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THEORY OF THE EFFECT OF THE CHANGE IN THE pH OF WATER UPON CONTACT WITH THE SURFACE OF FINELY DISPERSED SOLIDS (FLINT)

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Based on estimates of the parameters of the structure of water in a water–flint powder system and the structure of water adsorbed on the surface of the flint, an explanation is given for the effect of the increase in the pH of water in contact with the flint.

We consider the dependence of the pH of water on the number of cycles of contact with flint without regeneration of the latter revealed by us in experimental investigations (Fig. 1). A similar dependence can be obtained if the mass of the flint is decreased gradually with a constant mass of water in the water–flint system.

In the experiments we used flint from the Krasnosel'skii quarry of the Grodno region. We will not present here the technology of obtaining the form of flint that makes it possible to obtain the experimental relation given in Fig. 1, but we note that a substantial effect of the increase in the pH of water was discovered upon contact of it with other forms of flint: gray Devonian and white rock meal Devonian from the Gralevo quarry; white rock meal Devonian from the Ruba quarry; black chalky and gray chalky from the Beryoza quarry (all of these quarries are located within the Republic of Belarus).

The experiments carried out showed that the effect is attributable to the mineralogical composition of the flint, the dimensions of the particles of the solid phase, and the conditions of the heat treatment of the latter.

As follows from [1], in the majority of specimens of flints of the Cretaceous age the predominant mineral phase is α-quartz, with α-tridymite and α-cristobalite also being present.

Water in contact with opal (prepared in the same way as the flints), where amorphous SiO_2 is dominant and β-tridymite and β-cristobalite are also present, acquires a pH of 5.

It turned out to be impossible to explain the change in the pH of water by the content of salts dissolved in it as a result of contact with the solid phase. Then, it was assumed that, due to the technological operations in the production of water with a high pH, a portion of the highly dispersed fraction of the flint passes into the water, forming a colloidal (ultramicroheterogeneous) system. In point of fact, electron photomicrographs obtained at a magnification of 85,000 disclose the presence of flint particles with dimensions of up to 60 Å.

The mass of the dry residue obtained after evaporation of water with a pH of 13.5 amounted to 0.25% of the total mass of the flint by means of which the alkali water was prepared. Thus, the reason for the change in the pH of water is the existence of colloidally dispersed particles of flint in the volume of water. But the mechanism that determines the change in the pH of water should be associated with capture of hydroxonium ions by the surface of the flint. Why does this occur? To answer this question, it is necessary to estimate the change in the parameters of the structure of water in the water – flint system. This was partially done by us in [2–4], where it was shown that upon interaction of any solid phase with water the following parameters of the structure of water change: valence angle, distances between the oxygen atoms of two neighboring molecules, energies of hydrogen bonds, lengths of valence and hydrogen bonds, angle of bending of hydrogen bonds, and the dipole moment of the water molecule. The greatest changes were observed in the water – flint system, and for all the systems studied they were obtained from data of measurements of the longitudinal relaxation times of nuclear spins in the water molecule in nuclear magnetic resonance (NMR) spectra of high resolution. It should be noted that in NMR experiments

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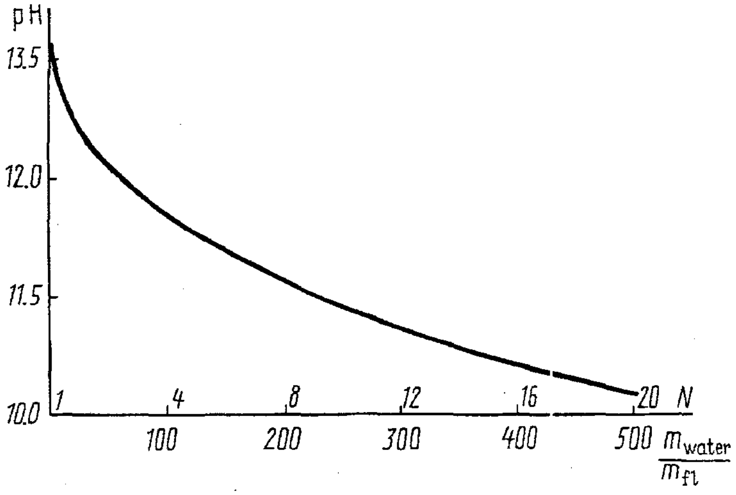

Fig. 1. Dependence of the pH of water on the number of cycles N of contact with flint (without regeneration of the latter) at $m/M = 0.3$ and on the mass ratio of water to flint m_{water}/m_{fl}.

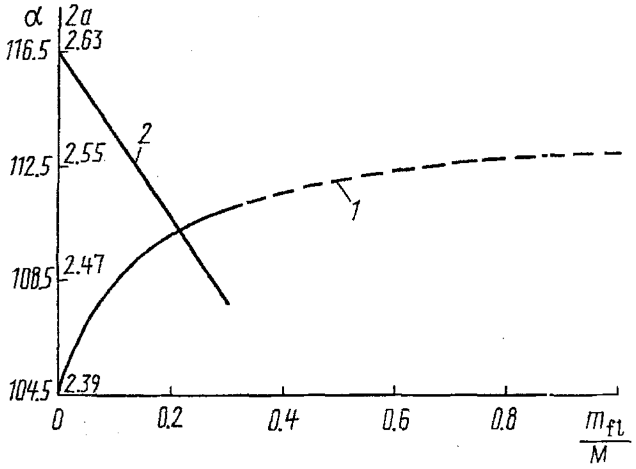

Fig. 2. Dependence of the valence angle α (deg) in a water molecule (1) and the spacing between the oxygen atoms $2a$ (Å) of two neighboring water molecules (2) on the mass ratio of flint to water and flint m_{fl}/M.

TABLE 1. Parameters of the Structure of Water in a System of Distilled Water and Flint Powder

m/N	b, Å	α, deg	τ, Å	$2a$, Å	ΔU kcal/mole	R, Å	θ, deg	T_1/T_1^0 (exp)	M_e, D
0.30	1.5828	110.7	0.962	2.4630	0.374	1.750	51.880	1.1931	1.8185
0.20	1.5775	110.15	0.962	2.4814	0.319	1.753	50.201	1.1771	1.8245
0.15	1.5696	109.5	0.961	2.5080	0.245	1.750	46.764	1.1533	1.8835
0.10	1.5490	107.4	0.961	2.5620	0.090	1.743	45.267	1.0919	1.8385
0.05	1.5390	106.4	0.961	2.5950	0.040	1.802	42.260	1.0595	1.8428
Parameters of the structure of adsorbed water									
1.0	1.6011	113.0	0.960	–	0.569	–	–	–	1.7781

[2–4] a coarsely dispersed flint with particles 2–3 mm in size was used. It was necessary to estimate the parameters of the structure of water for the water–flint powder system. All the calculational equations are presented in [5], and results of calculations are given in Table 1 and Fig. 2.

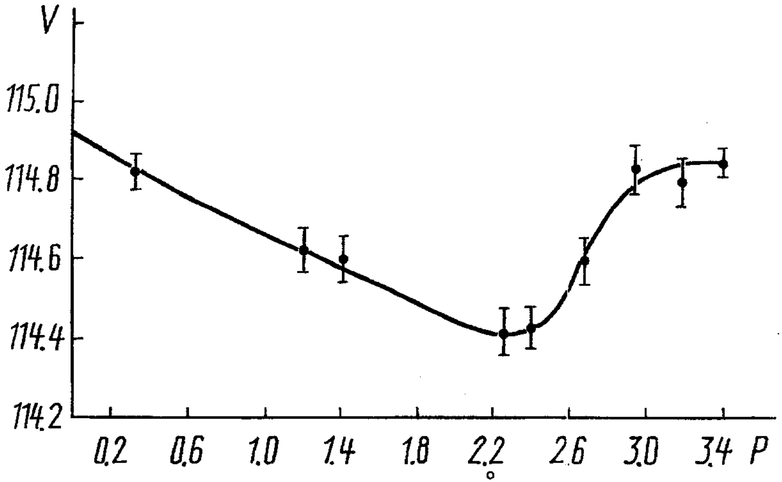

Fig. 3. Volume of an elementary cell of flint (Å) as a function of the content of adsorbed water (%).

In [3] it is shown that the value of the valence angle in a water molecule adsorbed on an oxygen atom in the surface layer of flint reaches 113°; in γ-alumina this angle is 107° in adsorption of a water molecule simultaneously on two oxygen atoms, while in the scheme of adsorption where one of the oxygen atoms of a water molecule enters into interaction simultaneously with a coordinationally nonsaturated aluminum atom (Lewis center) and an OH-group (Brönsted center) and the hydrogen atom of the molecule interacts with an oxygen atom of the crystal lattice, the valence angle amounts to 104.3°; in montmorillonite in adsorption of a water molecule simultaneously on two oxygen atoms the valence angle reaches 97.5°, while in the scheme of adsorption where one of the oxygen atoms of a water molecule interacts with an exchange cation or a hydroxyl group and the hydrogen atom of the molecule interacts with an oxygen atom of the crystal lattice, the valence angle turns out to be 104.5°.

Therefore, the valence angle in a water molecule changes substantially only upon its adsorption on oxygen atoms. But a change in the valence angle entails a change in the dipole moment of the water molecule and, consequently, a change of its electron charge.

The question arises as to why oxygen atoms located in the surface layers of various minerals determine the diverse transfer of electron charge to an adsorbed water molecule. We shall try to answer this question by estimating the distortion of the crystal lattice that occurs during adsorption of a water molecule. The magnitude of the distortion was determined experimentally on the basis of diffractometric measurements. For this purpose we employed the method of x-ray diffractometry using a DRON-2 diffractometer. Disperse flint was the object of investigation. The procedure of the measurements is described in [6].

The parameters and volume of the crystal lattice of quartz (flint of upper Cretaceous rock) were determined from the two reflections (112) and (203) by the formulas for a cubic system. The experimental results are presented in Fig. 3. As follows from the figure, the relative magnitude of the distortion of the crystal lattice of quartz (flint) attains a maximum at a moisture content of 2.3% and amounts to 0.00452 for this amount of water..

The experimental magnitude of the crystal lattice distortion was used to calculate the transverse charge that arises due to the shift of atoms within the lattice and characterizes the redistribution of charge between the atoms of oxygen and flint. This calculation was made according to Harrison [7].

In [7] the author uses extensively the notion of a transverse charge that determines the connection between transverse vibrations of the lattice and light waves and that characterizes the local polarization of atoms arising upon their relative displacement in the lattice.

The general expression for the transverse charge in any atom of the lattice and, in particular, in an oxygen atom is written as follows:

$$e_T = \sqrt{e_x^2 + e_y^2 + e_z^2}\,, \qquad (1)$$

where e_x, e_y, e_z are the components of the transverse charge in the direction of the coordinates.

According to [7],

$$e_x = Z^* + (3 \sin \theta_0 - 1) \beta_{px} (1 - \beta_{px}^2 + 3 \sin \theta_0 \beta_{pz}) (1 - \beta_{pz}^2) , \tag{2}$$

$$e_y = Z^* , \tag{3}$$

$$e_z = Z^* + 3 \cos^2 \theta_0 \beta_{px} (1 - \beta_{px}^2) + (3 \cos^2 \theta_0 - 1) \beta_{px} (1 - \beta_{pz}^2) , \tag{4}$$

$$Z^* = \beta_{pz} + \beta_{px} , \tag{5}$$

$$\beta_{pz} = W_3 (2 W_2^2 \cos^2 \theta_0 + W_3^2)^{-1/2} , \tag{6}$$

$$\beta_{px} = W_3 (2 W_2^2 \sin^2 \theta_0 + W_3^2)^{-1/2} . \tag{7}$$

Here Z^* is the effective charge of an oxygen atom in the lattice; β_{px} and β_{pz} are the fractions of the degree of ionicity of the bonds in the crystal; W_2 is the energy of a covalent bond in the crystal and W_3 the energy of an ionic bond in the crystal; θ_0 is the angle between the directions of Si–Si and Si–O.

The angle θ_0 changes upon deformation of the lattice. The value of θ_0 can be found as follows:

$$\frac{\Delta V}{V} = \Delta \theta_0 \tan \theta_0 , \tag{8}$$

where ΔV is the maximum change in volume (the maximum deformation) of an elementary cell. But simultaneously with a change in the angle θ_0 the length of the Si–O bond in the lattice changes. This change is determined thus:

$$\Delta d = d \Delta \theta \tan \theta_0 . \tag{9}$$

The energy of a covalent bond in the crystal depends on the length of the bond in the following way:

$$W_2 = \frac{c}{d^2} , \tag{10}$$

where c is a constant.

Thus, knowing the change in the angle θ_0, it is possible to determine the change in all the parameters entering in formulas (2)-(7), using for the calculation the values of these parameters at $\Delta V / V \to 0$ obtained from data of the Generalized Periodic System of Elements [7]. Results of the calculations are presented in Table 2.

Thus, due to the deformation of the SiO_2 lattice upon adsorption of water molecules the change in the transverse charge in an oxygen atom of the lattice is $\Delta e_T = 0.053\ e$. We now determine the change in the charge of a water molecule (the change in the unified atomic population) as a result of its adsorption on flint. For this purpose, we shall use the equation for the dipole moment that was derived in [3, 5]:

$$\Delta e_T = 0.053 \mathrm{e} .$$

$$M_e (\alpha , r) = 2 e r f_0 \left(\frac{r}{r_0} \right)^6 \cos \frac{\alpha}{2} - $$

$$- 4 \left[1 + f_0 \left(\frac{r}{r_0} \right)^6 \right] e \frac{\sqrt{- \cos \alpha}}{1 - \sqrt{\cos \alpha}} \cos \frac{\alpha}{2} \left(a_{sp} - r_0 + \frac{r}{2} \right) +$$

$$+ \frac{4 e \sqrt{- \cos \alpha}}{\cos^2 \frac{\alpha}{2} - \cos \alpha} \cos \frac{\alpha}{2} \left(\bar{x}'_{0_{sp}} + \frac{r - r_0}{2} \right) , \tag{11}$$

where r is a length of the valence bond in a water molecule in the water–flint system; r_0 is the length of a valence bond in an isolated water molecule, $r_0 = 0.96$ Å; e is the electron charge; f_0 is the charge of a bond at $r = r_0$; α is the magnitude of a valence angle; a_{sp}, $\bar{x}'_{0_{sp}}$ are parameters that are used to calculate the dimensions of the region of overlap of atomic orbitals and are determined from the coordinates of the point charges in an H_2O molecule.

We determine the value of the charge for each component of the dipole moment. According to [3]:

TABLE 2. Values of the Parameters Needed to Calculate the Electronic Structure of SiO_2, Obtained from the Generalized Periodic System, with Account for the Distortion of the Crystal Lattice

Parameter	$\Delta V/V \to 0$	$\Delta V/V = 0.00452$ (maximum value established in the experiment)
d, Å	1.61	1.617
Θ_0, deg	18.0	18.800
W_2, eV	10.95	10.850
W_3, eV	2.930	2.930
β_{px}	0.520	0.510
β_{pz}	0.200	0.198
Z^* (oxygen)	0.720	0.708
e_T	2.257	2.204

$$M_e = M_{e_1} + M_{e_2} + M_{e_3} \tag{12}$$

where M_{e_1} is the component characterizing the ionic bond in the O–H group; M_{e_2} is the component of overlap in the same O–H group; M_{e_3} is the component of the unshared pair in the oxygen atom.

In the first component of the dipole moment

$$e_1 = \frac{ef_0 r \left(\frac{r}{r_0}\right)^6 \cos\frac{\alpha}{2}}{r \cos\frac{\alpha}{2}} = ef_0 \left(\frac{r}{r_0}\right)^6, \tag{13}$$

i.e., the charge is independent of the valence angle α and is determined by the unified electron population of the hydrogen atom.

According to Herzberg [8], the unified atomic population (the electron charge of the oxygen atom) in a water molecule at $\alpha = 104.5^\circ$ is 8.349 a.u. Then $e_2 + e_3 = M_{e_2}/r_2 + M_{e_3}/r_3 = 8.349$ a.u. (r_2 and r_3 are the distances from the oxygen atom nucleus to the centers of the distribution of the electron charge of the atom in different directions), $M_{e_2} = -0.5587D$, $M_{e_3} = 1.6365\ D$, $r_3 = 0.179$ Å, and then $e_3 = 9.4052$ a.u., $r_2 = 0.259$ Å, $e_2 = -1.0561$ a.u.

In adsorption of a water molecule on flint α attains the value 113°. When $\alpha = 113^\circ$, $M'_{e_2} = -0.5556D$, $r_2 = 0.529$ Å, $e'_2 = -1.0503$ a.u., $M'_{e_3} = 1.6571\ D$, $r_3 = 0.179$ Å, $e'_3 = 9.5236$ a.u. Then the change in the electron charge of the oxygen atom of a water molecule due to its adsorption amounts to $\Delta e_{H_2O} = e'_2 + e'_3 - e_2 - e_3 = 0.1249$ a.u. or $0.0259\ e$.

Assuming that one oxygen atom of the SiO_2 crystal has interacted with two H_2O molecules by the time of the development of the maximum distortion, we obtain $\Delta e_T = 2\Delta e_{H_2O}$. But $\Delta e_T = 0.053\ e$ and $2\Delta e_{H_2O} = 0.052\ e$, i.e., $\Delta e_T \approx 2\Delta e_{H_2O}$.

Thus, the reasons for the formation of different valence angles in a water molecule adsorbed on the surface of different minerals become clear. These differences are caused by the degree of the change in the energy of the bond between the atoms in the crystal, i.e., by the different degree of compliance of the crystal under the effect of water molecules. It should be noted that the maximum value of $\Delta V/V$ for γ-Al_2O_3 is 0.0026, and the magnitude of the valence angle in an adsorbed water molecule on this mineral is $\alpha = 107^\circ$.

The experimental and predicted data presented in the present work for the parameters of the structure of the liquid water and adsorbed water in the water–flint system characterize a form of flint that creates a maximum value of the pH of water of 11.5. Results of investigating other forms of flint that give maximum values of pH of 12.5–13.5 will be presented in later publications.

Let us now consider works in which the structures of hydroxonium and OH-groups in liquid water and ice were investigated.

In [9] it is stated that a singly hydrated proton (H_3O^+) can have a length of an OH-bond of 0.963 Å and an HOH angle of 112.5°, and it is also noted there that the greatest stability of the $H_5O_2^+$ complex is observed for a length of an O–H...O bond of 2.36 Å.

In [10] the authors investigated the influence of the cooperative effect for H-bonds on the geometry of clusters that model the ionic defect H_3O^+ in an ice crystal. From their calculations it follows that the geometry of the H_3O^+ ion turns out to be intermediate between the plane and tetrahedral geometries with HOH valence angles of 115°; the spacing between neighboring atoms of oxygen – the H_3O^+ defect and H_2O – is 2.43 Å, the charge of the central ion (hydrogen in the defect) attains 0.63 *e* instead of 1.0 *e*, the magnitude of the electron density transferred to links of the chain from attached H_2O molecules is 0.04 *e*.

In [11] the geometry of clusters modeling the ion defect OH^- in an ice lattice was studied. From the calculations it follows that the spacing between neighboring oxygen atoms – the OH^- defect and H_2O – is 2.42 Å, and the magnitude of the electron density transferred to links of the chain from attached H_2O molecules is 0.05 *e*.

Comparing the results of our calculations of the parameters of the structure of water (Fig. 2, Table 1) with the calculations performed in [10, 11] we see that particles of highly dispersed flint occurring in water serve as a source of further dissociation of water molecules into hydroxonium and hydroxyl ions, since upon adsorption of water on the flint surface the water molecules deform and acquire a geometry close to that of the defect H_3O^+. But simultaneously capture of hydroxonium ions will occur on the surface of the highly dispersed flint with active transfer of charge from the oxygen atom of the crystal lattice of the flint (as follows from our calculations of the transverse charge in an SiO_2 crystal) to the central ion of H_3O^+. Precisely this process creates an excess of OH-groups in water.

In essence, a similar mechanism of capture of ahydroxonium ion not by flint but rather by nondissociated molecules [MeOH] is described in [12].

Our technique for obtaining alkali water seems to be possible not just with the use of flint. Other natural minerals may also be employed for this purpose, but justification of their use will require considerable theoretical and applied investigations.

NOTATION

m, mass of the solid phase (flint); M, mass of the solid phase and water; b, r, α, M_e, spacing between hydrogen atoms, length of a valence bond, valence angle, and dipole moment in a water molecule, respectively; $2a$, spacing between the oxygen atoms of neighboring water molecules; R, length of a hydrogen bond; θ, angle of bend of hydrogen bond; ΔU, change in the potential energy of the vibration of water molecules; T_1, T_1^0, longitudinal relaxation time of protons of water in NMR spectra (in the case of contact of water with a solid-phase surface and in the absence of a solid phase); e, electron charge.

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