The effect of ultrasound on the process of water softening

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Abstract. The application of ultrasonic vibrations in natural water conditioning technology is part of the scientific problem of using in this field of knowledge of physical methods, which also include magnetic, high-frequency, x-ray, ultraviolet, etc. Currently, ultrasonic vibrations are widely used in various industries: metallurgy, chemical, mechanical engineering, medicine, etc. Quite a wide application of ultrasound is explained by the variety of phenomena occurring in the ultrasonic field. Ultrasonic vibrations initiate dispersion and emulsification of substances, contribute to coagulation and degassing, affect the processes of crystallization and dissolution; it is known that ultrasound causes a variety of chemical transformations of the substance, among which are reactions of oxidation, reduction, polymerization, etc. the Explanation of these phenomena is found in a variety of ultrasonic effects: cavitation, shock waves, microflows, acoustic wind, etc. The schemes of ultrasonic generators are continuously improved, works on the development of methods of using ultrasound and on the search for new areas of its application are progressing.

1 Introduction

The relevance of the work. At present, physical methods of intensification of water purification are becoming widespread in water treatment technology. The use of ultrasonic vibrations is part of this scientific problem. The use of ultrasound is due to its specific effect on the liquid medium. Improvement of calculation methods extends the scope of ultrasound.

Theoretical background the softening of water in the ultrasonic field and the principles of the model calculation for this process is an urgent task.

Phenomena in the ultrasonic field.

1. Various physicochemical effects arising in the ultrasonic field are associated with the transformation of the energy of elastic vibrations. In this case, we can say that they are one of the types of mechanochemical reactions [1, 2]. These effects are accompanied by the phenomenon of cavitation [2].

On the other hand, the elementary processes of sound chemical reactions are close to radiolysis, reactions in an electric discharge, photolysis [3, 4].

Neipairas and Nolting advanced the theory of the occurrence of high temperatures in the adiabatic compression of a cavitation bubble in the process of its collapse [4]. According to their calculations, at a continuously increasing velocity of the bubble-liquid interface, the

temperature in the collapsing bubble can reach 10,000 ° K, and the pressure in the shock wave up to 104 bar. [5]. Such high temperatures appearing in the gas-filled bubble cavity can cause the appearance in it of electric charges of dissociated and ionized molecules, atoms, free radicals [6]. Thus, cavitation cavity can serve as a source of formation of products with high reactivity and initiation of physicochemical phenomena in ultrasound field.

Soviet physicist Ya. I. Frenkel suggested the occurrence of electric charges of the opposite sign on the walls of the lens-shaped cavity formed. In the initial stage of cavitation cavity formation, electric charges appear on it. Ya. I. Frenkel believes that when the continuity of the medium ruptures in the places of rarefaction, lens-shaped cavities, rather than spherical cavities, are formed of molecular dimensions. For such a break, a pressure amplitude of the order of 103-104 bars is required.

The transition from the lens-shaped cavity to the spherical cavity occurs as a result of the penetration of dissolved gases or vapors of the surrounding liquid [7].

According to the theory of Ya. I. Frenkel, under the conditions of an electric discharge, energy-rich particles, ionized molecules and ions, free radicals arise in the cavitation cavity [7].

Assuming that the charges were formed as a result of the uneven distribution of ions on the walls of the bubble when the liquid is ruptured, Ya. I. Frenkel determined the field strength inside the cavity at the time of its formation:

$$E_\text{п} = \frac{4\bar{e}}{r_\text{п}}\sqrt{N_\text{п}\delta_\text{п}},\qquad(1)$$

where $E_\text{п}$ – electric field strength, V/cm;
$\delta_\text{п}$ – the distance between the ruptured fluid layers, $\mathring{A}$;
$N_\text{п}$ – number of dissociated molecules per the volume unit;
$r_\text{п}$ – radius of cavitation cavity, cm;
$\bar{e}$ – electron charge, C.

Calculation of Frenkel: showed that the field strength $E_\text{п}$ = 600 V/cm, sufficient for breakdown of the cavity formed radius $r_\text{п} = 10^{-4}$ cm, when the pressure in it is small (up to 1/50 bar), occurs at $\delta_\text{п} = 5\ \mathring{A}$, i.e. barely exceeds the kinetic diameter of the water molecule H_2O. Therefore, here we are talking only about homogeneous liquids that do not contain "embryos" cavitation – microbubbles of dissolved gases, which reduce the cavitation strength by two orders of magnitude [7].

Gas bubbles of $\approx 10^{-5} - 10^{-4}$ cm size are considered to be "weak" places in the liquid and have spherical shape [4].

By its physical nature, ultrasound is an elastic wave and it is not different from sound.

The frequency boundary between sound and ultrasonic waves is conventional and corresponds to the average upper limit of the audible sound of 15 kHz.

However, due to higher frequencies and, consequently, low wavelengths, there are a number of features of the propagation of ultrasonic vibrations.

Sound-wave-like propagation of vibrations of particles of an elastic medium, characterized by values: sound pressure, sound energy density, sound energy flow, the level of intensity (force) of sound.

Water in a static state does not have shear viscosity and is not able to withstand and transmit any shear stresses.

Therefore, only longitudinal waves propagate in liquids and gases, in which the direction of tangential motions of particles coincides with the direction of wave propagation.

To generate ultrasonic vibrations, currently used a variety of devices that can be divided into two main groups:

- mechanical, in which the source of ultrasound is the mechanical energy of the flow of gas or liquid;

- electromechanical, in which ultrasonic energy is obtained by converting electrical.

The most widespread method of obtaining ultrasound is the conversion of electrical oscillations in mechanical.

In the range of low frequency ultrasound 15 kHz - 100 kHz application found ultrasound emitters using the effect of magnetostriction nickel, and in a number of special alloys, and also in ferrites.

For medium and high frequency ultrasound radiation (f > 100 kHz), the phenomenon of piezoelectricity is mainly used.

The main materials for emitters in this case are: quartz, lithium niobate, etc.

The maximum intensity of ultrasound radiation is determined by the strength nonlinear properties of the material of the emitters, as well as the features of their use.
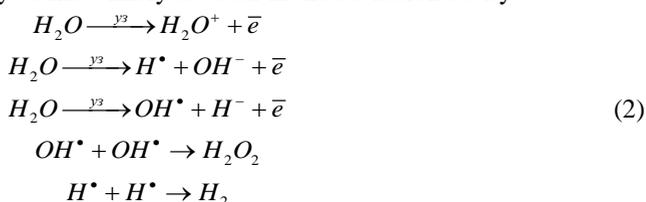
The choice of the generation method depends on the frequency range, the nature of the medium (gas, liquid or solid), the type of elastic waves and the required radiation intensity.

The types of radiation and frequency ranges for obtaining cavitation in water are given, as well as the scope of application:

a) – emitter type-Magnetostrictive,
   the range of frequencies – from 3 kHz to 3 MHz,
   applications in liquid environment, dispersing, emulsifying, mixing, deposition, polymerization;

b) – type of emitter-piezo-Quartz,
   the frequency range from 100 kHz to 3 MHz,
   application area - for dispersion, emulsification, deposition, oxidation, recovery and for laboratory research;

c) – emitter type-piezo-Quartz,
   the frequency range from 100 kHz to 3 MHz,
   application field-for dispersion, emulsification, deposition, oxidation, recovery and for laboratory research.

2. The study of the kinetics of ultrasonic chemical reactions [6] showed that the initial reaction rate does not depend on the concentration of the dissolved substance and after reaching the cavitation threshold is proportional to the acoustic power given. This allowed us to assume that ultrasonic waves do not act directly on the dissolved substance, but cause, similarly to ionizing radiation, the splitting of molecules into the free radical of hydroxyl $OH^{\bullet}$ and atomic hydrogen $H^{\bullet}$, which react with the dissolved substances. Recombination of these radicals leads to the formation of H_2 and H_2O_2 molecules in the voiced solution [8].

The following processes may be most likely to occur in the cavitation cavity:

$$H_2O \xrightarrow{y_3} H_2O^+ + \overline{e}$$
$$H_2O \xrightarrow{y_3} H^{\bullet} + OH^- + \overline{e}$$
$$H_2O \xrightarrow{y_3} OH^{\bullet} + H^- + \overline{e} \qquad (2)$$
$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$
$$H^{\bullet} + H^{\bullet} \rightarrow H_2$$

Valence-unsaturated atoms and radicals appear, which have a great reactivity. Thus, it can be considered that under the influence of ultrasound water molecules are split in the following scheme $H_2O \xrightarrow{y_3} OH^{\bullet}; H^{\bullet}; \overline{e}; H_2; H_2O_2$. In the presence of oxygen can also
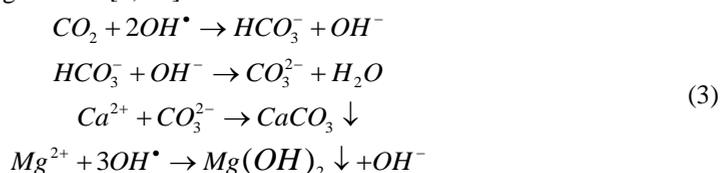
form a radical $HO_2^{\bullet}$.

It is believed that directly in the cavitation cavity the decay products of ionized particles interact with each other or react with diffusing gaseous substances. As a result of the

collapse of the bubble, the formed radicals are dispersed into the environment, where they react with dissolved substances. The life expectancy of the cavitation bubble is half of the period of applied ultrasonic vibrations $\approx 0{,}5 \cdot 10^{-6}$ s, and the lifetime of the formed ones radicals is approximately equal to $10^{-2} - 10^{-4}$ s.

This means that with the annihilation of the bubble, active hydroxyl groups pass into the aqueous medium, H^g- radicals, etc. depending on which radicals react with dissolved substances in water, the latter under the action of ultrasonic waves are subjected to oxidation or reduction processes.

It is believed that in the presence of oxygen in the water under the influence of ultrasonic vibrations, oxidative reactions are intensified, and in the atmosphere of hydrogen - reducing [6].

The outcome of the above and of the chemical reactions that occur during the reagent softening, we can assume the mechanism of the softening process in the ultrasonic field according to the following scheme [9, 10]:

$$CO_2 + 2OH^\bullet \rightarrow HCO_3^- + OH^-$$
$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \tag{3}$$
$$Mg^{2+} + 3OH^\bullet \rightarrow Mg(OH)_2 \downarrow + OH^-$$

Participate in the reaction, free hydroxyl radicals. Thus, along with the chemical reactions that usually occur with the reagent water softening, there arise in the ultrasonic field and the chemical reactions described above.

3. Prerequisites for the theoretical calculation of the use of ultrasound in reagent water softening. Reagent methods of softening are used in the practice of water treatment. They consist in the binding of water-contained cations of hardness, calcium and magnesium Ca^{++}, Mg^{++}, in low-soluble compounds that can be isolated from the solution by precipitation or filtration.

The use of different variants of reagent methods of water softening is determined by the quality of the source water and the necessary effect of softening. The process takes place in two stages: the first is the actual chemical reaction of interacting ions forming slightly soluble compounds $CaCO_3$ and $Mg(OH)_2$. After separation from the solution, the softening products are in a colloidal state. The second stage is the crystallization of the substance forming the precipitate and its agglomeration into flakes. The transition of reaction products from colloidal formation to the coarse state takes a long time − up to several hours.

The aim of the work is to develop a theoretical model of the softening process in the ultrasonic field.

The task is to obtain the equation of reduction of doses of alkaline reagents with water softening in an ultrasonic field.

2 Results

The dose of alkaline reagents, calculated according to the stoichiometric equations [11]:

$$\text{the dose of lime } D_и = 28\left(\frac{CO_2}{22} + \frac{HCO_3^-}{61} + \frac{Mg^{2+}}{12} + 0.5\right)$$

$$\text{and soda dose } D_c = 53\left(\frac{Ca^{2+}}{20} + \frac{Mg^{2+}}{12} - \frac{HCO_3^-}{61} + 1.0\right).$$

Suppose that the doses of alkaline reagents will provide a complete reduction in water hardness, i.e. the final stiffness will be 0. We denote the initial ion concentration (Ca^{2+} + Mg^{2+}) by $P_{1.0}$, and the intermediate value of P_1, the addition of alkaline reagents, the dose of

which will be a multiple of stoichiometric values, will cause a decrease in the initial concentration of $P_{1.0}$ proportional to additional reagents. Suppose also that all added reagents will react [12, 13, 14].

Ultrasonic treatment of water containing ions of calcium and magnesium can affect in two ways on the ions of calcium and magnesium, i.e. the impurity and enter the reagents because it is possible the connection of the ions obtained by the dissociation of the substance of the reagent and of free hydroxyl ions formed as a result of the action of ultrasound. Let the water contains an admixture, i.e. the content of ions $(Ca^{2+} + Mg^{2+})$, with a concentration of $P_{1.0}$. Based on the chemical reaction formula, i.e. the stoichiometric equation can be used to calculate the amount of reagent needed to fully extract all the impurities contained in water $(Ca^{2+} + Mg^{2+})$. The extraction of the impurity occurs under the condition of absence of any intensification of the process and with unlimited time of discharge of the solid phase of the sediment. Take this amount of reagent as 1. If in the same conditions to use not all quantity of the reagent necessary for full extraction of an impurity, i.e. accepted as 1, but only its x - part, the quantity of the precipitated impurity will be equal:

$$P_{1.0} \cdot x, \qquad (4)$$

and the remaining concentration of ions in water $(Ca^{2+} + Mg^{2+})$ will be P_M

$$P_M = P_{1.0} - P_{1.0} \cdot x = (1-x) \cdot P_{1.0}. \qquad (5)$$

The intensification of the process of ions $(Ca^{2+} + Mg^{2+})$ release from water under the condition of ultrasound exposure can be carried out in two ways:
- Due to the external energy supply, a certain number of atoms are split into a free hydroxyl group $OH^{\bullet}$ and a free hydrogen atom $H^{\bullet}$; hydroxyl groups can enter into the compound with both ions $(Ca^{2+} + Mg^{2+})$ and reagents. From the chemical reactions occurring in the softening processes, the attraction of free hydroxyl groups $OH^{\bullet}$ to Ca^{2+} and Mg^{2+} ions is characteristic. If the reaction of the $OH^{\bullet}$ ions to the impurity is more intense than their action on the reagent, the effect of free hydroxyl is the same as if an additional amount of reagent was added to the water.
- Due to the intensive mixing of the liquid mass, the processes of diffusion and release of the solid medium are accelerated with the reagent softening. Consider in more detail the possible influence of the additional free hydroxyl $OH^{\bullet}$ ions on the completeness of the process of separation of the reaction products of $CaCO_3$ and $Mg(OH)_2$ from the mass of water [15-17].

We will assume that the effect of the presence of additional free $OH^{\bullet}$ ions in water corresponds to the addition of an additional fraction to the amount of reagent x_0, that is, the total effect of the ions would be expressed in the fact that the content of the reagent x would increase by an additional amount x_0.
If these ions acted only on the admixture, their presence would be equivalent to the addition of x_0 parts of the reagent. However, free hydroxyl ions can be connected not only with the admixture, but also with the reagent, which should in turn lead to a decrease in its effective amount in the solution. Let us assume that the free hydroxyl groups $OH^{\bullet}$ are distributed in proportion to the masses of the impurity and reagent. If the amount of reagent is x, it can be assumed that the value x_0 is distributed between the reagents and the impurity as $\dfrac{x_0}{1-x}$.

After the deposition of reaction products, the precipitated concentration will be [18-20]:
- Due to the presence of ions arising from the action of ultrasound, the effect of the presence of the reagent is described by the expression (6)

$$P_{1.0} \cdot x + P_{1.0} \cdot (1-x) \cdot x_0. \tag{6}$$

- By "reducing" the amount of reagent, the effect will be reduced by the amount of

$$P_{1.0} \cdot x \cdot x_0. \tag{7}$$

The final concentration of impurities in water is determined from the equation (8)

$$P_1 = P_{1.0} - \left[P_{1.0} \cdot x + P_{1.0} \cdot (1-x) \cdot x_0 - P_{1.0} \cdot x \cdot x_0 \right]. \tag{8}$$

From this equation it follows

$$\frac{P_{1.0} - P_1}{P_{1.0}} = x + x_0 \cdot (1 - 2x). \tag{9}$$

We consider the special cases of existence of the equation (9).
If $x_0 = 0$, that is, there is no additional effect of ultrasound on water, then

$$\frac{P_{1.0} - P_1}{P_{1.0}} = x. \tag{10}$$

that is, the reagent is fully used.
If $x = 0$,
that is, the reagent is not added to the water, the dependence (9) is written

$$\frac{P_{1.0} - P_1}{P_{1.0}} = x_0. \tag{11}$$

that is, the change in the concentration of Ca^{2+} and Mg^{2+} ions occurs only due to the action of ultrasound. When the quantity of reagents $x = 0.5$, that is $\frac{P_{1.0} - P_1}{P_{1.0}} = x = 0.5$ the effect of the process is zero, since half of the free hydroxyl ions $OH^{\bullet}$ involved in reactions with the reagent. At a reagent concentration of $x < 0.5$, the presence of the $OH^{\bullet}$ formation process leads to a more effective action of the reagent. The opposite effect should be observed at reagent concentrations $x > 0.5$. The reagent is not fully used. For complete deposition of impurities must be the presence of a large quantity of the reagent than is conventionally equal to one. In this case

$$x = \frac{1 - x_0}{1 - 2x_0}. \tag{12}$$

3 Solutions

1. The analysis of the theoretical studies has shown that cavitation is a necessary condition for the softening of natural waters in the ultrasonic hearth.
2. Cavitation in the water and activates the hydrogen and hydroxyl ions.
3. To obtain a stable and adjustable cavitation in water, it is necessary to use an electromechanical method for its production.
4. As a result of theoretical studies, the dependence of the doses of alkaline reagents in water softening in an ultrasonic field was obtained.
5. The value of the proportion of alkaline reagents equivalent to the number of free hydroxyl groups $OH^{\bullet}$ is determined.

4 Conclusions

1. The obtained theoretical model of natural water softening relates the initial quality (hardness), the dose of alkaline reagents, and the physical and chemical effects of ultrasound.

2. This model makes it possible to predict the effect of ultrasonic vibrations on the water softening process

3. The theoretical model of natural water softening with the effect of ultrasound describes the relationship of the initial water quality (hardness), the dose of alkaline reagents, and the physical and chemical effects of ultrasound.

4. The obtained model makes it possible to predict the effectiveness of ultrasonic vibrations in the reagent water softening.

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