Journal of Engineering Physics and Thermophysics, Vol. 67, Nos. 5-6, 1994

THEORETICAL FOUNDATIONS OF A METHOD OF PRECIPITATION OF INORGANIC SALTS IN WATER UNDER THE INFLUENCE OF A DISPERSED SOLID (SILICA)

P. P. Olodovskii

UDC 541.1:42

A method of precipitation of inorganic salts is proposed based on NMR-spectroscopic investigations and calculations of the structure of water in contact with silica particles, as well as on estimates of the content of metal ions in the water.

The present work continues the investigations of [1–3]. In [3] the following general expression was obtained for estimating precipitation or dissolution of salts in water under the influence of solid phases (e.g., silica):

$$\frac{c}{c_0} = \frac{\rho^2 g^3 Me^6}{\rho_0^2 g_0^3 Me_0^6} . \tag{1}$$

The parameters with the subscript 0 refer to the systems in which the liquid does not interact with the surface of the solid phase.

At the present time we are developing two technologies for precipitating salts of inorganic compounds that are based on the use of silica. The first technology utilizes silica with particle dimensions of 1-10 mm (coarse-grained silica), whereas the second one utilizes fine-grained silica. The present communication presents the results related to the first technology.

Gray silica of the Upper Cretaceous layer was used as the subject of the study. For the salts we chose those of basic metals: KCl, NaCl, $CaCl_2$, $MgCl_2$, as well as salts of complementary metals: $AlCl_3$, $Zn(CH_3COO)_2$, $BaCl_2$, $SrCl_2$, CsCl, $CdCl_2$, $Pb(NO_3)_2$ with a concentration of 10^2-10^{-2} mg-eq/liter.

The first stage of the investigations consisted in a study of the effect of silica and the salts specified above (each individually) on the parameters of the structure of water. In the second stage the effect of silica and the salts was also studied, but initially we estimated the change in the parameters of the water structure under the effect of silica and salts of the basic metals with the following concentrations: $Ca^{2+}-3$, $Mg^{2+}-1$, $Na^{+}-1$, and $K^{+}-1$ mg-eq/liter; then salts of the complementary metals (each individually) with concentrations of 0.5-0.05 mg-eq/liter were introduced into the composition of the solution of salts of the basic metals. And, finally, in the third stage of the studies the effect of silica and the salts was investigated in cases where all salts or a group of salts of the complementary metals were introduced simultaneously into the composition of the solution of salts of the basic metals.

The concentrations of salts of the basic metals were chosen based on an analysis of data from "The State Water Cadastre on the Quality of Surface Waters."

The experimental investigations were based on measurements of the longitudinal relaxation times of water molecules in contact with the surface of a solid phase (silica) obtained from high-resolution NMR spectra in the pulsed regime, as well as on direct measurements of the content of metal ions in water by means of atomic absorption spectroscopy.

Central Research Institute of Multipurpose Utilization of Water Resources, Minsk, Belarus.Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 67, Nos. 5-6, pp. 437-445, November-December, 1994. Original article submitted July 12, 1993.

In all the experiments the ratio of the mass of silica to the mass of the whole system was taken equal to $m/M = 0.3$.

Using results of NMR spectroscopic measurements, the relative values of the longitudinal relaxation times T_1/T_1^0 were estimated for water molecules as a function of the original concentrations c_0 of metal ions in solutions of salts. The equation for calculating T_1/T_1^0 is as follows:

$$\frac{T_1}{T_1^0} = \frac{b^6}{b_0^6} \left[\frac{5a_0^2 + 3\pi b_0^6 N_0 a_0^{-1}}{5a^2 + 3\pi b^6 N_0 a_0^{-1}} \right], \tag{2}$$

where $b = 2r \sin \alpha/2$; $b_0 = 2r_0 \sin \alpha_0/2$. The parameters with the subscript 0 refer to reference systems.

In the preceding works [1–3] in the mineral-water systems r_0 was taken constant and equal to 0.96 Å. The presence of ions in the water is responsible for a change in r; consequently, in order to determine the parameters of the water structure one should use in addition to Eq. (2) an equation for the potential energy of molecular vibrations that accounts for changes in the length of the valence bond and the valence angle.

It can be written down as follows:

$$\Delta U = K_{rr}(r - r_0) + \frac{1}{2} K_\alpha r^2 (\Delta\alpha)^2. \tag{3}$$

However, the change in the potential energy of the molecular vibrations is also caused by a change in the mean bending of the H-bond and its length. Then, according to [4],

$$\Delta U = \frac{1}{2} K_\theta (R - r)\, r\, (\Delta\theta)^2 + 3\frac{\Delta R}{2.76} + 162 \left(\frac{\Delta R}{2.76} \right)^2 - 195 \left(\frac{\Delta R}{2.76} \right)^3, \tag{4}$$

where $\Delta R = R - R_0$; $\Delta\theta = \theta - \theta_0$.

It would appear reasonable that

$$K_{rr}(r - r_0) + \frac{1}{2} K_\alpha r^2 (\Delta\alpha)^2 = \frac{1}{2} K_\theta (R - r)\, r\, (\Delta\theta)^2 + 3\frac{\Delta R}{2.76} + 162 \left(\frac{\Delta R}{2.76} \right)^2 - 195 \left(\frac{\Delta R}{2.76} \right)^3. \tag{5}$$

To use Eq. (5) one should know R_0 and θ_0 corresponding to $\Delta U = 0$ (in this case $r_0 = 0.96$ Å). According to [5], in the ensemble of water J-structures at 300 K R_0 can be estimated with high probability as 1.825 Å, and the value of the angle φ of O...O—H is defined within the framework of the model of deformed H-bonds [4] as 26.8° at 300 K. Then it easy to show that $\theta_0 = 40.52°$ and $a_0 = 1.315$ Å. In order to determine the parameters α, r, R, θ from Eqs. (2) and (5) we proceeded from two principles: 1) those values of the parameters were admitted for which the change in the potential energy of molecular vibrations turned out to be minimum; 2) $R < R_0$ was taken at T_1/T_1^0 (exper.) > 1, and $R > R_0$ was taken at T_1/T_1^0 (exper.) < 1.

We proceed now to calculations of the parameters that appear in the Eq. (1). According to [4], the Kirkwood parameter g is determined as follows:

$$g = 1 + \sum_{i=1}^{\infty} N_i 3^{1-i} \cos^{2i}\frac{\alpha}{2} \left(1 - \frac{KT}{K_\varphi} \right)^{2i}, \tag{6}$$

where N_i is the number of adjoining molecules in the i-th coordination sphere; K_φ is the bending constant of the H-bond.

In order to calculate N_i and K_φ we turn to Pople's work (discussed in [4]), in which a model of liquid water is presented. Within the framework of this model the majority of H-bonds are considered as deformed rather than broken. In order to facilitate the explanation of the observed radial distribution on the basis of bending of H-bonds, Pople supposed that all the molecules in liquid water are connected by H-bonds with four neighbors, each of them being at a fixed distance $\overline{R}_0$. In accordance with this assumption, the closest neighbors should be situated at a distance $\overline{R}_0$ from the central molecule. However, the distance from the central molecule to the secondary (i.e., next to the closest neighbors), tertiary, and more distant neighbors will depend on the degree of bending of the hydrogen bonds. An H-bond in Pople model is considered as undeformed if the O—H group of the donor water molecule and the unshared electron pair that participates in H-bond formation lie along the oxygen-oxygen line of two molecules. In other words, the bending energy of an H-bond equals zero when all the angles of H_2O ...H_2O...H_2O are tetrahedral, as in the case of ice I. When the direction of the unshared pair deviates from the oxygen-oxygen line by the angle φ the H-bond is deformed and the energy of the system is increased by the quantity $\Delta U = K_\varphi(1 - \cos\varphi)$.

Pople considered the observed radial distribution function in the region of $\overline{R} = 0.6$ Å as a sum of contributions from the closest, secondary, and tertiary neighboring molecules and derived expressions for these contributions and then found a correspondence between the sum of the contributions and experimentally obtained distribution functions. In doing so, it was supposed that the four closest neighboring molecules are distributed within a Gaussian band at $R = R_0$. By varying the number of adjoining molecules, the H-bond bending constants, and the parameters of the Gaussian distribution, Pople achieved a good fit to the experimental distribution functions. The best fit was achieved using the following values of the parameters: a force constant of hydrogen bond bending of $3.78 \cdot 10^{-13}$ erg/rad^2, with 11 secondary and 22 tertiary neighboring molecules. Pople introduced one more assumption on the possibility of describing distorted hydrogen bonds by means of classical statistics and calculated the mean angle φ between the direction of the O—H bond and direction of O...O of adjoining molecules connected by a hydrogen bond. The following expression for the angle was obtained:

$$\cos\varphi = \coth\left(\frac{K_\varphi}{KT} - \frac{KT}{K_\varphi}\right).$$

Then

$$g = 1 + 4\cos^2\frac{\alpha}{2}\cos^2\varphi + \frac{11}{3}\cos^4\frac{\alpha}{2}\cos^4\varphi + \frac{26}{9}\cos^6\frac{\alpha}{2}\cos^6\varphi. \tag{7}$$

The value of the angle φ is found from the expression

$$\sin\varphi = \frac{R\sin\theta}{2a}.$$

Let us find the dependence of the dipole moment M_e of the water molecule simultaneously on the value of the valence angle (which is already done in [3]) and on the length of the valence bond.

It is shown in [3] that

$$M_e = f(\alpha)\,|_{r=0.96\text{Å}} = \text{erf}\cos\frac{\alpha}{2} - 4(1+f)\frac{\sqrt{-\cos\alpha}}{1-\cos\alpha}\cos\frac{\alpha}{2}\,\bar{x}_{sp}\,e + \frac{4e\sqrt{-\cos\alpha}}{\cos^2\frac{\alpha}{2} - \cos\alpha}\,\bar{x}'_{sp}\cos\frac{\alpha}{2}. \tag{8}$$

Recall that f (the bond charge) $= b_1^2 - a_1^2$, where b_1 and a_1 are the normalized coefficients in the molecular orbitals of the O—H bond. At $r = 0.96$ Å the mean value f between f_1 for the binding orbital $\overline{\varphi}_5(b_2)$ and f_2 for the molecular binding orbital $\overline{\varphi}_3(3a_1)$ is found to be equal to 0.133.

The question arises as to how f depends on the bond length in the water molecule. It should be emphasized here that the normalized coefficients a_1 and b_1 in the molecular orbitals of the O—H bond characterize the charge of the atoms and the order of the bond. At the same time, as follows from the quantum theory of the force constants in a molecule [7], these constants (e.g., K_{rr}) also dependent linearly on the density matrix of the electron distribution within the bond, i.e., on the charge of the atoms and the order of the bond.

It is shown in [6] that for the XH bond the following condition is satisfactorily fulfilled:

$$K_{rr} = \frac{b_0}{r^3}, \tag{9}$$

where b_0 is a constant. Therefore one can set $f = f_0(r/r_0)^6$, where f_0 is the bond charge for $r_0 = 0.96$ Å.

In Eq. (8) $\bar{x}_{sp}$ is the size of the area of overlapping of the atomic orbitals reckoned from the middle of the O—H bond: $\bar{x}_{sp} = a_{sp} - r_0/2$. The value of a_{sp} is determined from the coordinates of the point charges in the H_2O molecule (given, e.g., in [7]). When the length of the O–H bond is changed from r_0 to r it is obvious that

$$\bar{x}_{sp} = a_{sp} - \frac{r_0}{2} + \frac{r - r_0}{2} = a_{sp} - r_0 + \frac{r}{2}.$$

In Eq. (8) $\bar{x}'_{sp}$ is the size of the area of overlapping of the atomic orbitals reckoned from the nucleus of the oxygen atom. When the length of the O—H bond is changed from r_0 to r it is obvious that

$$\bar{x}'_{sp} = \bar{x}'_{0_{sp}} + \frac{r - r_0}{2},$$

where $\bar{x}'_{0_{sp}}$ is determined from the coordinates of the point charges in the H_2O molecule.

The expression for $M_e = f(\alpha, r)$ can be written in the following manner:

$$M_e(\alpha, r) = 2\,\mathrm{erf}_0\left(\frac{r}{r_0}\right)^6 \cos\frac{\alpha}{2} - 4\left[1 + f_0\left(\frac{r}{r_0}\right)^6\right] e\,\frac{\sqrt{-\cos\alpha}}{1 - \cos\alpha} \times$$
$$\times \cos\frac{\alpha}{2}\left(a_{sp} - r_0 + \frac{r}{2}\right) + \frac{4e\sqrt{-\cos\alpha}}{\cos^2\frac{\alpha}{2} - \cos\alpha} \times \cos\frac{\alpha}{2}\left(\bar{x}'_{0_{sp}} + \frac{r - r_0}{2}\right). \tag{10}$$

We proceed now to calculations of the density of water in a system of silica and aqueous solutions of salts.

Using Eq. (2) and (5) determine from minimization of ΔU the distances between the oxygen atoms of adjoining H_2O molecules. This distance is found to be equal to $2a_1 = \sqrt{R^2 + r^2 + 2Rr\cos\theta}$. The value of $2a_1$ depends on the composition and concentration of ions in water. Let us estimate the effect of $2a_1$ on the density of water. To do this, within a certain approximation we assume the structure of water to be similar to that of ordinary ice (ice I). The crystalline structure of the system of ice I belongs to the hexagonal syngony with the spatial group Pb^3/mnc. The parameters of the crystalline lattice are $\bar{a}_0 = 4.48$ Å, $C'_0 = 7.31$ Å. The number of molecules in a unit cell equals 4. The closest coordination sphere contains four oxygen atoms in a horizontal layer; at the same time at a somewhat different distance three oxygen atoms are situated on each side above and below. This distance can be calculated using the formula

$$d = \sqrt{\left(\frac{\bar{a}_0^2}{3} + \frac{(C'_0)^2}{4}\right)} \quad \text{or} \quad d_0 = 0.9995\bar{a}_0.$$

The change in the distance between two adjoining oxygen atoms $\Delta 2a_1$ is distributed uniformly between the upper and lower layers of these atoms. Then the new value is $d = \bar{a}_0 0.9995 - \Delta a_1$, and the new value of the crystalline lattice constant is $\bar{a} = (\bar{a}_0 0.995 - \Delta a_1)/0.9995$. The volume of an elementary unit of the hexagonal crystalline lattice $V_0 = \bar{a}_0^2 C'_0 0.866$. Consequently, the new volume of this lattice that appears as a result of the change in the distances between two adjoining oxygen atoms equals

$$V = \left[\frac{\bar{a}_0 0.9995 - \Delta a_1}{0.9995}\right]^3 \frac{C'_0}{\bar{a}_0}.$$

The new density of water that appears as a result of these changes is found to be equal to

$$\rho = \frac{\bar{a}_0^3}{\left[\dfrac{\bar{a}_0 0.9995 - \Delta a_1}{0.9995}\right]^3}. \tag{11}$$

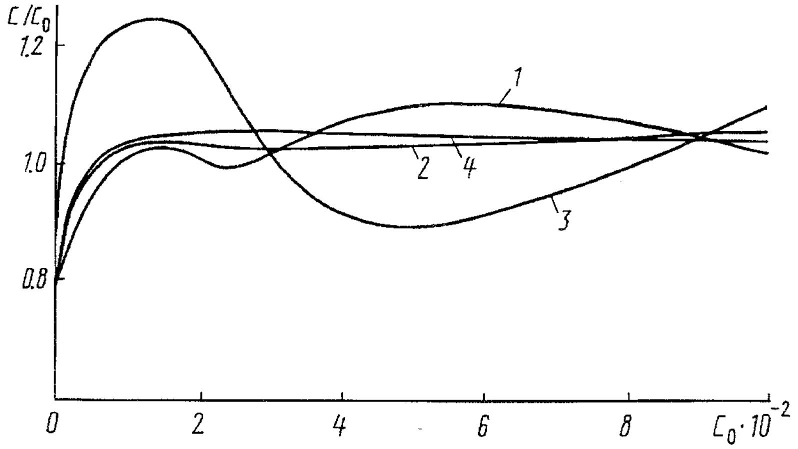

Fig. 1. Ddegree of precipitation (or dissolution) of salts of basic metals in contact with silica as a function of the original ion concentration in the solution: 1) KCl; 2) NaCl; 3) $CaCl_2$; 4) $MgCl_2$. c_0, mg-eq/liter.

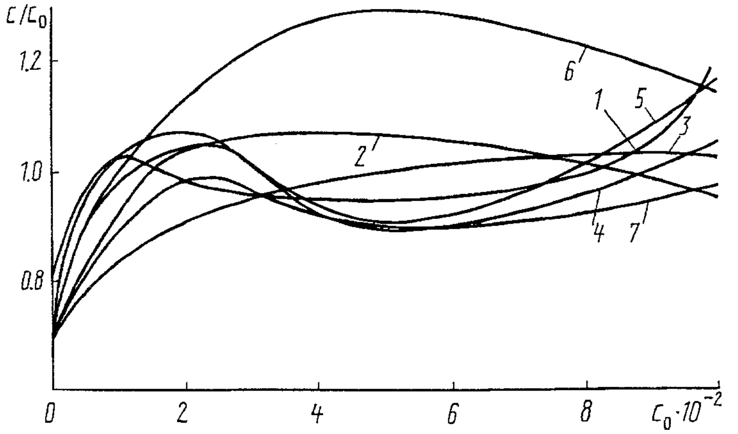

Fig. 2. Degree of precipitation (or dissolution) of salts of complementary metals in contact with silica as a function of the original ion concentration in the solution: 1) $Zn(CH_3COO)_2$; 2) $Pb(NO_3)_2$; 3) $AlCl_3$; 4) CsCl; 5) $CdCl_2$; 6) $BaCl_2$; 7) $SrCl_2$.

Using Eqs. (1), (2), (7), (10), and (11) we calculate the degrees of precipitation of salts of the basic and complementary metals dissolved individually in distilled water. The results are presented in Figs. 1 and 2.

Without going into the details of the complicated mechanism of interaction of ions with water molecules in the liquid phase (such mechanisms are considered in a series of works, e.g., in [8]) we present a brief analysis of the results of calculationsof c/c_0. As follows from Fig. 1, c/c_0 for sodium and manganese ions is close to 1 in the region of concentrations 0.05-0.01 mg-eq/liter, and only within the concentration range of 0.0-0.01 mg-eq/liter does it smoothly tend to its limit of 0.69 for pure water in contact with silica [3].

A different character of the dependence of c/c_0 is observed for potassium ions and especially for calcium ions. For calcium ions at a concentration of 0.005 mg-eq/liter the degree of precipitation of calcium salts equals 0.88, whereas at a concentration of 0.001 the solubility increases to 1.28.

As follows from Fig. 2, the ions Zn^{2+}, Cs^{+}, Cd^{2+}, and Sr^{2+} demonstrate approximately the same course of the dependence of c/c_0. Sharp distinctions are observed for barium ions: at a concentration of 0.005 mg-eq/liter the degree of solubility of barium salts reaches 1.43 (this distinctive feature of barium will be manifested in studies of other systems as well). Summarizing the results of the first stage of the investigations, it should be noted that no conclusions of practical importance follow from the results obtained. However, the method developed here for the calculation of the water structure parameters affected by silica and the ions was used in the second stage of the investigations.

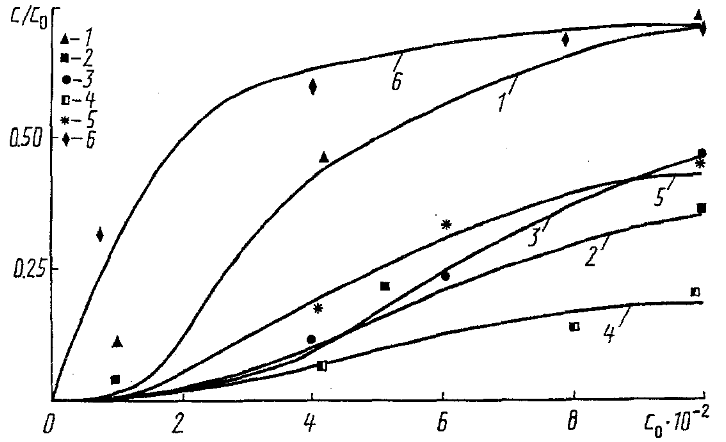

Fig. 3. Degree of precipitation of salts of complementary metals present individually in the solution of salts of basic metals in contact with silica as a function of the ion concentration in the solution: 1) $Zn(CH_3COO)_2$; 2) $Pb(NO_3)_2$; 3) $AlCl_3$; 4) CsCl; 5) $CdCl_2$; 6) $BaCl_2$; 7) $SrCl_2$.

Recall that in this stage we estimate change in the parameters of the water structure under the effect of silica and salts of the complementary metals present in the composition of the solution of salts of the basic metals.

The following parameters of the water structure are determined: α, r, R, M_e, ΔU, and ρ, as well as the degree of precipitation of salts of the basic metals $(c/c_0)_1$ and the degree of precipitation $(c/c_0)_2$ of salts of the basic and complementary metals in combination. The degree of precipitation of just the complementary metals was calculated in the following manner.

Let the original molar concentration of salts of the basic metals be m_0; then the concentration of salts of the basic metals whose solution is in contact with the solid phase (e.g., silica) will be equal to $m_0(c/c_0)_1$.

Let the original concentration of the salt of a complementary metal dissolved in the solution of salts of the basic metals be m_0', and the concentration of the salt of the same metal whose solution is in contact with the solid phase be m_0''.

Then

$$\left(\frac{c}{c_0}\right)_2 = \frac{m_0\left(\frac{c}{c_0}\right)_1 + m_0''}{m_0 + m_0'},$$

or

$$\left(\frac{c}{c_0}\right)_2 = \frac{\frac{m_0}{m_0'}\left(\frac{c}{c_0}\right)_1 + \frac{m_0''}{m_0'}}{\frac{m_0}{m_0'} + 1}.$$

Denoting $m_0''/m_0' = (c/c_0)_3$, we obtain

$$\left(\frac{c}{c_0}\right)_3 = \left(\frac{c}{c_0}\right)_2\left(\frac{m_0}{m_0'} + 1\right) - \left(\frac{c}{c_0}\right)_1\frac{m_0}{m_0'}. \tag{12}$$

In Eq. (12) m_0/m_0' is the ratio of the molar concentration of salts of the basic metals to the molar concentration of the salt of the complementary metal. In deriving Eq. (12) the degree of precipitation or dissolution of salts of the basic metals was supposed to be independent of the addition of the salt of the complementary metal. This

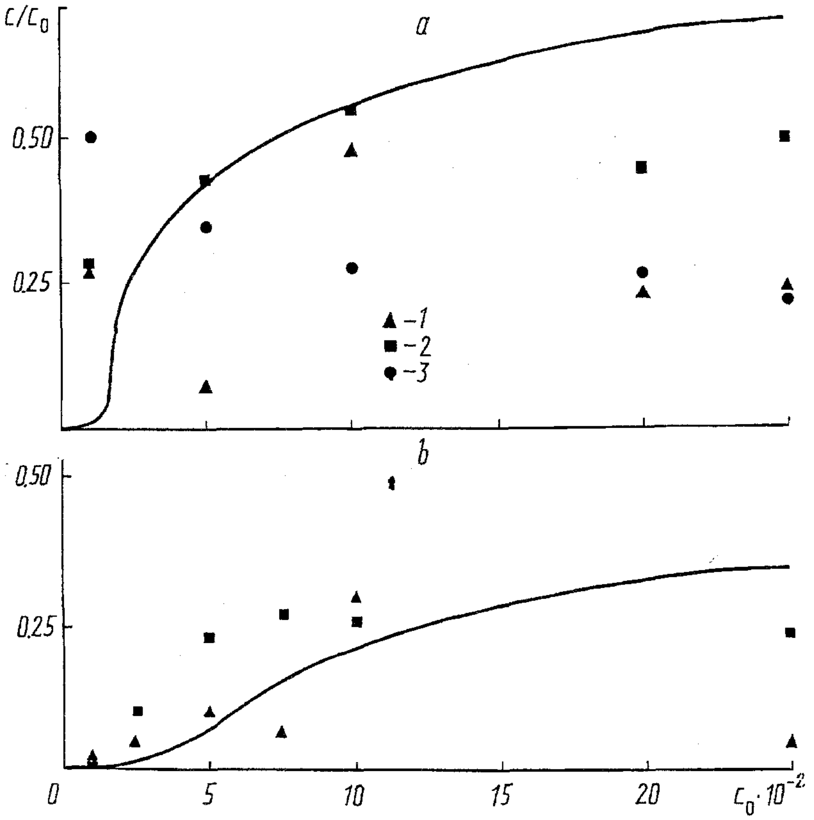

Fig. 4. Degree of precipitation of salts of complementary metals (a: aluminum, lead, cadmuium, zinc, cesium, and strontium; b: lead, cadmium, and zinc) present simultaneously in the solution of salts of basic metals (calcium, manganese, potassium, and sodium) in contact with silica as a function of the original total concentration of ions of the metals in the solution. The curves were obtained from NMR data and calculations; 1, 2, and 3) points corresponding to the degrees of precipitation of lead, cadmium, and zinc obtained from atomic-absorption analysis data.

hypothesis was confirmed for the zinc, lead, cesium, aluminum, and cadmium salts but was not confirmed for the strontium salts. Therefore in the case of strontium a correction was introduced into $(c/c_0)_1$ based on the linearization of the calculated values of $(c/c_0)_3$.

The calculated values of the degree of precipitation of salts of the complementary metals are represented in Fig. 3 by curves 1-6, and results of direct measurements of the concentration of zinc, lead, aluminum, cesium, and strontium by emission spectral analysis in salt solutions in contact and not in contact with a silica surface are shown by symbols.

As follows from this figure, a considerable degree of purification of the water from salts of the complementary metals is observed. Thus, at a concentration of $1 \cdot 10^{-2}$ mg-eq/liter, zinc, lead, aluminum, cesium, cadmium, and strontium ions are practically removed from water. At the same time silica stimulates dissolution of barium salts in the solution of salts of the basic metals.

Recall that the calculated values of c/c_0 were obtained from NMR spectroscopy data. This method encounters considerable difficulties when applied to paramagnetic ions. The results of measurements of the degree of precipitation of ferrous salts in the solution of salts of the basic metals under the effect of silica by the method of emission spectral analysis are as follows:

$$\text{at} \quad c_0 = 1 \cdot 10^{-1} \quad \text{mg-eq/liter} \quad c/c_0 = 0.19\,,$$

$$\text{at} \quad c_0 = 5 \cdot 10^{-2} \quad \text{mg-eq/liter} \quad c/c_0 = 0.13\,,$$

$$\text{at} \quad c_0 = 1 \cdot 10^{-2} \quad \text{mg-eq/liter} \quad c/c_0 = 0.10 .$$

And finally, the third stage of the investigations is devoted to the study of the process of joint precipitation of a series of salts of the complementary metals in the solution of salts of the basic metals.

The curve in Fig. 4a represents the calculated degrees of precipitation of lead, cadmium, zinc, aluminum, cesium, and strontium salts, and whereas the curve in Fig. 4b represents the calculated degrees of precipitation of lead, cadmium, and zinc present simultaneously in the solution of calcium, manganese, potassium, and sodium salts. The symbols in these figures represent the degrees of precipitation of individual salts according to data of emission spectral analysis.

It should be noted that the dependences represented by the curves in Fig. 4 can be fit with the function

$$\frac{c}{c_0} = A \exp(-mc_0^n) ,$$

where the empirical parameters A, m, and n are found using least-squares fitting of the function to the calculated data obtained using Eqs. (1), (2), (7), and (10)-(12).

Thus, we have succeeded in showing that in a system of silica and aqueous solutions of inorganic salts intense precipitation takes place for a series of metals: aluminum, iron, cadmium, cesium, zinc, lead, and strontium. These processes are extended in time and usually decay (as our experiments have shown) on the sixth or seventh day.

The technological system for purifying water is not complicated, the process itself does not require electric energy consumption, except for the consumption for transferring water to the settlers. Silica does not require regeneration in the technological process, and one load of silica can work for a long time. The greatest purification efficiency is achieved for the silica particle size of 1 mm.

NOTATION

c, c_0, final and original ion concentrations in the solution; g, Kirkwood correlation parameter in the equation for determination of the static dielectric constant of water; M_e, dipole moment of the water molecule; T_1, T_1^0, longitudinal relaxation time of protons of water in NMR spectra (for the case of water in contact with the surface of the solid phase and in the absence of the solid phase, respectively); b, distance between the protons in a water molecule; r, valence bond length in a water molecule; α, valence angle; a, half of the distance between the oxygen atoms of neighboring molecules; N_0, Avogadro's number; ΔU, change in the potential energy of molecular vibrations; R, length of the hydrogen bond; K_{rr}, force constant of the valence bond; K_α, force constant of the valence angle; K_θ, force constant of the angle at the hydrogen bond; θ, bending angle of the hydrogen bond; e, charge of an electron; $\bar{a}$, C_0', parameters of the crystalline lattice of ice I; ρ, density of water.

REFERENCES

1. P. P. Olodovskii and I. L. Berestova, Inzh.-Fiz. Zh., **62**, No.6, 853-858 (1992).
2. P. P. Olodovskii, Inzh.-Fiz. Zh., **62**, No. 6, 859-865 (1992).
3. P. P. Olodovskii, Inzh.-Fiz. Zh., **63**, No. 1, 80-87 (1992).
4. D. Eisenberg and W. Kautzman, Structure and Properties of Water [Russian translation], Leningrad (1975).
5. G. G. Malenkov, A. V. Teplukhin, and V. I. Poltev. Zh. Strukt. Khimii, **30**, No. 4, 79-87 (1989).
6. L. A. Gribov, Introduction to Molecular Spectroscopy [in Russian], Moscow (1976).
7. E. A. Melvin-Hughes, Physical Chemistry [Russian translation], Vol. 1, Moscow (1962).
8. K. P. Mishchenko and G. M. Poltoratskii, Problems of the Thermodynamics and Structure of Aqueous and Nonaqueous Electrolyte Solutions [in Russian], Leningrad (1968).