

MAGNETIC TREATMENT OF WATER: POSSIBLE MECHANISMS AND CONDITIONS FOR APPLICATIONS

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*(Received May 9, 1995. in the final form May 11, 1995, accepted
September 27, 1995)*

Abstract: In this paper, fundamental properties and parameters of water molecules, fine "structure" of water, hydration of ions and nature of the hydrogen bond are reviewed. A model is outlined of possible mechanisms of the effect of relatively weak magnetic fields on the statistically mean number of hydrogen bonds between water molecules, as a result of forbidden triplet–singlet transitions in the Zeeman electron–proton multiplets of the water molecule and its near surroundings. The effect of the influence of the magnetic field on the ion–colloidal subsystems of aqueous environment are analysed. It is shown that the energy of magnetic dipole interaction of colloidal particles of the magnetite type is sufficient for their flocculation and concentration in areas of high gradient of the magnetic field, and for their stability against hydrodynamic disruption of the flocs, possible centres of crystallisation of CaCO_3 . On the basis of the proposed calculations, and also based on data presented by other authors, particularly from ex–Soviet Union, conditions and regimes of anti–scale magnetic treatment of water are reviewed.

BRIEF CHARACTERISTICS OF WATER MOLECULES

A free water molecule H_2O is a three–nuclei formation. Two electrons 1S^2 are localised near oxygen, the other eight $2\text{S}^2\text{P}^6$ move along the lengthened elliptical orbitals. The axes of two orbitals coincide in bonds O–H and axes of the two other undivided electron pairs lie in a plane which is perpendicular to H–O–H and passing through the oxygen nucleus.

Electrostatic model of water molecules can be represented as a regular tetrahedron, in two vortices of which the mass centres of positive charges q_1, q_2 are situated, which are bound to protons, and in two other vortices there are centres of mass of negative charges e_1, e_2 , which are bound to undivided electron pairs. There is an oxygen atom with charge $+Q_0$ at the centre of the tetrahedron.

Table I The main parameters of water molecules

Parameter	Value
Length of O-H bond	$r = 0.96 \times 10^{-10} \text{ m}$
Angle H-O-H	$\alpha = 104.523^\circ$
Dipole moment	$d = 1.84 \pm 0.02 \text{ D} (6.13 \times 10^{-30} \text{ Cm})$
Volume magnetic susceptibility (SI)	$\chi_{xx} = 2.46 \times 10^{-6}$
	$\chi_{yy} = 0.77 \times 10^{-6}$
	$\chi_{zz} = 1.42 \times 10^{-6}$
Polarisability	$\beta = 1.48 \times 10^{-30} \text{ m}^3$
Ionisation potential	$I_w = 20.11 \times 10^{-19} \text{ J} (12.56 \text{ eV})$
Force constant in direction of O-H	$k = 8.256 \times 10^2 \text{ N/m}$
Energy of water formation, 0 K	$-918.333 \text{ kJ/mol} (9.511 \text{ eV})$
Energy of O-H bond, 0 K	$-459.205 \text{ kJ/mol} (4.40 \text{ eV})$
Energy of dissociation H-OH, 0 K	$-493.205 \text{ kJ/mol} (5.11 \text{ eV})$
The lowest energy of vibration	0.198 eV
The lowest energy of rotation	0.005 eV
Thermal energy kT , at $T=293 \text{ K}$	$2.52 \times 10^{-2} \text{ eV}$
Magnetic moment of proton	$\mu_p = 1.411 \times 10^{-26} \text{ A m}^2$
Magnetic moment of electron	$\mu_e = 9.285 \times 10^{-24} \text{ A m}^2$
Magnetic induction created by proton at a distance of 10^{-10} m	$1.4 \times 10^{-3} < B_p < 2.8 \times 10^{-3} \text{ T}$
Magnetic induction created by electron uncompensated spin moment at a distance of 10^{-10} m	$0.93 < B_e < 1.86 \text{ T}$

The main parameters of water molecules are shown in Table I [1]. The spectroscopic characteristics are depicted in Fig. 1 [2]. Every vibration changes the dipole moment and consequently it is active in the IR spectrum. The valency vibration O–H (weak shoulder) at 25° corresponds to the band 3615 cm^{-1} in the IR spectrum, and 3610 cm^{-1} in the combination scattering spectrum at 19°C.

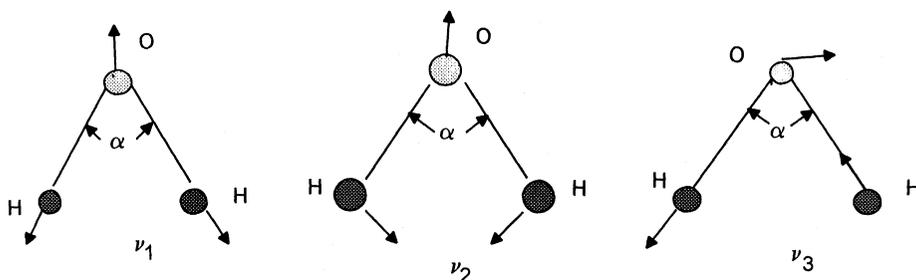


Fig. 1 Normal vibrations of free water molecule (H_2^{16}O).
 $\nu_1 = 3657 \text{ cm}^{-1}$, $\nu_2 = 1595 \text{ cm}^{-1}$, $\nu_3 = 3756 \text{ cm}^{-1}$.

LIQUID WATER AND ITS CHARACTERISTICS

Pure liquid water is a mixture of isotopes H_2^{16}O , H_2^{18}O , H_2^{17}O and HDO. According to this, the content of components in natural water is within the limits of 99.73, 0.20, 0.04 and 0.03% [1].

Distance between the molecules of liquid water, under normal conditions, which was determined on the basis of X-ray data is taken to be 2.76×10^{-10} m. At this distance, the water molecules interact with one another forming hydrogen bond $\text{H} \dots \text{H}-\text{O}-\text{H}$ arising as a result of the interaction between a proton of one of the molecules and an undivided electron pair of the other molecule. Each molecule can form maximum four such bonds which is proved by X-ray data [1].

It was found that in the temperature interval from 1.5 to 90°C, the number of close neighbours is $q = 4.4$. Water is thus a liquid with a pronounced short-range order arising owing to the hydrogen bonds.

Concept of "Water Structure"

When using the concept of "water structure" [1], its meaning must be defined. In view of the fact that we mean a liquid where the mass centres of molecules can produce not only vibrations but also movements at distances exceeding the diameter of a molecule D_m , the relative position and orientation of water molecules continuously changes. That is why the term "water structure" means the relative position of the water molecules averaged over the observation period $\Delta\tau$ of the configuration of the water molecule. By "observation" we also mean an act of a chemical conversion in water, or the effect of an external field on water.

It is possible to highlight several characteristic times:

–time of vibrations of the centre of mass of the molecules, $\tau_v = 10^{-13}$ s

–time of the rotational movement $\tau_r = 10^{-12}$ s

–time of translation of the centres of mass over distances exceeding D_m ,
 $\tau_t = 10^{-11}$ s.

According to this, the molecule configuration in water obtained from averaging over the period of time $\Delta\tau < \tau_v$ is called *I*–(ice) structure, or momentary structure. The result of averaging over a period $\tau_v < \Delta\tau < \tau_t$ is called the *V* (vibration) structure. A configuration obtained by averaging over a period $\Delta\tau > \tau_t$ is called the *D* (diffusion) structure.

X–ray and neutron–spectrographic experiments provide information about the *D*–structure. The same *D*–structure determines the equilibrium and quasi–equilibrium water properties. At the same time, the ion reactions with the conversion time $\Delta\tau < 10^{-11}$ s are determined by the *V* and *I* structures.

Information about the *V*–structure can be obtained also from a study of infra–red and Raman spectra, or of non–elastic scattering of slow neutrons. Thus, if changes of water have a characteristic time $\Delta\tau > 10^{-6}$ s, then only changes of the *D*–structure are meant, which can be determined with the help of corresponding experimental equipment.

To explain X-ray data, different V -structure models are proposed.

1. Nemethy and Scheraga model [3], or the mixed model: a momentary configuration of water at the present moment is a mixture of some number of clusters of water molecules, with completely closed H-bonds and free molecules which are not connected by hydrogen bonds.
2. Samoylov's vacuum model [4], which a special case of the mixed model. It is assumed that in the molecule network with H-bonds, a vacuum is formed which is occupied by free water molecules.
3. Pople's model of distorted hydrogen bonds [5]. It is assumed that all molecules are connected with each other by a flexible network of H-bonds. The dependence of the bond energy on the angle φ of deviation of the hydrogen bond is given by the relation:

$$\Delta U = K\varphi(1 - \cos\varphi)$$

where K is the constant of proportionality. It was found by Pople, from X-ray data, that

$$K = 3.78 \times 10^{-20} \text{ J/rad}^2$$

4. A model of occasional network [6] proposed by Bernal. Every molecule forms four bonds producing thus a non-regular network of ring structures. Rings can have 4, 5, 6 or 7 or more molecules.

Both models no. 3 and 4 are similar since they consider not broken but distorted H-bonds. The models describe well the X-ray data, heat capacity and water heat energy, large dielectric constant and mobility of protons, as well as energy of vaporisation.

There are data, however, that are difficult to explain within the framework of these models. This is a small spread of dielectric relaxation time which can be naturally described by mixed models.

CHARACTERISTICS OF THE HYDROGEN BOND

The energy of the hydrogen bond in liquid medium is found as the difference

$$\Delta E_{\text{hb}} = E(\text{O}-\text{H}) - E(\text{O}-\text{H}\dots\text{O})$$

where $E(\text{O}-\text{H})$ is the energy of the OH group in water, without the H-bond, while $E(\text{O}-\text{H}\dots\text{O})$ is the energy of the OH group with the H-bond.

It is clear that the energy of the H-bond found in this way depends on the pressure, temperature and momentary environment of the water molecule, and assumes a range of values [1]:

$$1.3 < \Delta E_{\text{hb}} < 4.5 \text{ kcal/mol bonds}$$

or

$$5.64 \times 10^{-2} < \Delta E < 1.95 \times 10^{-1} \text{ eV}$$

($T = 293 \text{ K}$, $kT = 2.52 \times 10^{-2} \text{ eV}$)

Different components contribute to the energy of the hydrogen bond. As a rule [7, 8], the main four components of energy are considered:

1. Electrostatic interaction of one of the undivided electron pairs with one of the protons of the neighbouring molecules. This contribution is considered to be large, about 7 kcal/mol bonds.
2. Electron interchange at approach $\text{O}-\text{HA}\dots\text{OB}$; this interchange is accompanied by mutual polarisation of shells. According to the way of calculation, this value changes within one order of magnitude.
3. Repulsion as a result of shell overlap. It is considered that in water this contribution is equal to the first one, as the distance $r_{\text{A}-\text{B}}$ is less than the sum of van der Waals radii.

4. The dispersion influence is also substantial through it is less than the others; its contribution is $\cong -1.5$ kcal/mol bonds.

It must be said that the energy of the H-bond is very sensitive to the non-local effects on the nearest neighbour state. Formation or break of H-bonds in the neighbouring molecules can increase or reduce ΔE_{hb} . It is important that small energy of the H-bond is a result of adding large contributions of electrostatic attraction and non-local repulsion.

ION HYDRATION

By ion hydration we mean all the changes that take place in the water medium during a process of introducing a molecule or ion into the water. There are two approaches to the process of hydration.

1. It is considered that the main factor in the process of hydration is the interaction of an impurity ion or molecule (admixture) with the molecules of water. Hydrated admixture in this model is a complex "admixture + strongly bonded water molecules".
2. It is assumed that the admixture influences mainly the dynamics and the structure of adjoining water volume and does not form strong-bonded complex with water molecules.

Interaction of ions with water molecules and with each other in the same medium must be studied considering their property to form H-bonds with water and the presence of these bonds between the water molecules. In the case of weak hydration, the admixtures substitute water molecules in the H-bond network, or are placed in its internods. Presence of admixture does not change the structure and the dynamics of the H-network substantially.

Under strong hydration the energy of interaction of the molecule with the admixture is larger than between water molecules. The admixture distorts and

partly breaks down the network of the H-bonds and determines the structure and dynamics of the H-network at a considerable distance.

Samoylov [4] proposed to describe the hydration phenomenon as a change of the mean time τ_i in comparison with τ time of the stationary state of the water molecule in a regular network of the H-bonds. Since the random motion of molecules from their temporary equilibrium positions has an activation character, i.e.

$$\tau = \alpha e^{-E/kT}$$

then we obtain

$$\frac{\tau_i}{\tau} = e^{\Delta E_i/kT}$$

where $E_i = E + \Delta E_i$, k is the Boltzmann constant and T is the absolute temperature.

The following situation are thus possible:

1. $\Delta E_i > 0$, $\tau_i > \tau$, positive hydration
2. $\Delta E_i < 0$, $\tau_i < \tau$, negative hydration

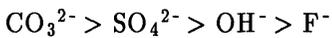
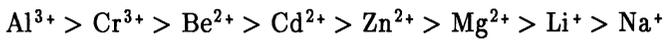
Under positive hydration, the strengthening of the H-bonds in a solution takes place (depression of temperature of the structure), while under negative hydration the H-bonds weaken (temperature of the structure increases).

Concepts of positive and negative hydration can also be used to describe processes of the water molecule sorption border. Table II shows values of the hydration energies ΔE_i (kcal/mol) calculated by [9].

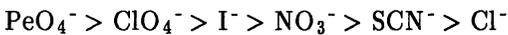
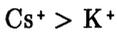
Spectroscopical study of the hydration phenomenon was made by measuring infra-red absorption frequency shift of the deformation vibrations of the O-H group [10]. The authors [10] classified ions by the degree of positive hydration:

Table II The energy of hydration

Ion	ΔE_i (kcal/mol)
Li ⁺	0.56
Na ⁺	0.14
K ⁺	-0.36
Cs ⁺	-0.31
NH ₄ ⁺	-0.35
Ca ²⁺	0.28
Mg ²⁺	0.8
Ba ²⁺	0.02
Cl ⁻	-0.21
NO ₃ ⁻	-0.44
SO ₄ ²⁻	0.15



and by the degree of negative hydration:



Positive and negative hydration phenomena are also accompanied by dissolution of non-electrolytes in water. Positive hydration of the molecules of dissolved gases can explain the diminishing dielectric permeability of the gas-saturated water, the formation of the gas-hydrates, change of the water solution capacity and so on.

THE EFFECT OF THE MAGNETIC FIELD ON WATER

Water is diamagnetic creating an internal field which is directed antiparallel to the external field with intensity H . The volumetric density of the energy $E(B)$ of free water when it is magnetised is given by:

$$\rho_f(B) = \frac{\delta E(B)}{\delta V} = \frac{1}{2} MB$$

where M is the magnetisation of water; $M = \chi H$, and B is the magnetic induction. For water $\chi = -0.722 \times 10^{-6}$, and magnetic field used in magnetic treatment is $B = 0.3$ T, or $H = 2.39 \times 10^5$ A/m. We thus have^{*}:

$$\begin{aligned} \rho_f(B) &= 2.59 \times 10^{-2} \text{ J/m}^3 \quad \text{or} \\ E(B) &= 4.66 \times 10^{-7} \text{ J/mol.} \end{aligned}$$

This value of the energy can be compared with the energy of the H-bonds for water, which is found in the interval:

$$5.43 \times 10^3 < E_{hb} < 1.88 \times 10^4 \text{ J/mol}$$

Even for the weakest H-bonds

$$\frac{F(B)}{E_{hb}} \approx 0.96 \times 10^{-10}$$

Thus the diamagnetic effects in the total energy of water are negligible.

^{*}The above analysis is incorrect. The value of magnetic susceptibility given above ($\chi = 0.722 \times 10^{-6}$) is the **mass** susceptibility in cgs units. The equation for $\rho_f(B)$ is written in SI units and, moreover, magnetic susceptibility in the relationship $M = \chi H$ is the **volumetric** susceptibility. The correct value to be used in the analysis is $\chi = -9.035 \times 10^{-6}$ (SI) (e.g. *Handbook of Chemistry and Physics, 62nd Ed. (1981-1982), CRC Press Inc., Boca Raton, FLA., USA*). The correct values of $\rho_f(B) = 0.3239 \text{ J/m}^3$, and of $E(B) = 5.83 \times 10^{-6} \text{ J/mol}$ are thus at least an order of magnitude larger than those used by the author. The fact that the magnetic energy is many orders of magnitude smaller than the energy of the H-bond is, however, not affected (*Editor's comment*).

SPIN MAGNETIC EFFECTS IN WATER

As has been mentioned in Section "Hydrogen bond Characteristics", the break energy of the first H–bond between water molecules is by 0.7 eV higher than the break energy of the second bond. It illustrates the cooperative character of the formation of H–bonds which is conditioned by the re–distribution (polarisation) of the electron cloud of molecules participating in these bonds.

Speaking about re–distribution, we mean that systems of protons and electrons interact with each other satisfying the law of conservation of impulse, of the moment of impulse (complete spin), and of energy. In view of the fact that water is diamagnetic, the minimum of the electron–vibrational energy of the water molecule with the H–bonds is obtain under the condition that its spin state is singlet. It must be noted that this condition does not require a singlet state of the proton spin as a separate system. Thus, it does not require a para–state of the water molecule, but it is necessary that the total spin of the proton ($S[^{16}\text{O}_8] = 0$) – electron system forming H–bonds is compensated.

Correlation of the spin of the electron–proton system can be evaluated by their mutual fields. Induction B_e of the magnetic field created by the uncompensated electron spin of molecule B (bond OA–HA...OB) at the position of proton HA is equal to 2 Tesla. Taking into account mutual spin compensation of the paired electrons, then

$$B_e = 2\alpha \quad [\text{Tesla}], 0 < \alpha < 1$$

$$\tilde{B}_e = \alpha B_e$$

where \tilde{B}_e is the magnetic induction generated by partially compensated electron spins and α is the coefficient of dynamic compensation.

Magnetic induction generated by proton HA in the region of undivided oxygen pairs O_B is $B_p \cong 3$ mTesla. Magnetic induction of the external field used in magnetic treatment is $B \cong 0.2$ Tesla. Thus, for $\alpha = 0.1$ the external magnetic field is commensurable with the field of partly non–compensated spins of an electron pair OB, and can change instantaneous multiplicity of the state. Thus, part of spectrum of the state which forms the H–bond can appear forbidden because of the

spin. The external magnetic field can cause the weakening and statistical average (as to V and D structures) diminishing the H-bond number between water molecules, and thus affecting its structure and consequently its reaction ability.

It must be noted that the proposed mechanism of the effect of the external magnetic field on the process of the dynamic formation of H-bonds is based not on the energy effects but is secured, as it takes place in the spin-radical reaction with the participation of the field [11], by the law of conservation of the total spin of the interacting particles.

It is quite probable that the external field affects, in the most efficient way, only those states of the electron-proton system which form the H-bond during the time that is less than that associated with the time of the thermal vibrations, namely $\tau < 10^{-13}$ s. We must also note that under this mechanism of the effect of the magnetic field the values of the effective magnetic induction are in the range $3 \text{ mT} < B < 1000 \text{ mT}$.

MAGNETIC FIELD INFLUENCE ON THE ION AND COLLOID SUBSYSTEMS

It has been already mentioned that the diamagnetic interaction of the water itself with magnetic field can hardly be related to technological effects including the anti-scale effect.

Let us investigate the effect of the magnetic field on a system of impurities in the water medium. It consists of neutral and charged particles, molecular and colloidal dispersibility degree. Some of the particles can acquire non-compensated spin magnetic moment, other particles can be diamagnetic, as for instance CaCO_3 , which has a pronounced anisotropy of diamagnetic susceptibility [12]:

$$\chi_{\perp} - \chi_{\parallel} = 4.02 \text{ to } 4.89 \times 10^{-6}$$

where χ_{\perp} and χ_{\parallel} are perpendicular and parallel components of magnetic susceptibility. The anisotropy is determined by the type of the crystalline system

(orthorhombic or trigonal). The ions widely found in natural waters are also diamagnetic, as is shown in Table III. Oxygen is paramagnetic, and $\mu_{O_2} = 2\mu_B$, where μ_B is the Bohr magneton, equal to $9.274 \times 10^{-24} \text{ Am}^2$.

In view of technological magnetic effects, the colloidal particles exhibiting ferro-, ferri-, antiferro- and superparamagnetic properties are the most interesting. It is known [12, 13] that when particles reach a critical radius $R_{cr} = 0.5$ to $1.0 \times 10^{-8} \text{ m}$,

Table III Magnetic susceptibilities of diamagnetic ions

Ion	$\chi \times 10^6$ (SI)
Mg^{2+}	-3.2
Ca^{2+}	-10.4
K^+	-14
Na^+	-6.5
NO_3^-	-20.1
SO_4^{2-}	-35.2
CO_3^{2-}	-28.1
CO_2	-4.23

they behave in the external magnetic field as mono-domain particles. The saturation magnetisation of these particles is equal approximately to 0.05 T, while for multi-domain particles the saturation magnetisation amounts to about 0.2 T. Magnetic moment of mono-domain particles is comparatively large:

$$\mu_s = 2.5 \text{ to } 9.0 \times 10^{-18} \text{ Am}^2$$

In the external magnetic field, the magnetic moment rotates around the field while a particle itself rotates in the water medium. Behaviour of a system of mono-domain particles in the external magnetic field was investigated in [14, 15]. When the size of a particle decreases further, i.e. $R < 0.5 \times 10^{-8} \text{ m}$, particles lose their ferromagnetic properties and turn into a superparamagnetic state [16]. Paramagnetic susceptibility in this state is $\chi \approx 10^{-4}$ to 10^{-3} .

An estimate of the interaction energy of the magnetised monodomain particles at a distance $r = 10^{-8}$ m gives $E_m \cong 2.5 \times 10^{-18}$ J, or $E_m/kT \cong 15$. Thus such particles flocculate immediately and form chain structures. It must be noted that for concentration of particles from 10^{15} to 10^{18} m $^{-3}$, the average distance between them is 10^{-5} to 10^{-6} m, and their interaction energy is several orders of magnitude lower than the thermal energy.

Thus, to obtain an effective flocculation of magnetic particles, their concentration must increase. It can be provided by ponderomotive forces acting in non-homogeneous magnetic field on magnetisable particles. The condition of concentration of magnetisable spherical particles in a liquid stream can be expressed as:

$$\frac{F_m}{F_d} \geq 1$$

where $F_{mi} = \mu \frac{dB}{dx_i}$ is the magnetic force on a particle and $F_d = 6\pi\eta r_0 v$ is the hydrodynamic drag. r_0 is the radius of a particle, η is the coefficient of the dynamic viscosity of water, v is the velocity of the water flow and μ is the magnetic moment of a particle.

Assuming $T = 20^\circ\text{C}$, $\eta = 10^{-3}$ kg/m.s, we obtain

$$2.6 \times 10^{-8} \frac{dB}{vdX} \geq 1$$

Consequently, taking into account real velocity profile in a channel, the concentration condition is satisfied in a thin wall layer of 10^{-4} to 10^{-3} m of the channel of the magnetic device. The corresponding effects of concentration of ions or electrodynamic particles by electrodynamic forces are by 2 to 3 orders of magnitude lower.

It thus seems probable that effects of changes of dispersion of the colloidal suspension in natural and technical waters during their magnetic treatment, including the anti-scale effects are caused mainly by suspensions of particles that have magnetic moments which are sufficient to resist hydrodynamic and thermal destruction. Naturally, the mechanism of magnetic treatment of

ferro-admixtures does not exclude the effect of the magnetic force on the water structure as discussed in previous section.

QUANTITATIVE ESTIMATE OF THE CONCENTRATION EFFECTS IN ION-COLLOIDAL SYSTEMS IN MAGNETIC DEVICES

Majority of studies [17] which try to explain the effect of magnetic treatment propose to consider the magnetic device as a magnetohydrodynamic unit in which Lorentz force F_L is the driving force. The electrolyte movement in the cross magnetic field causes a cross ion current which produces a concentration of ions with opposite sign in the vicinity of the opposite walls of the channel of the magnetic device. The situation is depicted in Figure 2.

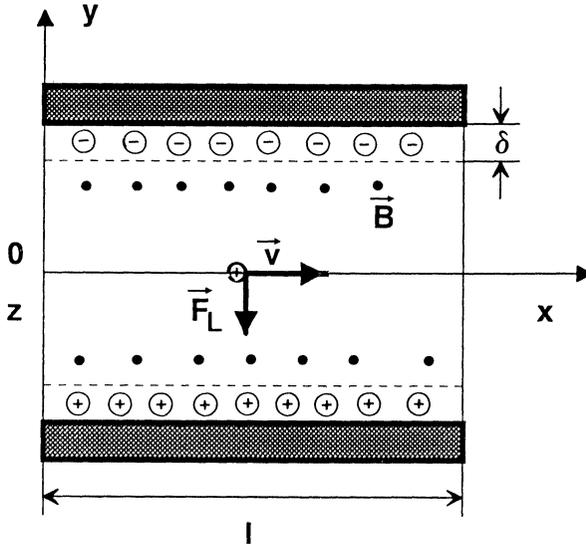


Fig. 2 Cross section through a rectangular channel of the magnetic device. Magnetic induction B denoted by dark circles is perpendicular to the plane of the channel ($B \parallel OZ$) while l is the length of the magnetic zone and δ is the thickness of a layer of concentration of ions and charged colloidal particles.

In the case of a rectangular section of the channel in the YOZ plane which is oriented along the OX vector (vector $\mathbf{B} \parallel \text{OZ}$), the change of the ion concentration near the wall perpendicular to YO is given, in the non-diffusion approximation, and ignoring the Hall field, by the expression [18]:

$$\frac{\Delta n(x, y)}{n_0(y)} = \alpha x \frac{\{ \ln[n_0(y)v(y)] \}}{dy}$$

$$\alpha = \frac{qBD}{kT}$$

In the above equations, $n_0(y)$ is the distribution of ions at the entrance into the channel, Δn is the change of the concentration of ions as a result of the action of the magnetic field, q , k and D are the ion charge, Boltzmann constant and the ion diffusion coefficient (for instance, for CO_3^{2-} or Ca^{2+} in solution), respectively, and $v(y)$ is the mean velocity in the channel of the magnetic device. For Ca^{2+} and CO_3^{2-} ions at $T = 300 \text{ K}$ $\alpha = 10^{-7}$ to 10^{-8} .

Using a parabolic profile of the flow velocity:

$$v(y) = v_0 [1 - (y/d)^2]$$

where d is the radius of the channel and v_0 is the flow velocity at $y = 0$, we get, for $n_0(y) = n_0 = \text{const.}$:

$$\frac{\Delta n(x, y)}{n_0(y)} = -\alpha \frac{2xy}{d^2 - y^2}$$

This expression allows to estimate the amplitude of relative change of the ion concentration in the wall layer of thickness δ . Assuming that $y = d - \delta$, $x = \ell$, length of the channel of the magnetic device, and bearing in mind that $\delta/d \ll 1$, we obtain

$$\frac{\Delta n}{n_0} = \frac{\alpha \ell}{\delta}$$

Consequently, in order to attain $\Delta n \cong n_0$, it is necessary that $\delta = 10^{-7}$ to 10^{-8} m, at $\ell = 0.1$ m. Thus, an appreciable change of concentration ($\approx 10\%$) of ions, as a result of magnetohydrodynamic effects, appears in the wall layer of thickness $\delta =$

10^{-6} to 10^{-7} m. It is easy to see that a change of the ion concentration in such a thin layer cannot essentially affect the crystallisation process of CaCO_3 in the magnetic device.

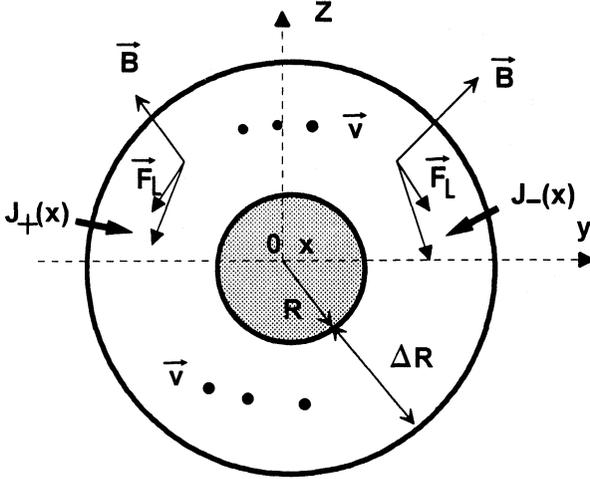


Fig.3 Cross section of the cylindrical channel of the magnetic device. The fluid moves along the OX axis, $\mathbf{v} \parallel \text{OX}$, the magnetic induction \mathbf{B} is oriented radially, $J_+(x)$ and $J_-(x)$ are the flux densities of positive and negative ions created by the action of the Lorentz force.

There is another condition associated with the Lorentz force, which is worth of attention. In a circular channel of a magnetic water device, with radial magnetic field $B_r(x)$, it is assumed that that the field is not homogeneous along the axis OX of the channel. The vortex current this arises whose dissipation energy can be easily calculated. We have, for the tangential component of the vortex current density:

$$J(x) = GE_r(x) = Gv(x)B_r(x)$$

where v is the mean velocity of the water flow, G is the specific electrical conductivity of the treated water.

According to this, a specific power of the vortex current energy dissipation is equal to:

$$-\frac{dW}{d\Omega dt} = G(x)v^2(x)B_r^2(x)$$

where W is the energy of dissipation of the electric current generated by the Lorentz force, while Ω is the volume of a channel of the magnetic unit. From the above, power released in the working space of the device is given by:

$$\frac{dW}{dt} = \int_0^{2\pi} \int_{R_1}^{R_2} \int_0^L G(x)v^2(x)B_r^2(x)\rho dx d\varphi d\rho$$

and complete work done by permanent stream of water is

$$W = 2\pi R \Delta R \int_0^L G(x)v^2(x)B_r^2(x)dx \int_0^L \frac{dx}{V(x)}$$

where L is the length of the channel, R is the radius of channel and ΔR is its height. For a cylindrical channel with the side surface R , $R + \Delta R$, under the condition that $v(x) = \text{const.}$, $G(x) = \text{const.}$, and we obtain:

$$W = \Omega G v L B_r^2; \quad B_r^2 = \frac{1}{L} \int_0^L B_r^2(x) dx$$

For realistic values $R = 10^{-1}$ m, $\Delta R = 10^{-2}$ m, $L = 10^{-1}$ m, $v = 2$ m/s, $B = 0.2$ T, $G = 10^{-2}$ Sm, we find that $W = 5 \times 10^{-8}$ J.

Assuming that the work of formation of the crystallisation centres $\Delta A = 10^2$ kT, with efficiency $\zeta = 0.01$, then the number of the centres formed at $T = 300$ K is:

$$N_{cc} = \frac{5 \times 10^{-8}}{10^2 \text{ kT}} \eta = 10^9$$

which gives the concentration per unit volume:

$$n_{cc} = \frac{N_{cc}}{\Omega} = 1.6 \times 10^{12} \text{ m}^{-3}$$

If we assume that, on condition of over-saturation, the crystallisation centres entering a heat exchanger reach the size of a $\cong 0.5 \times 10^{-6} \text{ m}$, and it is possible to obtain their specific surface

$$S_{cc} = 4\pi a^2 n_{cc} = 5.0 \text{ m}^{-1}$$

This can be compared with specific surface of a standard pipe of a heat exchanger, with inside diameter of $1.8 \times 10^{-2} \text{ m}$, $S_{\text{pipe}} = 1.11 \times 10^2 \text{ m}^{-1}$. Thus, the anti-scale effect will represent approximately 5 per cent.

Besides by Lorentz forces, the colloidal particles (if they are charged) are affected by the gradient ponderomotoric forces of both magnetic and electrical nature. Estimation shows that the electric gradient forces can be neglected in comparison with the magnetic forces.

Therefore, when considering a cylindrical channel of circular cross-section, oriented along the OX axis, with radial magnetic field, it is possible to obtain (if the diffusion process is neglected) an expression for the change of the concentration of particles on the walls of the channel:

$$\frac{\Delta n(x, y)}{n_0(r)} = \epsilon(r) \frac{1 - e^{-b(r)x}}{1 - \epsilon(r)[1 - e^{-b(r)x}]}$$

$$\epsilon(r) = \frac{\mu \frac{dB_r}{dx}}{6\pi\eta r_0 v(r)} \qquad b(r) = \frac{6\pi\eta r_0}{mv(r)}$$

where m and r_0 are the mass and the radius of a particle, respectively, and x is the coordinate along the channel axis. For realistic values of r_0 , m , η , μ and dB/dx we obtain, in SI units:

$$\beta(r) = \frac{10^6}{v(r)} ; \qquad \epsilon(r) = \frac{10^{-4}}{v(r)}$$

It thus transpires from the above that $\Delta n(x,r)/n_0(r)$ reaches its maximum along the OX axis at a distance of 10^{-6} to 10^{-5} m from the channel entrance, i.e. almost instantaneously. Thus

$$\max \frac{\Delta n(x,r)}{n_0(r)} = \frac{\epsilon(r)}{1 - \epsilon(r)}$$

From the last formula we find that concentration of magnetic particles changes substantially in the wall layer with thickness of $\delta = 10^{-4}$ to 10^{-3} m. Rapid flocculation is thus possible in the wall layer of the magnetic device, and generation of supercritical crystallisation centres CaCO_3 is probable.

It must be stressed that for the magnetic flocculation mechanism of magnetic treatment of water to be effective, magnetisable particles must be present. As a rule, colloidal particles of magnetite Fe_3O_4 are those that are needed. Conditions of thermodynamic stability of magnetite in water medium are determined by Purbe diagram [19]. In the {Eh, pH} plane the values

$$-0.8 \text{ V} < \text{Eh} < -0.2 \text{ V}; \quad 7 \leq \text{pH} \leq 14$$

correspond to the zone of magnetite stability. It corresponds to the alkali medium and presence of Fe^{2+} in water.

Such conditions do not often occur in nature. Natural magnetite can arise as a result of bioprocesses or be formed in deep underground waters. Probability of the magnetite formation in a feed water into low-pressure boilers is not high though our studies have shown that approximately 20 to 30 per cent of deposit from ferrous boiler water passed through a filter paper (blue or white strips) exhibits pronounced ferromagnetic properties.

It was described in [20] that the formation of magnetite had been experimentally observed in a magnetic unit and a heat exchanger supplied with magnetised water. Formation of ferromagnetic particles formed in magnetic devices was also observed by streaming ultramicroscopy [21] and using a laser television analyser [22]. In these publications the number of registered particles in the size range 10^{-7} to 10^{-6} m increased during the magnetic treatment by a factor 2 to 8. The authors stressed

the necessity of direct contact of the magnetised water with steel components of a magnetic unit.

HYDRODYNAMIC AGENT IN MAGNETIC TREATMENT OF WATER

The agent affecting the stability of the flocculated particles, and ultimately their ability to become crystallisation centres of the scale-forming compounds, namely $\text{Ca}(\text{Mg})\text{CO}_3$ and $\text{Ca}(\text{Mg})\text{SO}_4$, is the hydrodynamic regime of the water in the magnetic device, in the transportation path to a heat exchanger and in the heat exchanger itself.

Taking into account that flocculation occurs only in a thin layer under the surface, with thickness of $\delta \cong 10^{-4}$ to 10^{-3} m, it is important that intense exchange of colloidal particles between the stream core and the wall layer takes place as a result of turbulent diffusion in the magnetic device. In the transportation path, the stream regime must not destroy the flocs, and in the heat exchanger itself the conditions must be similar to those in the magnetic device, namely that turbulent mixing of the medium is necessary not to create over-saturation in the vicinity of the walls of the heat exchanger.

It is clear that in case of special ability of the wall of the heat exchanger to absorb a suspension (bio-coating, electropotential etc.) intense repeated scale formation is possible. As transpires from the above, the hydrodynamic regime must provide good fluid mixing and must not lead, at the same time, to the destruction of the flocs. Physically it means the following: the energy of the hydrodynamic turbulent pulsation must not be larger than the work required to destroy the flocs.

Let us estimate the situation when the above condition is satisfied. The above condition can be written as:

$$\rho \frac{v_{\lambda}^2}{2} < \frac{U}{V} \frac{\varphi}{\varphi}$$

where ρ is the density of water, v_{λ} is the velocity of pulsation corresponding to the

scale of pulsation λ , U_φ is the energy of the floc bond, V_φ is the volume of the floc.

Taking into account [23] that

$$v_\lambda = v \left[\frac{\lambda}{\ell} \right]^{1/3} \quad \ell = \frac{D_h}{m_t} \quad m_t = \frac{\lambda_h Re}{64}$$

where v is the mean flow velocity, D_h is the hydraulic diameter of the channel through which the liquid is flowing, m_t is the scale of turbulence, Re is the Reynolds number and λ_h is the hydraulic coefficient of friction. According to Blasius

$$\lambda_h = \frac{0.3164}{Re^{1/4}}$$

Using these relations we can obtain the value of the energy of pulsation of the water medium in a volume of a floc with radius a :

$$U_{cr}^\lambda = 1.95 \times 10^{-2} \pi a^3 v \rho Re^{1/2} \left[\frac{\lambda}{D_h} \right]^{2/3}$$

Assuming the following experimental conditions: $a = 10^{-7}$ m, $v = 1.3$ m/s, $Re = 2.6 \times 10^4$, $\rho = 10^3$ kg/m³, $\lambda = 10^{-7}$ m, $D_h = 10^{-2}$ m, we find

$$U_{cr} \cong 0.1 \text{ eV} \gg kT, \quad kT \text{ (at 300 K)} = 2.52 \times 10^{-2} \text{ eV}$$

Thus the energy of the hydrodynamic velocity pulsation is, in these circumstances, comparable to the magnetic dipolar energy of interaction which is at this distance equal to 0.08 eV.

Let us further define a connection between magnetic and hydrodynamic parameters of the process of magnetic treatment, which ensures efficient flocculation of magnetisable particles.

1. Magnetisable particles must be magnetised, consequently $B > 0.05$ T.

2. The concentration condition must be observed, i.e. $\epsilon(r) \cong 1$, or in the wall layer $v(r) \cong 10^{-4}$ m/s.
3. It is necessary for intense turbulent mixing of the fluid to take place, i.e. $D_{\text{turb}} \gg D_{\text{heat}}$, where D_{turb} and D_{heat} are the diffusion coefficients for turbulent and thermal mixing, respectively.
4. Hydrodynamic pulsations must not destroy magnetically flocculated particles.

Let us explore the last condition thoroughly. To do so we shall use an equation

$$U_{\text{cr}} < U_{\text{m}}; \quad U_{\text{m}} = \frac{2\mu^2}{a^3} \times 10^{-7}$$

where U_{m} is the energy of the magnetic interaction of two parallel dipoles having a magnetic moment μ . Magnetisation of a particle is given by:

$$M = \frac{\mu}{V_{\mu}} = \frac{3\mu}{4\pi a^3}$$

where V_{μ} is the volume of a particle with magnetic moment μ . Condition of the efficient flocculation can be written as:

$$M \geq 1.32 \times 10^3 v \rho^{1/2} \text{Re}^{1/4} \frac{\lambda^{1/3}}{D_{\text{h}}^{1/3}}$$

Using the relationship between the scale of pulsation λ and the Reynolds number Re [23] we obtain, for hydraulic smooth pipes:

$$M \geq \beta v \rho^{1/2} \text{Re}^{1/4}$$

$$\text{Re} < 35 \frac{D_{\text{h}}^{2/3}}{a \frac{2}{c_{\text{r}}}^3}$$

$$\beta = 7.81 \times 10^3 \left[\frac{C \text{ kg}^{1/2}}{\text{m}^{7/2}} \right]$$

where a_{cr} is the critical size of a centre determined by the equation [24]:

$$a_{\text{cr}} = \frac{b(a)}{\ln \gamma - \frac{U(a)}{kT}}$$

$$b(a) = \frac{2G(a)\xi(a)}{\rho(a)RT}$$

where $\xi(a)$, $G(a)$ and $\rho(a)$ are the mole mass, surface energy and density of centres of size a , respectively. $U(a)$ is the potential energy of interaction of a scale-forming element (molecules CaCO_3 or ions Ca^{2+} , CO_3^{2-}) with the crystallisation centres of radius a , and γ is the coefficient of over-saturation of the medium. Thus the following equations control the interval of values of parameters of the magnetic treatment, in which the process can be efficient:

$$B > 0.05 \text{ Tesla}$$

$$M \geq \beta v \rho^{1/2} \text{Re}^{1/4}$$

$$\text{Re} < 35 \frac{D_h^{2/3}}{a_{\text{cr}}^{2/3}}$$

According to the equations given above, the parameters characterising the process of magnetic treatment are the following:

magnetic induction B

magnetisation M of the magnetisable particles

flow velocity v of liquid in the magnetic device

density ρ of the liquid

Reynolds number Re

hydraulic diameter D_h and length L of the channel of the magnetic unit

over-saturation coefficient γ of the medium

temperature T

critical size a_{cr} of the crystallisation centres.

REQUIREMENTS FOR A REGIME OF THE TREATMENT AND FOR DESIGN OF THE MAGNETIC DEVICES

These requirements developed by various authors transpire from theoretical pre-conditions and from the level of understanding of the processes occurring in the water environment and of the mechanisms of the anti-scale magnetic treatment, as well as of the corresponding requirements.

Yu. V. Myagkov [25] assumes that the effect of the anti-scale magnetic treatment is based on an increase in the probability of formation of molecules CaCO_3 (or MgCO_3 and MgSO_4), as a result of the opposing movement of cations and anions produced by Lorentz forces.

Considering the opposing drift of the ions, product of the magnetic induction B and the length L of the active zone must be within the range 0.1 to 0.2 Tm:

$$Z = BL = 0.1 \text{ to } 0.2 \text{ [Tm]}$$

The same study proposes to use the anti-scale magnetic treatment only for over-saturated water with concentration of magnetisable particles:

$$C_f < 0.5 \text{ mg/dm}^3$$

The flow regime in the treatment zone is supposed to be optimum.

Using data from numerous installations of magnetic devices on ships and small boilers, the authors of [26] proposed an empirical formula which can be used to determine the optimum regime of the anti-scale magnetic treatment:

$$H = \beta \frac{L_0 v_0^{1/2}}{L_q v_0^{1/2} n} [A + D(\alpha H_g - 1)]$$

where $A = 171 \text{ kA/m}$, $D = 58.9 \text{ kA/m}$, $0.1 < \beta < 1$, $L_0 = 0.18 \text{ m}$. L_q is the length of the active zone of the magnetic field, n is the number of zones of the magnetic field, v is the water flow velocity, H_g is the hardness in meqv/dm^3 .

$$\alpha = \frac{[\text{Ca}^{2+} + \text{Mg}^{2+}]}{[\text{Ca}^{2+}]}$$

The authors of [27] confirm that magnetic treatment changes the rate of dissolution of CO_2 in water and destroys equilibrium of carbon dioxide changing the kinetics of dissolution of CaCO_3 or CaSO_4 . A proposition was made to use magnetic treatment to remove the existing scale. For $H_g \cong 0.4 \text{ meqv/dm}^3$, $v = 2.4 \text{ m/s}$ $B = 100 \text{ mT}$ is suggested.

An original approach to the mechanism of the anti-scale magnetic treatment is discussed in [20]. "water-pipe-line metal" system is considered as a magnetothermic couple, the cold end of which in the magnetic device generates the ion current, closed in the heat exchanger, polarising the surface of the heat exchanger and thus protecting it from scale.

The efficiency of the magnetic device is proposed to be determined by a difference between the potentials of the magnetic device and the heat exchanger. There are no concrete proposals as far as the regimes of the anti-scale magnetic treatment, and construction of the magnetic device are concerned. Nevertheless, an efficient application of the original construction of the magnetic device in the evaporating ship devices is described.

Considerable factual material about the applications of magnetic devices in heating systems, power engineering and industry is given in papers [28] and [29]. The authors point out that magnetic induction $B < 50 \text{ mT}$ is not effective, as we discussed above. At the same time, the anti-scale magnetic treatment in magnetic field $B \cong 0.4$ to 0.5 T attains the efficiency of 60 to 80 per cent, when applied in heaters and low-pressure boilers.

Publication [29] underlines efficient performance of a magnetic device with pulse field with the frequency ν ranging from 3 to 10 Hz, and the number of the active zones of the magnetic field $n = 4$ to 8. It is claimed that the anti-scale magnetic treatment is efficient for water with

$$H_g = 1.5 \text{ to } 8.0 \text{ meqv/dm}^3$$

$$H_g = 1.0 \text{ to } 4.5 \text{ meqv/dm}^3$$

while the water flow velocity in the treatment zone is recommended to be

$$v = 0.5 \text{ to } 2.5 \text{ m/s}$$

Besides, the author of [29] proposes to install magnetic devices at a distance of $L \leq v\tau$, where $\tau = 60$ seconds. It should be pointed out that in [21] the technique of ultramicroscopy allowed to observe particles of CaCO_3 and MgCO_3 which arise during magnetic treatment and are preserved in water for two to three days.

Publication [30] gives the most detailed analysis of conditions and regimes of the anti-scale magnetic treatment. It is noted that the requirements must be divided into the following sections:

- requirements for water system
- requirements for the treatment regime and water transport in a heat exchanger
- requirements for the heat exchanger and its operating regime
- requirements for the mode and position of installation of a magnetic device.

1. Requirements for water system are considered in [30] and [31]. It is found that magnetic treatment is expressed in the best way under the following parameters of the water:

General salinity $S \cong 1000$ to 1500 mg/dm^3 , $H_g < 10 \text{ meqv/dm}^3$

$$\frac{H_g}{H_{\text{Ca r bon}}} < 1.4 \text{ to } 1.5 \qquad \frac{[\text{Mg}^{2+}]}{[\text{Ca}^{2+}]} < 0.2$$

$$\frac{[\text{Na}^+]}{[\text{Ca}^{2+}]} < 2 \qquad \frac{[\text{Cl}^-]}{[\text{HCO}_3^-]} < 0.5 \qquad \frac{[\text{SO}_4^{2-}]}{[\text{HCO}_3^-]} < 0.5$$

$$0.03 \text{ mg/dm}^3 < C_{f,\text{gen}} < 1.0 \text{ mg/dm}^3$$

where $C_{f,\text{gen}}$ is the concentration of general ferromagnetic particles.

The most preferable temperature of the magnetic treatment is between 10 and 45°C. Water must be over-saturated with compound responsible for scale formation, e.g. CaCO_3 . In this case

$$\gamma = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}] f_a^2}{J_{\text{CaCO}_3}} > 4$$

where f_a is the activity of ions and J_{CaCO_3} is the solubility of CaCO_3 in water.

2. Requirements for the regime of treatment.

It transpires from analysis of large amount of data obtained from successful applications of anti-scale magnetic treatment [28, 29, 30], and from theoretical analysis that the following conditions must be met:

- 2.1 Magnetic induction in the channel of a magnetic device must be in the interval $0.1 < B < 0.6$ T.
- 2.2 Gradient of the magnetic field $\text{dB}/\text{dx} > 50$ T/m
- 2.3 The magnetic field can be either permanent or pulse. For the pulse field the frequency must be in the interval $3 < \nu < 10$ Hz.
- 2.4. The length of the zone of treatment $L = 0.15$ m and 60 per cent must correspond to a zone with $\text{dB}/\text{dx} > 5$.
- 2.5 For salinity $S > 500$ mg/dm³, $B > 0.2$ T.
- 2.6 The desirable flow velocity in the zone of the magnetic field: 0.5 m/s $< v < 5$ m/s. The following relationship is a more precise criterion:

$$3.0 \times 10^{-2} [\text{m}^2/\text{s}^{3/2}] \leq v^{3/2} D_H^{1/2} \leq 12 \times 10^{-2} [\text{m}^2/\text{s}^{3/2}]$$

where D_h is the hydraulic diameter of the channel of the magnetic device.

- 2.7 Specific surface of the channel $\Omega = S/V$ where S and V are the surface and the volume, respectively, of the channel [30]:

$$2 \times 10^2 \text{ m}^{-1} \leq \Omega \leq 6 \times 10^2 \text{ m}^{-1}$$

3. Requirements for heat exchangers and their operating regime.

It is considered that magnetic treatment is efficient for heat exchangers where specific heat transfer surface

$$\Omega_{\text{HE}} \leq 2.5 \times 10^2 \text{ m}^{-1}$$

and heat loading

$$\frac{dQ}{dS dt} \leq 3 \times 10^2 \text{ kW/m}^2$$

while the surface boiling must be absent. Special attention during the application of the magnetic device to a heat exchanger must be paid to anti-sludge measures [25]. To achieve this, we must increase the number of boiler blow-offs two to three times, or to use a by-pass sludge separation for the circulation system.

4. Position of installation must be chosen so that the residence time in the heat exchanger of the magnetically treated water does not exceed 60 seconds. The flow regime during transportation must be transitive.

There are many other factors that effect the efficiency of the anti-scale magnetic treatment, for instance season variations of the water quality, floating currents in pipe-lines, vibration of pipes, local liquid turbulence, composition and concentration of suspended particles, level of saturation with CO_2 and O_2 gases, surface-active substances and others. All these factors are also responsible for

possible failures of anti-scale magnetic devices. Nevertheless, according to our research [18] and data obtained by other investigators [28, 29], in more than 60 per cent of cases the magnetic devices installed in the territory of the former USSR were effective (i.e. quantity of scale was reduced by a factor of two or more). In the former East Germany and Czechoslovakia, the efficiency of the anti-scale magnetic treatment in 1980–1983 was 75 to 80 per cent.

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Keywords: water, magnetic treatment, hydrogen bond, anti-scale effect, ion-colloidal system