. The excess negative charge of the layer is neutralised and the mineral loses its capacity for ion exchange. When the non-stoichiometric substitutions are located in the tetrahedral network, the Li-form fully retains its ion-exchange properties after heating. The above observation holds also in the presence of isomorphous substitutions in both tetrahedral and octahedral networks.

†This implies H^+, Al^{3+}, and Fe^{3+} ions capable of being exchanged for other cations.

The influence of the positions of the non-stoichiometric substitutions in the structures of layer silicates on the nature of their exchangeable acidity was examined on the basis of the above results [15]. Pyzhevskii [Pyzhev?] montmorillonite, the Bug region nontronite, Kovdorskii [Kovd?] vermiculite (particle size < 40 μm), Gorbskii [Gorbi?] beidellite, Cherkassy palygorskite, and Glukhov kaolinite were chosen for investigation. The acid forms of the above aluminosilicates were prepared from the Na-forms by the ion-exchange method under static conditions [16]. The content and nature of the exchangeable acid ions on the surface were determined electrochemically[17,18] and also by analysing the equilibrium solution after treating the acid forms of the minerals with 0.5 *N* $BaCl_2$ solution. A detailed analysis of other methods for the investigation of the surface acidity of solids has been described by Ovcharenko and Vasil'ev [18].

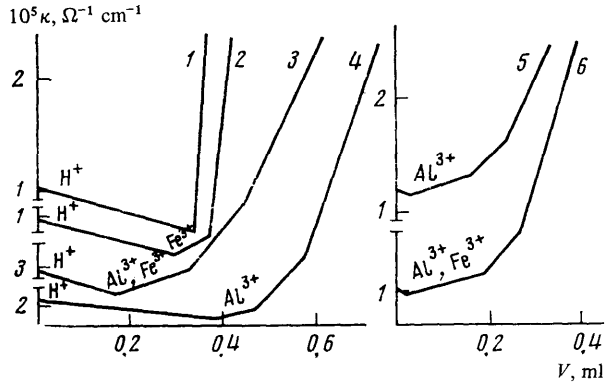


Figure 1. Curves for the conductimetric titration of acid forms of layer silicates with 0.095 *N* NaOH solution: 1) montmorillonite (0.027 g); 2) nontronite (0.037 g); 3) palygorskite (0.22 g); 4) kaolinite (0.19 g); 5) beidellite (0.041 g); 6) vermiculite (0.014 g).

Fig. 1 presents conductimetric titration curves for aqueous suspensions of freshly prepared acid forms of layer silicates. It follows from the data in the Figure that, after the complete or partial distribution of non-stoichiometric substitutions in the octahedral network (montmorillonite, nontronite, palygorskite, and kaolinite, see Table 1), the H-form of this type of mineral acquires strongly acid properties and contains on its surface freely mobile exchangeable hydrogen ions (Fig. 1, curves *1–4*). A completely different behaviour is observed in the titration of the acid forms of both vermiculite and beidellite in which non-stoichiometric isomorphous substitutions are almost completely distributed in the tetrahedral network. Their titration curves are analogous to the titration curves of a weak acid by a sodium hydroxide solution (Fig. 1, curves *5* and *6*). Analysis of a salt extract (0.5 *N* $BaCl_2$) showed that Al^{3+} ions are present on the surface of beidellite, while the vermiculite surface contains Al^{3+} and Fe^{3+} ions in approximately equal amounts. These results lead to the conclusion that, after the substitution of the exchangeable Na^+ ions of the mineral by the H^+ ions of the resin [15], the exchangeable protons immediately interact with the tetrahedra where silicon has been substituted by aluminium or tervalent iron.

According to the proposed model [15] (Fig. 2), three exchangeable protons compensate the ruptured bonds (i.e. there is a conversion of $\equiv SiO^-$ into $\equiv SiOH$ groups) and the Al^{3+} (or Fe^{3+}) ion liberated from the tetrahedron neutralises the charges of two neighbouring intact tetrahedra and one charge formed at the apex of the disrupted tetrahedron. Al^{3+} (or Fe^{3+}) ions can also compensate the charges of the intact tetrahedra located in neighbouring basal planes. The simultaneous disruption of all the defective tetrahedra is impossible owing to the deficiency of the exchangeable H^+ ions, since three protons are required to transfer Al^{3+} or Fe^{3+} ions to a site where exchange is possible.

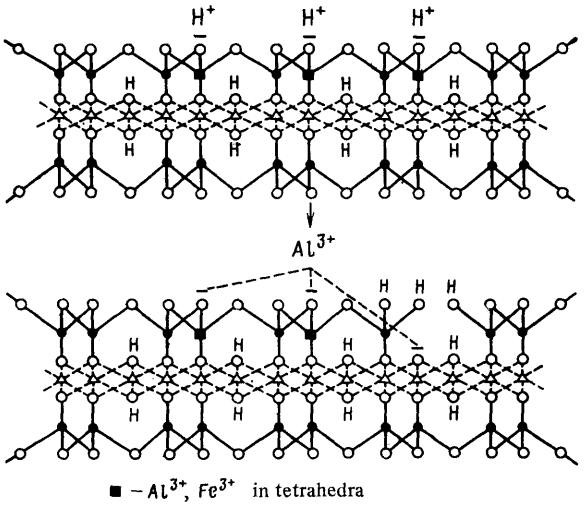


Figure 2. The disruption by exchangeable protons of the tetrahedra in which silicon has been substituted by aluminium or tervalent iron.

The transfer of the charge of the mineral from the tetrahedral to the octahedral network is confirmed by the constancy of the exchange capacities of the silicates before and after treatment with the KU-2 resin in the H-form [15,19]. Furthermore, it follows from Fig. 2 that, after the complete substitution of the exchangeable Na^+ ions of the silicate by the H^+ ions of the resin and rapid conversion of the H-form into the Al-Fe-form, one-third of the surface charge of the mineral is transferred from the tetrahedral to the octahedral network. After the conversion of Al-Fe-vermiculite into the Na-form and after the regeneration of the acid mineral, one-third of the exchange capacity should be due to the exchangeable H^+ ions. The results of these experiments are presented in Table 2, which shows that approximately one-third of the exchange capacity of vermiculite after the above operations have been carried out is indeed due to the exchangeable hydrogen ions. The H-Al-Fe-form of vermiculite obtained proved to be chemically unstable and was converted after 6 h (at 25°C) into the Al-Fe-Mg-form. The homoionic H-forms of vermiculite and beidellite could not be obtained after several (>2) treatments with the resin, since their structure was disrupted by protons [15,19].

The above considerations concerning the decomposition of defective tetrahedra by hydrogen ions have been confirmed by ESR studies [19]. The ESR spectra of the specimens were recorded in the X-range. The ESR spectrum of Kovdorskii [Kovd?] Na-vermiculite (Fig. 3, curves *1* and *2*) contains a very broad and intense band of complex shape with the absorption centre at $g \simeq 4.3$ and a relatively weak band at $g \simeq 2$. The low-field signals ($g = 4$–6) are usually assigned [20,21] to ions in the S-state (Mn^{2+}, Fe^{3+}) in a strong crystal field of low symmetry, for example in glasses. In vermiculite, the majority of Fe^{3+} ions exist in the form of isomorphous substitutions in the tetrahedral network [22].

Table 2. The exchangeable acidity of Na-vermiculite after two cycles of treatment of the mineral with the KU-2 resin in the H-form (c_{susp} = 0.6 wt.%; V_{susp} = 200 ml; V_{resin} = 200 ml).

Time of contact with resin, h	Amount of exchangeable acid ions on surface, μequiv. g^{-1}		Amount of exchangeable ions in salt extract (0.5 *N* $BaCl_2$), μequiv. g^{-1}			Total exchange capacity w.r.t. Ba^{2+}, μequiv. g^{-1}
	H^+	$Al^{3+}+Fe^{3+}$	H^+	$Al^{3+}+Fe^{3+}$	Mg^{2+}	
1	410	820	360	780	165	1400
2	380	800	300	750	200	1380
4	340	760	300	700	260	1300
7	60	660	45	590	470	1210

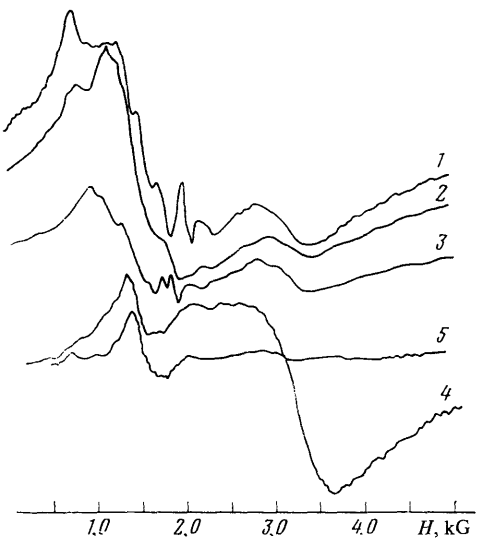


Figure 3. ESR spectra of Kovdorskii [Kovd?] Na-vermiculite: 1) air-dry; 2) dried at 105°C; 3) treated with 2 *N* HCl for 1 h; 4) treated with the KU-2 resin in the H-form for 6 h; 5) treated with the resin for 8 h.

The exchangeable cations, located directly at the iron–oxygen tetrahexra, greatly reduce the symmetry of the crystalline environment about the Fe^{3+} ions (to orthorhombic and below). In terms of the approximation of the crystal field to orthorhombic or similar symmetry, the solution of the Hamiltonian [19] yields the ESR absorption in the region [23] of $g \simeq 4.3$. Consequently the intense band in the ESR spectrum of vermiculite must be assigned mainly to Fe^{3+} ions in the tetrahedral network. The Fe^{3+} ions in the octahedral layer of vermiculite involved in the exchangeable complex may contribute to this band. It follows from a comparison of spectra *1* and *2* in Fig. 3 that adsorbed water is present in the immediate environment in the Fe^{3+} ions and has a significant influence on the form of the ESR spectrum. When vermiculite is treated with an acid (Fig. 3, curve *3*), the main change in the ESR spectrum consists in a decrease of the intensity of the band at $g \simeq 4.3$. This is associated with the removal of part of the tetrahedral and ion-exchange iron.

Table 3. The exchangeable acidity of vermiculite after its Na-form has been in contact with the KU-2 resin in the H-form (c_{susp} = 0.9 wt.%; V_{susp} = 200 ml; V_{resin} = 200 ml).

Time of contact with resin, h	Amount of exchangeable ions on surface, μequiv. g^{-1}		Total exchange capacity, w.r.t. Ba^{2+}, μequiv. g^{-1}	Time of contact with resin, h	Amount of exchangeable ions on surface, μequiv. g^{-1}		Total exchange capacity, w.r.t. Ba^{2+}, μequiv. g^{-1}
	$Al^{3+}+Fe^{3+}$	Mg^{2+}			$Al^{3+}+Fe^{3+}$	Mg^{2+}	
0.33	490	—	1420	5.0	1200	180	1410
0.50	680	—	1420	6.0	1260	200	1410
1.0	850	—	1420	8.0	1030	260	1400
2.0	890	180	1410	9.0	950	350	1380
3.0	1120	280	1410	11.0	840	420	1260
4.0	1160	240	1410	14.0	480	740	1240

Table 3 shows that the interaction of Na-vermiculite with the KU-2 resin in the H-form leads to the complete substitution, even in the first few hours, of Na^+ by Al^{3+} and Fe^{3+} ions, which appear as a result of the disruption of the tetrahedral network of the mineral. For example, the complex band at $g \simeq 4.3$ disappears almost completely from the ESR spectrum of vermiculite treated with the cation-exchange resin for 6 h (Fig. 3, curve *4*). In this part of the spectrum, a narrow signal remains, while the broad band at $g \simeq 2$ hardly changes but diminishes appreciably on further contact with the resin (Fig. 3, curve *5*), but the narrow signals with $g \simeq 4.3$ remain unaltered. Spectra *4* and *5* (Fig. 3) are characteristic of montmorillonite [24,25]. Analysis of the infrared spectra [19] also shows that, when Na-vermiculite is treated with the ion-exchange resin for 8 h, a montmorillonite structure with the absorption bands characteristic of this mineral is formed. X-Ray diffraction analysis indicates the appearance on the diffractometer trace of the resin-treated vermiculite of distinct reflections characteristic of montmorillonite [19].

Thus, when Na-vermiculite comes into contact with the cation exchanger in the H-form, the substitution of Na^+ ions by H^+ ions is followed by the dissociation of the oxygen bridges joining the defective tetrahedra to neighbouring tetrahedra and octahedra, as a result of which structural Al^{3+} and Fe^{3+} ions pass to exchange sites and then to the resin. This is manifested in the ESR spectrum to the disappearance of the broad band at $g \simeq 4.3$ due to the Fe^{3+} ion located initially in the tetrahedral network.

It follows from the above data that, when the non-stoichiometric isomorphous substitutions are fully or completely distributed in the octahedral network, it is possible to obtain under certain conditions [17,18] the hydrogen- or mixed H-Al-Fe-form of the layer aluminosilicate with strongly acid properties. When the non-stoichiometric substitutions are located in the tetrahedral network, the exchangeable protons rapidly decompose the defective tetrahedra, as a result of which exchangeable Al^{3+} or Fe^{3+} ions appear on the aluminosilicate surface.

III. CHEMICAL STABILITY OF THE H-FORMS OF LAYER SILICATES AND THE MECHANISM OF THEIR AGEING

It was established as early as 1934 [26] that the H-forms of argillaceous minerals are chemically unstable and are converted spontaneously into the Al-Fe-Mg-forms (age). The authors of one of the earliest investigations of this problem found [27] that, after storage for one month, the exchange capacity of air-dry H-montmorillonite is virtually determined solely by hydrogen ions. In the specimen of the same mineral which had been repeatedly saturated with water and dried, a large proportion of the total exchange capacity was due to the fraction of aluminium ions. Similar data were obtained in other investigations [28-31]. In some of these, the influence of various factors on the ageing of H-clays was studied [30,31]. Our investigations showed that, with increase of temperature, the rate of ageing of the H-forms of natural aluminosilicates investigated‡ increases sharply [17,18,32-34]. Fig. 4 illustrates the temperature dependence of the ageing process of H-montmorillonite§. [33] A study of the rate of ageing of H-days in methyl, ethyl, and n-propyl alcohols and dioxan showed [17,18,32-35] that ageing is not observed in pure organic solvents, while in their mixtures with water the rate of this process depends on the content of the organic component in the mixture (Fig. 5). Fig. 5 shows that, compared with alcohols, dioxan has a stronger influence. The influence of the content of the disperse phase in the suspensions on the ageing of H-minerals was also studied. The experiments showed that, with increase of the content of the solid phase, particularly when it exists in the form of a dense deposit, the rate of ageing falls. Continuous stirring of the suspension accelerated the ageing of the specimen somewhat [17,18,36].

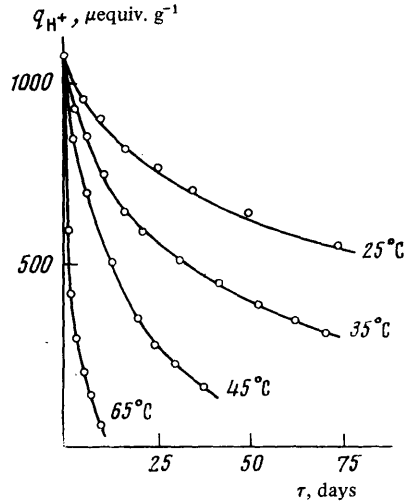


Figure 4. The influence of temperature on the rate of ageing of a 0.3% suspension of H-montmorillonite.

‡The kinetic experiments were performed on dilute suspensions of the H-forms with constant stirring.

§Here and henceforth data are presented only for H-montmorillonite. Similar results were obtained for other minerals.

Only a few studies have been devoted to the elucidation of the mechanism of the ageing of the hydrogen-forms of natural aluminosilicates. Miesserov believes [37,38] that the ageing of the H-form of montmorillonite involves the octahedral layer and is a result of the interaction of the hydrogen in the hydroxy-groups in the tetrahedral layer with the hydroxy-groups located at the aluminium atoms. Mitra and Singh [30] concluded that H-montmorillonite ages owing to the exchange of the hydrogen ions located in the basal planes of the clay particles for the aluminium ions on the crystal faces. As a result of the Brownian movement of the particles, the double layers formed by H^+ and Al^{3+} ions overlap, which leads to exchange. However, if this mechanism is adopted, one cannot understand why the process ceases completely in a polar solvent such as methyl alcohol.

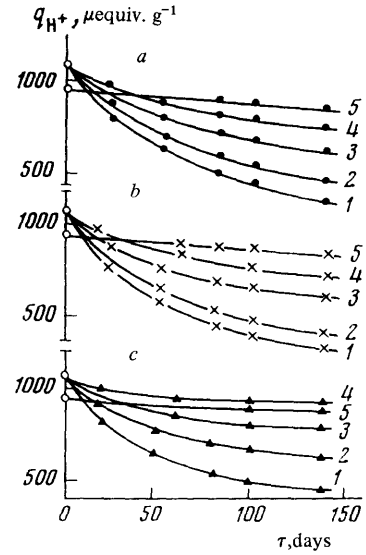


Figure 5. The influence of the content of organic solvent in the intermicellar medium on the rate of ageing of a 0.3% suspension of H-montmorillonite; content of solvent in the mixture (wt.%): 1) 10; 2) 30; 3) 60; 4) 60; 5) 100; *a*) ethanol; *b*) propanol; *c*) dioxan.

Eeckman and Loudelaut [31] established by a series of experiments that the rate of ageing of montmorillonite in the hydrogen-form is described empirically by the equation of a parabola. They suggested that the ageing mechanism involves the mutual diffusion of H^+ and Al^{3+} ions. Aluminium ions diffuse along the surface of the particles from the crystal faces to the centre and there is a flux of hydrogen ions in the opposite direction. As soon as the hydrogen ions reach the crystal faces, they interact with the lattice, as a result of which a constant concentration of Al^{3+} ions is maintained on the lateral surface. According to the authors, the rate of ageing is determined solely by the diffusion of H^+ and Al^{3+} ions. To test the diffusion mechanism of ageing which they proposed, Eeckman and Loudelaut [31] used the following procedure. Assuming that the empirical parabolic equation which they derived is equivalent to Fick's Second Law, they obtained, after a

series of mathematical transformations, an expression susceptible to an experimental test. The test showed that the mutual diffusion coefficient of H^+ and Al^{3+} ions is extremely small during the ageing of H-montomorillonite (10^{-20} cm^2 s^{-1}), which is inconsistent with the observed rate of ageing and its temperature dependence [17,18]. By comparing the principal results of the application of the diffusion mechanism to the description of the ageing of H-montmorillonite, it can be easily shown that these ideas suffer from significant disadvantages [17]. In particular, the use of Fick's Second Law to characterise the mutual diffusion of H^+ and Al^{3+} ions during ageing is completely unjustified. It is well known that Fick's Laws do not describe satisfactorily the diffusion of charged species, because in the given instance the occurrence of the process depends on many specific factors, primarily on the electric field arising during the migration of ions (the diffusional potential jump) [39,40]. The mutual diffusion coefficient calculated by the authors [31] is therefore doubtful. We may also recall that the theoretical calculations performed by Eeckman and Loudelaut are in poor agreement with their own experimental data.

Another attempt to interpret the mechanism of the ageing of the hydrogen-form of montomorillonite was undertaken recently [41,42]. To describe the ageing of the H-forms of this mineral, the authors used hyperbolic functions. This empirical approach to the process, without a definite physical basis, appears to be unjustified. The conclusion reached [41,42] about the kinetics of the ageing process (reaction order $n = 1$) is therefore unconvincing.

On the basis of the analysis of the entire set of the available literature data and our own experiments [18,33], we suggest that the ageing of the H-forms of clay minerals is a heterogeneous chemical reaction involving hydronium ions and not free protons. The involvement of water molecules in the given reaction is indicated by the results presented in Fig. 5, from which it follows that, when an organic solvent is added to the intermicellar medium, the rate of ageing of the H-form of the layer silicate falls. This is because in a water–organic solvent mixture some of the H^+ ions of the clay are solvated with formation of lyonium (and not hydronium) ions, for example $C_2H_5OH_2^+$, which are produced to a greater extent the higher the content of the organic component in the mixture. In non-aqueous media, where hydronium ions are altogether absent, ageing ceases completely. Together with the above factors, the rate of ageing of H-clays in water–organic solvent mixtures may be influenced by the association of the organic solvents with water, which results in a decrease of the activity of water molecules [43]. The validity of the above ideas concerning the decisive role of water in this reaction is confirmed very convincingly by the results [33] presented in Fig. 6. They show that the air-dry specimens of the H-forms of aluminosilicates, which still contained a certain amount of water, aged gradually. On the other hand, the specimens subjected to additional dehydration *in vacuo*, with simultaneous freezing out of water by liquid nitrogen, and then stored in sealed bulbs showed no signs of ageing whatever.

As shown above (Fig. 4), the rate of ageing of the H-forms of silicates increases sharply with increasing temperature, like the rate of any chemical reaction. This finding proves the chemical nature of the phenomenon investigated. We used a general kinetic equation for the mathematical description of this reaction. It was assumed [18,33] that the rate of ageing of H-minerals is determined mainly by the content of exchangeable H^+ ions, since the concentrations of other reactants—aluminium, iron, and magnesium present in the solid phase and the water present in the system in excess—may be regarded as constant. Therefore

$$-dq_{H^+}/d\tau = kq_{H^+}^n, \quad (1)$$

where q_{H^+} is the content of exchangeable H^+ ions in μequiv. g^{-1}, τ the time in days, k the reaction rate constant, and n the power exponent corresponding to the order of the chemical reaction. Having plotted the dependence of the reaction rate on the concentration of exchangeable H^+ ions in terms of logarithmic coordinates, it is easy to determine from the slopes of the straight lines the orders of the chemical reactions [17,18,32–34]. Calculations showed that at the beginning of the ageing process is of third order, after which there is a decrease of the order to second and below. The activation energies were calculated separately for the second- and third-order reactions by plotting lg k against the reciprocal of temperature. The results fit on parallel straight lines corresponding to the following activation energies: 20 kcal g-ion^{-1} for the ageing of H-montmorillonite and H-nontronite; 17 kcal g-ion^{-1} for the ageing of H-palygorskite; 25 kcal g-ion^{-1} for the ageing of H-kaolinite. [18] Fig. 7 presents examples of the above determinations for the ageing of H-montmorillonite. These results show that the ageing of the hydrogen-forms of layer silicates is indeed a heterogeneous chemical reaction.

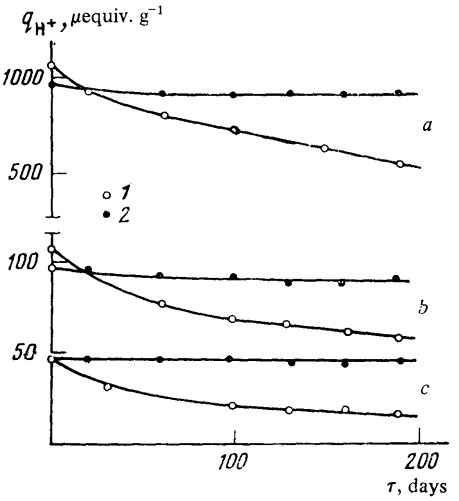


Figure 6. Kinetics of the ageing of air-dry (1) and fully dried specimens (2) of the H-forms of montmorillonite (*a*), palygorskite (*b*), and kaolinite (*c*) at 25°C.

Fig. 8 illustrates the model proposed [44] for the disruption by the exchangeable protons and water molecules of the crystal structure of montmorillonite. Evidently, three exchangeable H^+ ions are involved in the fundamental reaction step. One proton (Fig. 8*a*) reacts with a basic OH group (=Al–OH) and forms a water molecule. Simultaneously, two other protons attack via an electrophilic mechanism the ≡Si–O–Al= bonds, as a result of which the latter are broken with formation of two silanol groups and the liberation of an Al^{3+} ion. The loss of the aluminium

ion from the octahedral network reduces the stability of the silicon–oxygen tetrahedra. The presence of a water molecule in the system and the catalytic effect of the exchangeable H^+ and Al^{3+} ions [45,46] lead to the dissociation of the ≡Si–O–Si≡ bonds, as a result of which two molecules of silicic acid are released into the equilibrium solution¶:

$$2\left[\begin{array}{l}\equiv Si-O\\ \equiv Si-O\end{array}\!\!>Si(OH)_2\right] + 4H_2O \rightarrow 4\,[\equiv SiOH] + 2\,Si(OH)_4\,. \qquad (2)$$

When the next three exchangeable protons interact, the same products are obtained (Fig. 8*b*). In this case, the siloxane linkages are ruptured in accordance with the equation

$$2\,[\equiv Si-O-Si(OH)_3] + 2H_2O \rightarrow 2\,[\equiv SiOH] + 2Si(OH)_4\,. \qquad (3)$$

In contrast to the first reaction step (Fig. 8*a*), in this instance two exchangeable H^+ ions apparently rupture initially the ≡Si–O–Al≡ bond, after which one proton reacts with a hydroxy-group at an aluminium atom.

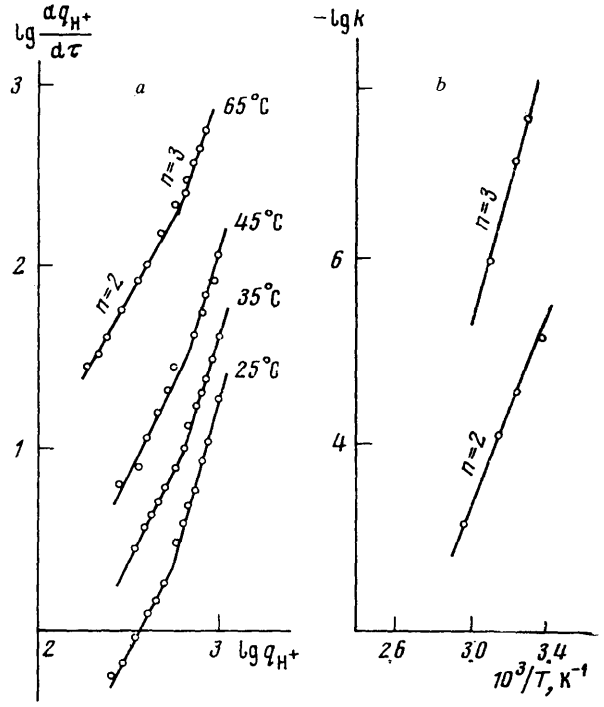


Figure 7. Dependence of the ageing of a 0.3% suspension of H-montmorillonite in water on its content of exchangeable H^+ ions at different temperatures (*a*) and of the logarithms of the rate constants for the second- and third-order reactions on the reciprocal of temperature (*b*).

It follows from Eqns. (2) and (3) that water is one of the reactants in the ageing of H-silicates. In is now understandable why ageing of the H-forms is not observed in non-aqueous media [17,18,33–35].

¶Silicic acid was determined in terms of SiO_2 by a standard method [47,48].

Subsequently the reaction under consideration proceeds analogously to those illustrated in schemes *a* and *b* in Fig. 8. After the complete conversion of the hydrogen-form of the aluminosilicate into the Al-form (the ageing cycle), its exchange capacity falls [31], because during the ageing of the H-forms of the minerals some of the Mg^{2+} ions emerge from the octahedral layer (Fig. 8*c*), i.e. the number of non-stoichiometric isomorphous substitutions in this structure diminishes. The decrease of the number of isomorphous substitutions leads in its turn to a decrease of the exchange capacity of the aluminosilicate. Studies have shown [44] that the exchange capacity decreases by 130–140 mequiv. g^{-1} in each ageing cycle of H-montmorillonite (five cycles in all were carried out).

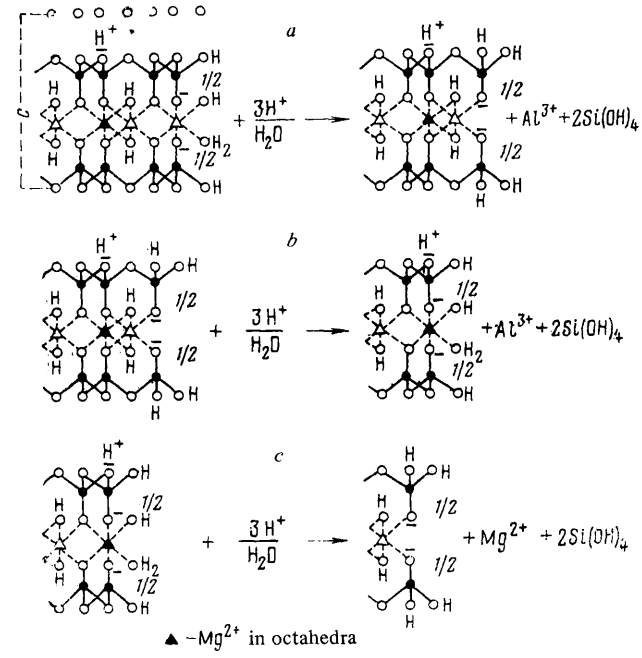


Figure 8. The disruption of the crystal structure of montmorillonite by protons.

It follows from the structure of layer silicates that the exchangeable protons, which neutralise the ruptured bonds at the crystal faces, are the first to enter into the reaction investigated. Since the exchangeable H^+ ions located on the basal planes are highly mobile [5,17,18,49,50], they reach the faces of the mineral and interact with the latter, liberating aluminium (iron, magnesium) ions from the lattice. The latter diffuse onto the basal plane and compensate its excess negative charge, generated after the removal of H^+ ions. At the same time, ions may migrate also in a different way. As a result of the Brownian movement or stirring of the suspension, the silicate particles can be oriented in such a way that the basal plane of one approaches closely to that of another. During the ion exchange between two solid phases in an aqueous medium, protons are adsorbed on the crystal faces and aluminium ions are adsorbed on the basal plane of a neighbouring particle [30]. However, it must be emphasised that neither

the mutual diffusion of H^+ and Al^{3+} (or Fe^{3+}, Mg^{2+}) ions nor ion exchange between the aluminosilicate particles [30,31] determines the rate of reaction.

It has been shown [17,18,32-34] that the dependence of the logarithms of the rate constants for the ageing of H-silicates on the reciprocal of temperature is linear. These data as well as the high activation energies show that the process under consideration proceeds only under kinetic conditions [51]. Consequently the kinetics of the ageing of dilute suspensions of the H-forms are determined mainly by the rate of reaction of the exchangeable protons with the face of the mineral, i.e. by the rate of dissociation of the ≡Si–O–Al= and ≡Si–O–Si≡ bonds, while ion transport is of secondary importance. Basic hydroxy-groups play an important role in this process [52]. Only in the ageing of paste-like and air-dry specimens of the H-forms can the mutual diffusion of ions exert some influence on the rate of the process.

As already mentioned, the calculated activation energies for the ageing of H-silicates are the same for the second- and third-order reactions. This equality and also the observed stoichiometric amounts of Al^{3+}, Fe^{3+}, and Mg^{2+} ions released from the mineral lattices suggest that the order of the reaction is in our case three, in conformity with the proposed model (Fig. 8). The observed decrease of the reaction order is caused mainly by the decrease of the concentration of the exchangeable H^+ ions during ageing. Only at the beginning of the process, where the surface concentration of H^+ ions is high, are the necessary conditions created for the occurrence of the third-order reaction. With decrease of their content, the rate of dissociation of the aluminosiloxane linkages falls. At the same time, the substitution of hydronium ions of the exchangeable Al^{3+} ions located on the lateral faces of the silicates becomes more difficult. The validity of this interpretation is confirmed by a number of data [17,53]. It follows from the latter that, with decrease of the exchange capacity of montmorillonite and kaolinite†, the orders of the ageing reactions of the H-forms decreased by unity. Together with the causes described above, one cannot exclude the influence of other factors, such as the imperfection of the crystal structure of the aluminosilicate, the accumulation of silicic acid in the equilibrium solutions and its polymerisation on the surface of the particles with formation of secondary particles [54], etc.

Apart from their direct involvement in the dissolution of the aluminosilicate, water molecules play a number of additional functions. For example, owing to the considerable hydration energies of the Al^{3+}, Fe^{3+}, and Mg^{2+} ions, water promotes their liberation from the octahedral layer. As a consequence of the formation of hydronium ions, it ensures a high mobility of the exchangeable protons. The addition of alcohols of dioxan to the intermicellar medium leads, as already stated above, to the appearance of lyonium ions, which are formed to a greater extent the higher the content of the organic solvent in the mixture. As a result of this, the mobility of the exchangeable protons falls with a consequent decrease of the rate of the ageing process.

It has been shown [44] that a similar pattern in the disruption of the aluminosilicate structure is observed when the aluminosilicate comes into contact with an inorganic acid. Table 4 shows that, in the interaction of the Ba-form of montmorillonite with a 0.01 *N* hydrochloric acid solution (with constant stirring of the suspension), aluminium ions and silicic acid are released into the equilibrium solution‡. As for exchangeable H^+ ions, the rate of reaction of the silicates with protons from the solution increases with increase of temperature. We therefore also used a general kinetic equation for the mathematical description of this process [18,33,44]. It was assumed that the rate is determined by the number of H^+ ions reacting, since the concentrations of the other reactants — aluminium and silicic acid present in the solid phase and the excess water in the system — can be regarded as constant. Fig. 9 shows that the dependence of the rate of reaction on the concentration of H^+ ions which have reacted, plotted in terms of logarithmic coordinates, consists of two linear sections. The orders of the corresponding reactions were determined from the slopes of these sections and were found to be 2 and 1. The decrease of the order of the reaction by unity compared with the ageing of the H-forms of layer silicates can be explained as follows. In contrast to the ageing reaction when Ba-montmorillonite interacts with HCl, a considerable amount of Al^{3+} ions accumulates in the equilibrium solution. Since silicic acid molecules also pass to the solution, this leads to the formation of the strong aluminosilicic acid and the interaction of each aluminium ion with $Si(OH)_4$ yields one H^+ ion [55]. Three protons are involved in the fundamental reaction step (Fig. 8). However, after the liberation of the Al^{3+} ion and two silicic acid molecules from the lattice, aluminosilicic acid is formed and one proton returns to the equilibrium solution.

Table 4. Kinetics of the interaction of Ba-montmorillonite with 0.01 *N* HCl solution at different temperatures (V_{HCl} = 300 ml).

τ, days	$[H^+]_a$, μequiv. g^{-1}	$[Al^{3+}]_s$, μequiv. g^{-1}	$[Al^{3+}]_{soln}$ μequiv. g^{-1}	c_{SiO_2}, μmole g^{-1}
45° C, c_{susp} = 0.455%				
5.94	380	130	360	870
9.10	420	230	520	1420
12.94	480	280	560	1710
19.94	540	350	610	2100
30.0	580	380	690	2180
41.12	620	420	750	2760
65° C, c_{susp} = 0.405%				
0.56	150	80	230	390
1.58	285	150	280	910
2.50	370	190	370	1230
4.54	510	300	590	2110
5.54	570	340	680	2480
6.54	620	410	700	2640
98° C, c_{susp} = 467%				
0.05	200	90	160	280
0.10	305	130	350	790
0.125	340	150	390	1120
0.167	390	190	480	1590
0.25	450	230	510	1710
0.37	520	240	520	1920
0.46	560	250	550	2030

Notation: $[H^+]_a$ is the amount of sorbed H^+ ions, $[Al^{3+}]_s$ and $[Al^{3+}]_{soln}$ are the amounts of Al^{3+} liberated from the mineral onto its surface and into the equilibrium solution respectively, and c_{SiO_2} is the amount of silicic acid, in terms of SiO_2 evolved from the mineral.

†The H-forms were prepared from specimens of these minerals subjected to preliminary activation with an inorganic acid.

‡The amount of amorphous silicic acid was determined by a standard method [48].

This is confirmed by Table 4, which shows that the amount of aluminium ions evolved from the mineral lattice is approximately one-third greater than the amount of absorbed hydrogen ions. Furthermore, the decrease of the concentration of H^+ ions as a result of their interaction with the montmorillonite crystals faces leads to an increase of the order of the reaction.

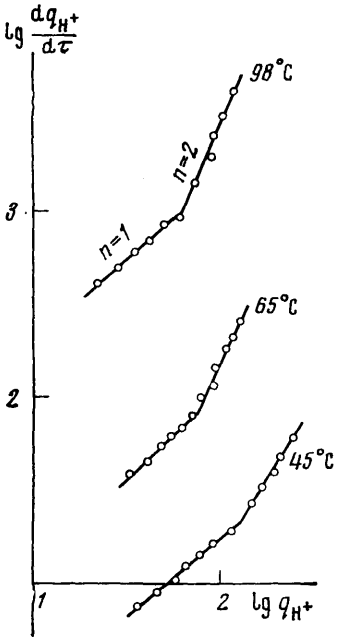


Figure 9. Dependence of the rate of interaction of H^+ ions with montmorillonite on the number of such ions reacting at different temperatures.

In order to calculate the activation energy for the dissolution of the mineral in an acid, we plotted[44] the logarithm of the reaction rate constant against the reciprocal of temperature. The data found for the first- and second-order reactions fit on parallel straight lines, which correspond to an activation energy of 24 kcal g-ion^{-1}. This value is close to that obtained earlier for the decomposition of the montmorillonite structure by exchangeable protons.

The mechanism proposed for the decomposition of natural aluminosilicates by H^+ ions is valid for all minerals in which non-stoichiometric substitutions or other defects, responsible for their ion-exchange capacity, are located in the octahedral network. A difference may be observed only in the quantitative release of silicic acid into the equilibrium solution (depending on the crystal-chemical type of the mineral). When layer silicates interact with inorganic acids one must bear in mind that aluminium ions exist in the intermicellar solution as cations derived from aluminosilicic acid. These cations may be adsorbed on the surface of the natural aluminosilicate instead of Al^{3+} ions[56]. One should also note that, when clay minerals interacted with concentrated hydrochloric acid solutions (0.05 and 0.1 *N*), the absorption of protons was not observed[44]. This is apparently associated with the formation under certain conditions of aluminosilicic acids of different composition and the liberation of H^+ ions into the equilibrium solution.

IV. THE ION-EXCHANGE PROPERTIES OF THE ACID FORMS OF NATURAL SILICATES

Extremely valuable information about the strength of binding of acid ions to the surfaces of clay minerals can be obtained from the analysis of the ion-exchange properties of the latter. At room temperature, H-silicates do not undergo appreciable changes during the first hours of ageing, which makes it possible to rule out the influence of this process when adsorption experiments are performed. The Langmuir equation has been used[17,18,57-59] to describe the ion-exchange interaction of the hydrogen- and electrodialysed (Al- and Fe-)forms of silicates with solutions of alkali and alkaline earth metal salts. The constant b (adsorbability) of this equation serves as a quantitative characteristic:

$$a = a_\infty \frac{bc_e}{1+bc_e}, \qquad (4)$$

where a is the degree of adsorption of the ions in μequiv. g^{-1}, a_∞ the maximum degree of adsorption of the ions corresponding to complete coverage of the mineral surface by the latter in μequiv. g^{-1}, and c_e the equilibrium concentration of the ions in solution in μequiv.ml^{-1}.

Table 5. The constants of the Langmuir equation (a_∞, μequiv.g^{-1}; b, ml μequiv.$^{-1}$) characterising the adsorption of cations on the hydrogen- and aluminium-forms of the minerals.

Cation	Ba^{2+}	Ca^{2+}	Cs^+	Rb^+	K^+	Na^+
Montmorillonite						
a_∞ (H)	1150	1150	1170	1170	1150	1200
a_∞ (Al)	800	820	800	800	860	800
b (H)	1.8	1.8	1.5	1.5	0.50	0.10
b (Al)	0.064	0.062	0.104	0.100	0.018	0.005
Palygorskite						
a_∞ (H)	150	150	145	145	140	140
a_∞ (Al)	80	80	80	80	75	85
b (H)	0.25	0.25	0.20	0.20	0.16	0.14
b (Al)	0.035	0.033	0.048	0.043	0.017	0.011
Kaolinite						
a_∞ (H)	55	53	53	52	53	55
a_∞ (Al)	47	48	46	47	47	48
b (H)	1.5	1.5	0.36	0.36	0.12	0.06
b (Al)	0.06	0.05	0.15	0.10	0.023	0.007

The sorption isotherms obtained for the cations on both acid forms of clay minerals are described satisfactorily by the Langmuir equation[17,18]. The experimental points fitted satisfactorily on the straight line obtained in terms of the coordinates of Eqn. (4), from which the constants a_∞ and b were found by a graphical method[60]; the constants are listed in Table 5. Evidently a_∞ remains invariant, within the limits of experimental error, and equal to the content in the initial specimen of hydrogen

and aluminium ions§ which are exchanged for the salt cations. This indicates the independence of the exchange capacity (due to isomorphism) of clay minerals of the nature of the adsorbed cation. The constant b, characterising the adsorbability of the cations investigated, varies as a function of both the properties of the salt cation and the nature of the exchangeable ion in the acid form of the aluminosilicate. The latter is manifested by the fact that the adsorbability of alkali and alkaline earth metal cations on the H-forms of minerals is an order of magnitude greater than on the aluminium-forms. Consequently the bonds between the exchangeable hydrogen ions and the silicate surface of the particle are much weaker than those linking the exchangeable Al^{3+} ions.

Aluminium ions are strongly hydrated in solution and their mobility is low[61], while the acid proton is not even permanently attached to a particular water molecule with which it forms a hydronium ion, migrating continuously from one water molecule to another[62]. Presumably H^+ and Al^{3+} ions retain their properties also in the adsorbed state. This explains our observation of the greater adsorbability of cations on the hydrogen-forms of clay minerals than on the aluminium-forms. Thus it follows from the literature[57-59] that exchangeable H^+ ions exhibit a high mobility and behave similarly to univalent cations. The anomalous behaviour of hydrogen ions[63] can be explained by the fact that aluminium-forms of clay minerals and not hydrogen-forms were in fact investigated.

The differences in the properties of exchangeable hydrogen and aluminium ions influence also the positions of alkali and alkaline earth metal cations in the series based on their adsorbability on the acid forms of layer silicates. Whereas the cations considered can be arranged in the sequence

$$Ba^{2+} = Ca^{2+} > Cs^{+} = Rb^{+} > K^{+} > Na^{+},$$

in terms of their capacity to enter into the exchangeable complex of H-minerals, another series holds for the aluminium-forms:

$$Cs^{+} > Rb^{+} > Ba^{2+} > Ca^{2+} > K^{+} > Na^{+}.$$

The change in the cation adsorbability series as a function of the nature of the exchangeable cation of the acid form can be accounted for from the standpoint of modern ideas about the behaviour of electrolytes in solution. According to these ideas, hydrogen ions as well as alkali and alkaline earth metal cations migrate in solution without a hydration shell[64]. Such data are lacking for aluminium ions, but, by analogy with the behaviour of beryllium ions, Al^{3+} ions presumably migrate together with water molecules. In ion-exchange processes, the fundamental step in the substitution of one type of ion by another may occur, depending on the properties of the cations, both with and without the involvement of the hydration shell. This apparently leads to the fundamental difference between the ion-exchange processes on the H- and Al-forms of minerals. Whereas in the former case unhydrated cations are exchanged, in the latter the process is determined by the fact that Al^{3+} ions can be displaced only together with their hydration shells. When the fundamental exchange step on the surface of a layer silicate is not complicated by the hydration of cations, their adsorption from solutions should occur more effectively the stronger their attraction to the surface of the particle. This attraction is greater the higher the charge of the ion and, for the same charge, the greater its polarisability. In the exchange of hydrogen ions for alkali and alkaline earth metal cations, doubly charged ions are therefore adsorbed more strongly than singly charged ions and, in individual groups of cations, the adsorbability increases with increasing radius of the unhydrated ion.

In the exchange processes on the aluminium-forms of clay minerals, Al^{3+} ions are probably involved together with their hydration shells. Their substitution might be facilitated if their shell were disrupted in some way. This apparently actually occurs in the exchange of Al^{3+} ions for Rb^+ and Cs^+ ions, which are characterised by negative hydration, consisting in the fact that, under the influence of these ions, water molecules, as it were, become more mobile than in the pure solvent[64]. This is why the adsorbability of Rb^+ and Cs^+ ions on the Al-forms of the minerals is greater than that of the remaining cations investigated, including bivalent cations. Thus the results presented show that the exchangeable H^+ ions of clay minerals do not exhibit any anomalous properties and retain the features characterising them in aqueous electrolyte solutions.

V. THE INFLUENCE OF THE MOBILITY OF THE EXCHANGEABLE H^+ IONS ON THE NATURE OF ^1H NMR SPECTRA

Apart from their strongly acid properties the exchangeable H^+ ions manifest yet another interesting property—they influence proton magnetic resonance spectra. The ^1H NMR spectra of the water present in oriented preparations of the H-, Li-, and H-Li-forms of montmorillonite have been analysed[65]. The investigation showed that the shape of the ^1H NMR spectrum of the protons in the water molecules adsorbed by the Li-form of montmorillonite depends on the disposition of the film of the partly oriented mineral in the magnetic field. Together with a narrow line in the centre of the spectrum (Fig. 10, curve *2*), there is a distinct doublet, the distance between the peaks of which is described satisfactorily by the relation $3\cos\theta - 1$ [sic], where θ is the angle between the normal to the plane of the aluminosilicate packets and the external magnetic field H_0. These data indicate the anisotropic movement of H_2O molecules in the interlayer space of the Li-montmorillonite obtained previously in a study of powdered specimens[66]. It is noteworthy that the maximum splitting of the doublet for the oriented preparation, when the magnetic field is applied at right angles to the plane of the film ($\theta = 0$, Fig. 10, curve *2*), amounts to approximately 4 G, which exceeds by a factor >2 the corresponding value for powdered specimens with the same moisture content[66]. The angle γ_{iR} between the interproton vector and the normal to the plane of the packet was determined from the calculated second moment of the doublet (6 G^2) and was found to be ~38°. This value agrees satisfactorily with the results from a number of studies[67,68]. The ^1H NMR spectrum of the water in the H-form of montmorillonite shows a single narrow line, regardless of the orientation of the films in the magnetic field (Fig. 10, curve *1*). The absence of the doublet from the spectrum can be accounted for both by the different state of the water molecules in the interlayer space of H-montmorillonite and by the specific influence of the mobile exchangeable H^+ ions on the form of the ^1H NMR spectra. The nature of the mobility of the water in the Li- and H-forms should not differ significantly.

§The decrease of the content of exchangeable Al^{3+} ions relative to hydrogen ions is due to the decomposition of the silicates during electrodialysis.

Studies have shown[65] that the introduction of even an insignificant amount (1–2% of the exchange capacity of the mineral) of exchangeable hydrogen ions leads to the disappearance of the doublet from the spectrum of the Li-form of the aluminosilicate. The change in the state of water under these conditions must be slight. One can therefore postulate that the introduction of small amounts of hydrogen ions into the mineral accelerates significantly only the proton exchange in the system. The role of this factor in the disappearance of the doublet structure of the ^1H NMR spectrum of water in the montmorillonite gels had been noted earlier[69,70] in a comparison of pulsed proton and deuteron magnetic resonance signals. It also follows from the results presented that the mechanism of "relay" proton exchange is more probable, since the formation of short-lived H_3O^+ ions requires a rearrangement of the electronic configuration of water molecules. Furthermore, it is difficult to suppose that all the water molecules participated in the formation of H_3O^+ ions in the proton exchange process in the presence of such a low concentration of H^+ ions on the surface of Li-montmorillonite.

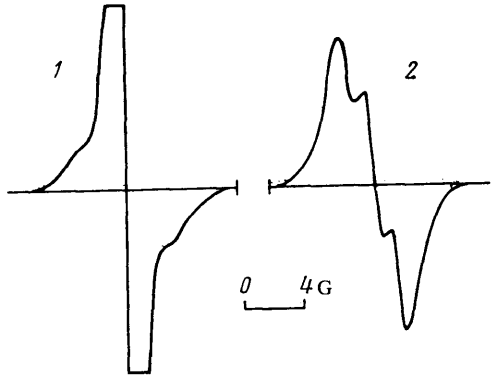


Figure 10. The ^1H NMR spectra of the oriented specimens: 1) air-dry H-montmorillonite; 2) air-dry Li-montmorillonite.

The narrow line in the centre of the ^1H NMR doublet spectrum of the Li-form of montmorillonite (Fig. 10, curve *2*) was assigned to the state of water whose mobility is close to that of isotropic water[66]. However, the appearance of the narrow line can also be accounted for by the influence of proton exchange, which occurs when montmorillonite is hydrated[71]. The protolytic dissociation of water molecules which takes place in this case owing to the polarising action of the cations and the surface may influence the proton exchange in the system. This effect should become more pronounced with increase of the ionic strength due to the cations. This may explain the difficulty of observing the doublet structure of the NMR spectra of the water protons when the exchangeable complex contains certain bivalent metal cations[72].

VI. THE INFLUENCE OF TEMPERATURE ON THE STATE OF THE EXCHANGEABLE ACID IONS

The catalytic activity of natural aluminosilicates is related mainly to their surface acidity. As already stated, the hydrogen forms of layer silicates are chemically unstable and undergo the ageing process. In order to elucidate the mechanism of the chemical reactions, it is therefore necessary to take into account, under certain conditions in the catalytic process, both the composition and the state of the acid aluminosilicate ions on the surface.

Table 6. The influence of the temperature and duration (τ) of heat treatment on the content of exchangeable Al^{3+} and Fe^{3+} ions (μequiv.g^{-1}) on the surface of layer silicates.

τ, h	25–400° C	500° C	600° C
Al-montmorillonite			
1.0	1100	750	100
2.0	1100	680	90
3.0–4.0	1100	600	90
Al, Fe-palygorskite			
1.0	145	140	70
2.0–4.0	145	140	60
Al-kaolinite (Prosyanovskii [Prosyanaya?] deposit)			
1.0–4.0	55	55	53

Tables 6 and 7 present data for the influence of the temperature and duration of the heat treatment on the content of exchangeable Al^{3+}, Fe^{3+} and H^+ ions on the surface of air-dry specimens of minerals. They show that the Al-forms are chemically stable at fairly high temperatures, while the H-forms of the minerals are chemically unstable and the mechanism of their ageing changes significantly as a function of temperature.

Below 200°C, the ageing of air-dry specimens of H-clays proceeds only as far as a definite content of hydrogen ions on the surface of the aluminosilicate and then becomes sharply retarded. Such inhibition can be accounted for by the fact that the ageing process under the given conditions is determined by the rate of the spontaneous conversion of the H-form of the mineral into the Al-form and by the evaporation of water from the surface of the silicate particles[18,36]. After the removal of water, this process ceases. The proposed explanation is confirmed by the results of a study of the ageing of a completely dried H-specimens¶—even at 200°C it is hardly converted into the aluminium-form (Table 7). A completely different behaviour was observed in the ageing of the H-forms above 200°C (Table 7). In contrast to the ageing mechanism already known, the exchangeable H^+ ions disappear completely from the surface without the removal from the mineral structure of a stoichiometric amount of Al^{3+} ions. After the heat treatment of the H-forms of clay minerals for 1 h at 300–400°C, the

¶The dry specimen of the H-mineral was prepared from the air-dry specimen by prolonged evacuation accompanied by the freezing out of moisture by liquid nitrogen, after which it was stored in a sealed bulb.

exchange capacity of the mineral decreases irreversibly by an amount equal to the number of exchangeable hydrogen ions.

The observed phenomenon is probably similar to the migration of Li^+ ions in the octahedral layer of the clay mineral noted earlier. The small Li^+ cations may be located either at vacant octahedral sites [13] or in the interstices between them [14].

Table 7. The influence of the temperature and duration (τ) of heat treatment on the chemical stability of the hydrogen-forms of layer silicates (the contents of exchangeable acid ions are quoted in μequiv.g^{-1}).

τ, h	25° C		100° C		200° C		300° C		400° C	
	H^+	Al^{3+}	H^+	Al^{3+}	H^+	Al^{3+}	H^+	Al^{3+}	H^+	Al^{3+}
					H-montmorillonite					
1.0	890	260	760	390	550	600	80	250	0.0	250
2.0	890	260	720	430	480	670	40	250	0.0	250
3.0	890	260	720	430	470	680	0.0	250	0.0	250
6.0	890	260	720	430	470	680	0.0	250	0.0	250
2.0*	900	250	900	250	850	250	0.0	250	0.0	250
					H-palygorskite					
1.0	105	35	62	78	36	104	10	36	0.0	36
2.0	102	38	53	78	27	113	0.0	36	0.0	36
3.0	102	38	41	99	19	121	0.0	36	0.0	36
6.0	102	38	40	100	18	122	0.0	36	0.0	36
2.0*	105	35	103	37	84	56	0.0	35	0.0	36
					H-kaolinite					
1.0	49	9	28	27	16	39	0.0	11	0.0	10
2.0	45	10	20	35	9	46	0.0	11	0.0	10
3.0	45	10	20	35	8	47	0.0	11	0.0	10
6.0	44	11	20	35	8	47	0.0	11	0.0	10
2.0*	46	9	45	10	38	17	0.0	10	0.0	10

*In vacuo.

In order to elucidate the causes of the loss of exchange capacity by H-montmorillonite on heating to 300–400°C, a study was made of the NMR spectra of both acid forms [78]. It was observed that the NMR spectra of the initial air-dry specimens of the H- and Al-forms show an intense narrow band due to the adsorbed water molecules and hydrogen ions. The difference between the NMR spectra of the H- and Al-forms is manifested only after the removal of sorbed H_2O molecules. For example, the NMR spectrum of the Al-form heated for 1 h at 200°C (Fig. 11, 1*a*) contains a broad band due to hydroxy-groups. The calculated second moment, which is approximately 4 G^2, agrees well with data for OH groups obtained for other cation-substituted forms of montmorillonite [14].

In contrast to the Al-form, the NMR spectrum of H-montmorillonite heated to 200°C shows a distinct narrow line with $\Delta H \simeq 0.5$ G (Fig. 11, 2*a*), against the background of the band due to hydroxy-groups, which we assigned to mobile exchangeable hydrogen ions. Quantitative study of the form of the NMR signal obtained reveals a downfield shift of the band due to H^+ ions relative to the signal of hydroxy-groups. Owing to the considerable width of the bands observed in the spectrum, it is difficult to estimate the shift quantitatively. If it is assumed that, on raising the temperature to 300°C, hydrogen ions become located at the ion-exchange centres on the aluminosilicate, then the NMR spectrum should exhibit a broadening of the band due to hydroxy-groups as a result of the increase in proton density. In fact, a narrow proton line is observed even at a heat treatment temperature of 500°C and the content of protons decreases (only) above this temperature, where the loss of the structural hydroxy-groups of the mineral already takes place (Fig. 11, *b*). Since at 300°C and above there are no exchangeable protons on the surfacd of montmorillonite (Table 7), it is reasonable to suppose that they migrate into its crystal structure. It also follows from the results presented that the protons captured by the lattice are not located at definite electron-donating centres, but diffuse throughout the crystal structure.

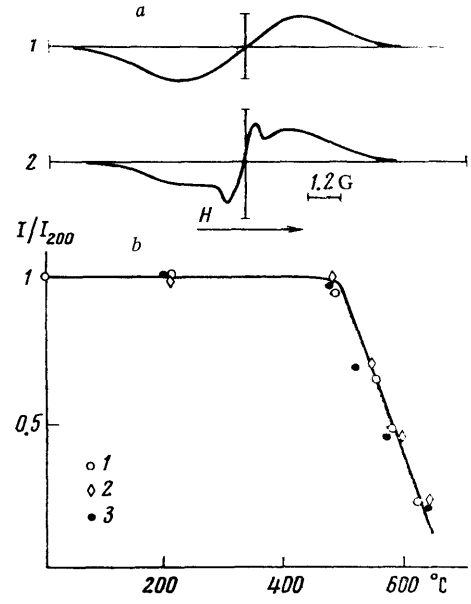


Figure 11. *a*) NMR spectra of the protons of the specimens of the Al-form (*1*) and the H-form (*2*) of montmorillonite dehydrated at 200°C; *b*) variation of the integral intensities in the NMR spectra of the hydroxyl protons and H^+ ions in the acid form of montmorillonite as a function of the temperature of the heat treatment of the specimens; 1) OH groups in the Al-form; 2) OH groups in the H-form; 3) H^+ ions.

X-Ray diffraction studies on the H-form of montmorillonite heated at different temperatures (25–450°C) showed that its crystal lattice does not undergo appreciable changes during the ageing processes. The non-basal reflections (4.39, 3.12, 2.48, 1.66, 1.48, and 1.27 Å, etc.) for both acid forms of the mineral are characteristic in the experimental temperature range also of other cation-substituted forms of montmorillonite [74].

Thus the available data show that the nature of the surface of the acid forms of layer silicates depends to a large extent on their heat treatment temperature. In the study of chemical transformations, it is therefore necessary to take into account the change in the chemical nature of the surface under certain conditions of catalysis. Thus, in the investigation of the catalytic process on the aluminium-form, one must bear in mind the decrease of the content of exchangeable Al^{3+} ions of silicates above 500°C. The study of the mechanism of catalytic reactions on the minerals in the hydrogen-forms must be approached with

even greater caution. The elucidation of the true mechanism of the catalytic reaction is complicated in this case by the ageing processes of the H-form. Under conditions where there is no water in the system, the H-form is a chemically stable complex up to 200°C. Above this temperature exchangeable protons migrate spontaneously in the crystal structure of the mineral, which is reflected in its catalytic activity. A slight activity may be manifested under these conditions owing to the thermal dissociation of the surface hydroxy-groups [75] or other active centres in the crystals.

VII. THE EXCHANGEABLE ACIDITY OF SILICATES ACTIVATED BY INORGANIC ACIDS AND OF ELECTRODIALYSED SILICATES

Considerable advances have been made in the study of the adsorption-structural and physicochemical properties of acid-activated minerals [1,7,76]. These investigations have established that the sorbents and catalysts obtained in this way exhibit enhanced adsorption, bleaching, and catalytic properties. The studies performed have shown[53] that both the composition of the exchangeable cations and the exchange capacity of montmorillonite depend on the activation time (Table 8). With increase of activation time, the content of hydrogen ions on the surface of the mineral falls and that of the aluminium ions increase. When the sorbent is treated with a 20% hot solution of H_2SO_4 for 6 h, its virtually homoionic Al-form is produced.

Table 8. The influence of the activation time on the amount of exchangeable H^+ and Al^{3+} ions of montmorillonite (μequiv.g^{-1}) and on the concentration of Al^{3+} ions in the mother liquor $[Al^{3+}]_{soln}$ (activation temperature 98°C).

Treatment time, h	Exchange capacity, μequiv. g^{-1}	Washing without cooling		Washing after cooling		$[Al^{3+}]_{soln}$ N
		H^+	Al^{3+}	H^+	Al^{3+}	
1	960	350	615	500	465	0.06
2	880	300	580	390	490	0.07
3	790	190	605	310	485	0.10
4	780	80	710	180	610	0.13
5	700	50	655	100	605	0.17
6	650	40	660	40	660	0.21
8	630	30	640	30	640	0.22

The decrease of the number of exchangeable H^+ ions during the activation process can be explained as follows. When a hot solution of sulphuric acid comes into contact with the clay mineral, the mineral faces dissolve, as a result of which aluminium ions and polysilicic acid gradually accumulate in the mother liquor. On washing the specimen, the selective adsorption of tervalent aluminium (or aluminosilicate [56]) ions results in the partial or complete substitution by the latter of the hydrogen ions in the equilibrium solution depending on the concentration of the tervalent ions. At the same time, one cannot rule out also the possibility of the ageing of the H-form of the aluminosilicate during activation and particularly during the washing of the hot specimens. This is indicated by the dependence of the composition of the exchangeable cations of the activated mineral on the washing conditions: samples which were washed free of the excess electrolyte without cooling contain fewer exchangeable hydrogen ions compared with samples which had been subjected to preliminary cooling for 24 h (Table 8). This is because on cooling a suspension of the mineral in an acid solution, the Al^{3+} ions cannot be distributed on the surface, since they are readily displaced by protons owing to the high concentration of the latter. During the washing of the hot specimen, the H-mineral ages after the first portion of the mother liquor has been decanted, with migration of exchangeable aluminium ions onto the surface.

The hydrogen-aluminium-form of the activated montmorillonite thus obtained is chemically unstable and is converted after a time into the homoionic Al-form. As for the homoionic H-forms of clay minerals, this process depends on the content of the disperse phase in the system, the composition of the intermicellar medium, and temperature. With increase of the concentration of the suspension and following the introduction of methanol into the dispersion medium, the rate of ageing of the activated specimens falls. In dehydrated methanol and in the dried state, the specimens investigated do not show any signs of ageing. With increase of temperature, the rate of ageing of the specimens in the aqueous suspension increases sharply. These results show that the ageing process of the activated mineral is similar to the ageing of the homoionic H-forms of layer silicates described above and is a heterogeneous chemical reaction of the exchangeable protons on the aluminosilicate faces. A necessary condition for this reaction is the presence of water molecules in the system. The calculated activation energy for the ageing of the H–Al-form (21 kcal g-ion^{-1}) proved to be equal to the value for the ageing of the homoionic H-form of the mineral.

Table 8 shows that the exchange capacity of the silicate after activation for 6 h changes insignificantly. This is because a large amount of aluminium ions and silicic acid accumulates in the mother liquor, as a result of which a chemical equilibrium is established in the system. At the same time, the inhibition of the dissolution of minerals may be influenced by the polymerisation processes of the above compounds. Amorphous polyaluminosilicic and polysilicic acids may be deposited on the lateral faces of silicates and prevent the interaction of hydronium ions with the latter.

It follows from the analysis of the extensive literature on the acid activation of minerals that solutions of concentrated acids (up to 20%) are used as a rule for this process [1,7,76,77]. However, in these solutions the degree of dissociation of the acid is greatly reduced and the activity of H^+ ions is insignificant. In order to intensify the above treatment, it is therefore desirable to use more dilute solutions of inorganic acids. One must also take into account the fact that, when unpurified minerals are used, part of the acid is consumed in the dissolution of impurities such as oxides, carbonates, organic substances, etc., which are always present in natural specimens.

Electrodialysis of aqueous suspensions of minerals is a very convenient method of obtaining their acid forms [17]. Its advantage is due to the fact that, in contrast to acid activation, it does not require additional operations involved in the removal of electrolytes from the dispersed silicate by washing, particularly since both methods frequently lead to minerals in the Al-(Fe-, Mg-)forms [17]. It has been shown in a number of studies [1,78,79] that electrodialysis of suspensions of aluminosilicates causes

the disruption of their lattices. The mechanism of the dissolution process is apparently similar to that described above and consists of the following steps. When a constant electric field is applied, the exchangeable cations in the suspension† migrate to the cathode and accumulate in the cathodic compartment. The negatively charged silicate species diffuse to the anode, becoming concentrated near the cellophane partition. During electrodialysis, water molecules are known to decompose:

$$6H_2O \rightarrow 2H_2 + O_2 + 4H^+ + 4OH^-, \quad (5)$$

OH^- ions accumulating at the cathode and H^+ ions at the anode. When the cathodic compartment is washed with distilled water, the exchangeable cations are removed in the form of metal hydroxides. The excess negative charge of the individual mineral particles is compensated by hydrogen ions. As shown above, the H-form of the natural aluminosilicate is chemially unstable and is converted into the Al-Fe-Mg-form. Since electrodialysis is almost always accompanied by an increase of temperature, the ageing reaction proceeds under these conditions at a high rate. As a result, the mineral faces break down (Fig. 8) with liberation of silicic acid, which is always observed in the anodic compartment [17,80].

One should also note that the intensity of the given process depends both on the nature of the exchangeable cation and on the potential difference applied to the electrodes. The stronger the binding of the exchangeable cation to the surface, the greater the potential gradient required for the transfer of the exchangeable cation to the cathodic compartment. If a potential difference capable of causing the desorption of the exchangeable Al^{3+} (Fe^{3+}) ions from the surface and of transferring them to the cathodic compartment is applied to the system, a continuous dissolution of the mineral is observed. In order to obtain the acid form of the aluminosilicate by the electrodialysis of aqueous suspensions, it is therefore necessary to monitor the process carefully. The monitoring consists in analysing the electrolyte in the cathodic and anodic chambers. As soon as the flow of exchangeable cations into the cathodic compartment ceases and silicic acid appears in the anodic compartment (in the form of SiO_3^{2-} ions), electrodialysis is stopped. The composition and amount of exchangeable acid ions on the surface of the silicate are determined at the same time.

In order to obtain reliable data on the nature of the exchangeable acidity of powdered specimens, one must bear in mind the fact that the drying of their pastes must be carried out at room temperature or below. Such drying conditions inhibit the ageing of the H-forms of the minerals.

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†The suspension in the working compartment of the electrodialyser is stirred continuously [17].

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