Influence of ultrasound on the concentration of hydrogen ions in water

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Abstract. The paper deals with the physical and chemical effects arising in water under the action of the energy of elastic vibrations of ultrasonic frequency in the cavitation mode. Cavitation state is characterized by the formation of the gas and air cavities - bubbles in the aquatic environment. The theory of occurrence of high temperatures at the moment of collapse of a cavitation bubble in water is given. It is noted that there is a dissimilation of the substance of free active radicals, dissociated and ionized molecules. The kinetics of chemical reactions in the ultrasonic field under the cavitation regime is described. Methods for obtaining ultrasonic cavitation in a liquid medium with a description of the generation of ultrasonic vibrations and a list of transducers and types of emitters are given. A relatively wide spectrum of radiated frequencies and instability of frequency and amplitude of oscillations are considered. The choice of ultrasonic generator is justified due to the necessary frequencies and intensities for the excitation of cavitation in water \( f = 18-22 \text{ kHz}, \ I = 2.0 \text{ W/cm}^2 \), technological considerations about the possibility of mounting the transducer in an existing production line, as well as safety and efficiency issues. The relevance, purpose and objectives of the work are formulated. The equipment and methods of experimental research are presented. Laboratory experimental studies on the effect of ultrasonic vibrations in the cavitation mode on the change of water pH were carried out. It is shown that bubbles formed in the ultrasonic field in the studied water collapse and create micro-explosions, shock waves and micro-flows. The results of studies on the change of pH in water are shown and the analysis of experimental data is performed. The experimental studies made it possible to substantiate the conclusions of this work and to formulate a conclusion about the influence of the ultrasonic field in the cavitation mode on the pH of the aqueous medium and its further application in water treatment processes.

Introduction

1. In the aqueous medium under the influence of cavitation obtained in the ultrasonic field, there are physical and chemical effects associated with the energy of elastic vibrations. There is an initiation of biochemical reactions, which depend on the phenomenon of cavitation \[1,2\]. There are indications in the literature that these reactions are close to radiolysis and photolysis \[3,4\]. The authors Napiras and Nolting \[4\] put forward the theory of the occurrence of high temperatures at the time of collapse of the cavitation bubble in water, consistent with its adiabatic compression. The order of these temperatures is 10000 °K, there is a shock wave with a pressure of 104 ATM. \[5\]. At high temperatures in the bubble cavity filled with dissolved gas, electrification occurs with the formation of atomic oxygen and hydrogen, free active radicals, dissociated and ionized molecules \[6\].
In addition, in the aqueous medium during cavitation, intermediates are formed with a high activating ability in the rate of physical and chemical reactions. There are literature data on the appearance of opposite sign charges on the walls of the lenticular cavity of the cavitation bubble [7].

Author Frenkel Ya. I. put forward a theory about the formation of a lenticular cavity of molecular size and calculated the pressure amplitude for the discontinuity of the continuity of the medium at rarefaction [7]. The theory of formation of cavitation bubble in water, emergence of charges and formation of extremely highly reactive elements is generally recognized. The field strength at the time of bubble formation is calculated by the formula:

\[ E_n = \frac{4\varepsilon}{r_n} \sqrt{N_n \delta_n}, \]

where \( E_n \) – electric field strength, V/cm;
\( \delta_n \) – the distance between the ruptured fluid layers, Å;
\( N_n \) – number of dissociated molecules per the volume unit;
\( r_n \) – radius of cavitation cavity, sm;
\( \varepsilon \) – electron charge, Kл.

When the radius of the bubble \( r_n = 10^{-4} \) cm field has a strength \( E_n = 600 \) V/cm, and the distance between the collapsing layers of liquid \( \delta_n = 5 \) Å. This distance corresponds to the kinetic diameter of the water molecule H₂O.

In real natural water there are dissociated molecules, inorganic inclusions, dissolved gases, which are the natural nuclei of cavitation bubbles. They lead to a decrease in the cavitation strength of water by two orders of magnitude [7].

2. The kinetics of chemical reactions in the ultrasonic field is proportional only to the acoustic power and does not depend on the concentration of dissolved substances [6].

In the literature there are data, experimentally proven, on the formation of the free radical hydroxyl \( \text{OH}^- \) and atomic hydrogen \( \text{H} \) under the action of cavitation, recombination of which leads to the formation of \( \text{H}_2 \) and \( \text{H}_2\text{O}_2 \) molecules in water [8].

Under the influence of ultrasound in the cavitation cavity, the following reactions occur:

\[ \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^- + \varepsilon; \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- + \varepsilon; \]

\[ \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ + \varepsilon; \text{OH}^- + \text{OH}^- \rightarrow \text{H}_2\text{O}_2; \text{H}^* + \text{H}^* \rightarrow \text{H}_2 \]

The presented reactions (2) show that free electrons, activated atomic hydrogen, activated hydroxyl groups, hydrogen ions, hydroxyl ions, ionized water, hydrogen pyroxide are formed in ultrasound-treated water [4,10,11,14,16,17].

Recombination of elements obtained by ultrasound in water leads to the formation of substances according to the following scheme \( \text{H}_2\text{O} \rightarrow \text{OH}^-; \text{H}^*; \text{H}_2; \text{H}_2\text{O}_2 \).

From the above it follows that it is necessary to perform experimental studies on the effect of ultrasonic cavitation on the pH of water. The pH is the negative decimal logarithm of the concentration of hydrogen ions in water. The formation of hydrogen ions occurs by the following reaction

\[ \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- . \]

The equilibrium constant of this reaction will be

\[ K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}, \]

where

\[ \frac{K}{[\text{H}^+]} = [\text{HCO}_3^-]/[\text{H}_2\text{CO}_3], \text{ where } K = 10^{-4.3} . \]
If the quantities $HCO_3^-$ and $H_2CO_3$ are equal (for example, $10^{-2}$ mol/l), then $H^+ = 10^{-6.5}$ mol/l and pH = 6.5. The total amount $HCO_3^-$ and $H_2CO_3$ is $2 \cdot 10^{-2}$ mol/l. When added to the acid solution, the equilibrium shifts to the left to form $H_2CO_3$. To change the ratio $\frac{HCO_3^-}{H_2CO_3}$, for example to $1/3$, you will need to add acid about $5 \cdot 10^{-3}$ mol per liter of solution. The added amount of $H^+$ is almost $10^4$ hfpf higher than the original content of hydrogen ions. The new pH value can be calculated:

$$\frac{10^{-6.5}}{H^+} = \frac{1}{3}; \quad \left[ H^+ \right] = 3 \cdot 10^{-6.5} \cdot \left[ HCO_3^- \right]; \quad \text{pH} = 5.9.$$

The above reactions characterize the state of water [17,18,19,23].

Physical methods, which include ultrasonic cavitation, affect water by changing the pH.

3. Methods for obtaining ultrasonic cavitation liquid medium.

To generate ultrasonic vibrations, a variety of devices are currently used, which can be divided into two main groups: mechanical, in which the source of ultrasound is the mechanical energy of a gas or liquid flow, and Electromechanical, in which ultrasonic energy is obtained by converting electrical energy.

Mechanical ultrasound emitters-air and liquid whistles and sirens-are characterized by comparative simplicity of the device and operation, do not require high frequency electrical energy for operation, the efficiency of such emitters is $\eta = 10$-20 %. The main disadvantage of all mechanical ultrasonic emitters is a relatively wide range of emitted frequencies and instability of the frequency and amplitude of oscillations, which allows them to be used mainly in industrial ultrasonic technology and partly as a means of signaling.

All aerodynamic converters are designed to operate in gaseous environments so they are not applicable.

Table 1 shows ultrasonic technological equipment [20,21].

| ## | Name | Emitter type | Frequency range | Application |
|----|------|--------------|-----------------|-------------|
| 1  | Low frequency continuous ultrasonic generators (UZG-109; UZG-0,4 / 22; UZG-1,6 / 22; UZG-2-10; UZG-2-4; UZG-2-0,1; 27-UZG I-M-1,5). | Magnet ostrictive. | From 3 to 100 kHz. | Designed to power the magnetostRICTive Converter for operation in a liquid environment, for welding, tinning, cleaning parts. |
| 2  | Continuous ultrasonic generators covering a wide range of frequencies (GU-3). | Magnet ostrictive; removable quartz movement | From 3 to 100 kHz. From 100 kHz to 3 MHz | Designed to work in a liquid environment, for dispersion, emulsification, mixing, deposition. |
| 3  | Ultrasonic generators of continuous action of high frequency (UPG-2; UZGV-10). | Piezo quartz | From 100 kHz to 3 MHz | For dispersion, emulsification, deposition and laboratory testing. |
| 4  | Ultrasonic pulse generators (TUIG-2M; EP-P; IGUR-611M; UZGI-325). | Magnet ostrictive | – | Generation of the required frequency and power of the ultrasonic field |
5. An electromagnetic device of the type of BPU. Electromagnetic emitters 4-10Hz. It is used instead of agitators (anchor, turbine, propeller), if necessary, sealing process V = 1.0 m³.

6. Ultrasonic column apparatus type UPHA. MagnetostRICTIVE 4.8-18kHz. Performance in three modifications: for processing of low-viscosity components-UPHA-R, for processing of viscous and pasty products-UPHA-sh, for processing of products in a thin layer-UPHA-TS.

7. Hydrodynamic ultrasonic devices. Ultrasonic whistle Range of 0.5 – 40 kHz. For emulsification and mixing of liquid components-UGS, for homogenization of liquids-AGB. Rotary apparatus type GARTH-PR for processing products in the chamber for single processing.

8. Acoustic filter (AF-2, AF-100). Electromagnetic vibrator – It is intended for cleaning of suspended substances, for determination of suspensions.

9. Acoustic centrifuges and hydrocyclones. MagnetostRICTIVE and piezoelectric Depending on the type of generator and emitter For separation in centrifuges and thickening in hydrocyclones of suspensions

Hydrodynamic converters of the type of plate liquid whistles, the action of which is based on the excitation of resonant vibrations of the vibrator – plate or rod – by a jet of liquid flowing under high pressure, have become widespread. The frequency of such emitters is 8-30 kHz.

In the low frequency ultrasound range 15 kHz ÷ 100 kHz, ultrasound emitters using the magnetostriction effect of Nickel, and in a number of special alloys, and also in ferrites, have found application. For the emission of ultrasound of medium and high frequencies (f > 100 kHz), the phenomenon of piezoelectricity is mainly used. The main materials for emitters in this case are: piezoquartz, lithium niobate.

Magnetostriuctive emitters are a core of rod or ring shape with a winding through which alternating current flows, and piezoelectric-a plate or rod of piezoelectric material with metal electrodes to which an alternating electric voltage is applied.

The limiting intensity of ultrasound radiation is determined by the strength non-linear 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 most difficult choice of ultrasound frequency to obtain acoustic cavitation by various devices. To excite cavitation in a liquid medium, the following conditions must be created:

- frequency f = 20 kHz-intensity I = 0.3 -1.0 W/cm²;
- frequency f = 200 kHz-intensity I = 10.0 W/cm²;
- frequency f = 20 kHz-intensity I = 200.0 W/cm²;
- frequency f = 20 kHz-intensity I = 50.0 kW/cm²;

Thus, we choose such a frequency for the excitation of cavitation in water, for which the minimum sound input power is required-f = 15-30 kHz, the intensity for the excitation of cavitation in water corresponding to this frequency is 0.3 – 2.0 W/cm².

In the range of low frequency ultrasound – 15 – 100 kHz, emitters using the effect of magnetostriction in a number of alloys and ferrites were used. The vast majority of industrial installations operate in the frequency range 18-44 kHz. This is the optimal frequency range in terms of technological effect,
process efficiency and safety.
The ultrasonic generator UZG-2-4 produced by our industry operates in the selected frequency and intensity range.
In combination with it can work magnetostrictive Converter PMS-6-22 one or two, depending on the flow of treated water. Magnetostrictive transducers of this type can operate in a liquid medium.
The choice of this ultrasonic generator was due to the necessary frequencies and intensities for the excitation of cavitation in water \( f = 18-22 \text{ kHz}, I = 2.0 \text{ W/cm}^2 \), technological considerations about the possibility of mounting the transducer in an existing production line, as well as safety and cost-effectiveness issues.

Relevance of the work
Research of influence of ultrasound on change of properties of water, in particular change of pH in water, is very actual problem.

Purpose of work
Experimental studies on the effect of ultrasound on the pH of water.

Job task
Determination of parameters of ultrasonic field, duration of treatment and influence on change of pH of water.

Equipment and methods of experimental research
1. To determine the pH of the water used potentiometric method of analysis is based on measuring the electrode potential and on finding a relationship between its size and concentration, or rather activity potential component in the solution.
   Used universal ionomer brand EV-74 complete with glass electrode type ESL-43-07.
   The pH measurement of the water was repeated three times, each time removing the electrodes from it and re-immersing them in water. The measurement error is ± 0.01 pH [9,13].
2. Ultrasonic equipment generator UZG – 2 – 4 complete with magnetostrictive transducer of ultrasonic vibrations PMS – 6 – 22 was used [11,15,22].

| ##. | Name of characteristics | Characteristic |
|-----|-------------------------|---------------|
| 1   | Generator output power, kW | 4.5 ± 0.5 |
| 2   | Output voltage, V | 360 ± 80 |
| 3   | Output frequency (adjustable), kHz | 16.8 – 23.5 |
| 4   | Efficiency, %, not less | 75 |
| 5   | Supply voltage (three-phase, with neutral wire), V | 360 ± 5% |
| 6   | The frequency of the supply voltage, Hz | 50 |
| 7   | Weight, kg, not more | 250 |
| 8   | Overall dimensions, mm (l x b x h) | 720 х 580 х 1350 |

These characteristics correspond to the passport data of the equipment.
The transmission of the electrical signal to mechanical vibrations was carried out thanks to the Converter PMS-6-22.
Table 3. The main parameters of the Converter PMS-6-22.

| No. | Name of characteristics | Characteristic |
|-----|-------------------------|----------------|
| 1   | Power consumption, max  | 2.5 kW         |
| 2   | Voltage supply          | 360 ± 80 V     |
| 3   | Operating frequency     | 22 ± 1.65 kHz  |
| 4   | Weight, not more than   | 11 kg          |
| 5   | Overall dimensions      | 300 x 300 x 191 mm |

Description of laboratory installation.
Generator UZG-2-4 is adjusted to the specified parameters: frequency-22 kHz, intensity - 2 W/cm². Further, the transfer of the established parameters of the ultrasonic field to the magnetostrictive transducer PMS-6-22 is carried out. The Converter is built into the ultrasonic reactor, with a capacity of 5.0 liters, made of stainless steel grade XI8HICT. The position of the transducer in the reactor is determined by the direction of radiation of ultrasonic vibrations and the placement of the test water. In the case of these conditions, acoustic radiation was carried out from the bottom up, and the water surface was at atmospheric pressure.

The scheme of the experimental installation for liquid treatment in the ultrasonic field is presented in figure 1.

Figure 1. Scheme of the experimental installation.
1. The reactor of stainless steel of grade XI8HICT.
2. A membrane that emits ultrasonic waves from the bottom to the top.
3. Magnetostrictive Converter PMS-6-22.
4. Water discharge. 5. Cooling liquid.
6. Electrical connection with the generator.
7. Treated source water.
8. Feed water supply.
Laboratory experimental studies on the effect of ultrasonic vibrations in the cavitation mode on the change in the pH of water were carried out over the liquid in the reactor at rest. Bubbles formed in the ultrasonic field in the studied water collapse and create micro-explosions, shock waves and micro-flows. The movement of bubbles starts from the transducer membrane and continues to the open surface of the liquid.

**Results**

Source water for pH studies was used of two types:
- artesian water from the well "7zh", faustovo village, Moscow region (total hardness 16.6 mg-eq/l; carbonate hardness 4.8 mg-eq/l; Ca\textsuperscript{2+} content 7.7 mg/l; Mg\textsuperscript{2+} content 8.9 mg/l; pH 7.8; sulfates 576 mg/l; chlorides 12.0 mg/l);
- tap water of the city of Moscow (total hardness 4.6 mg-eq/l; Ca\textsuperscript{2+} content 2.7 mg/l; Mg\textsuperscript{2+} content 3.2 mg/l; pH 5.9).

The duration of ultrasonic water treatment was 30 seconds, 60 seconds, 120 seconds and 300 seconds. Water samples for analysis were taken from three points of the reactor at each sounding time. Each exposure was repeated three times. After that, the pH of the water of each sample was determined by a potentiometric method using an ionomer of the EV-74 brand. The results of the obtained arithmetic mean values of water pH are placed in table 4.

| ## | Sample designation. | Source water. | The frequency of the sound. | Voice time, t, s. | The pH of the water. |
|----|---------------------|---------------|------------------------------|-------------------|---------------------|
| 1  | 2                   | 3             | 4                            | 5                 | 6                   |
| 1  | a.                  | Artesian water| 22 kHz                       | 0                 | 7.80                |
| 2  |                     |               |                               | 30                | 8.55                |
| 3  |                     |               |                               | 60                | 8.63                |
| 4  |                     |               |                               | 120               | 8.70                |
| 5  |                     |               |                               | 300               | 8.75                |
| 6  | b.                  | Tap water     | 22 kHz                       | 0                 | 5.90                |
| 7  |                     |               |                               | 30                | 6.22                |
| 8  |                     |               |                               | 60                | 6.30                |
| 9  |                     |               |                               | 120               | 6.30                |
| 10 |                     |               |                               | 300               | 6.30                |
| 11 | c.                  | Tap water     | 22 kHz                       | 0                 | 5.70                |
| 12 |                     |               |                               | 300               | 6.30                |
| 13 | d.                  | Tap water     | 8 kHz                        | 0                 | 5.90                |
| 14 |                     |               |                               | 300               | 5.90                |
| 15 | e.                  | Tap water     | 1 MHz                        | 0                 | 5.90                |
| 16 |                     |               |                               | 300               | 4.90                |

Figure 2 plots the change in pH from exposure time.
Figure 2. Changes in the pH value of water depending on the time of sounding.

- a. Artesian water;
- b. Tap water;
- c. Frequency 22 kHz;
- d. Frequency 8 kHz;
- e. Frequency 1 MHz;

- c, d, e - according to the literature.

The initial pH of natural artesian water was 7.8 and tap water was 5.9.

When sounding with a frequency of 22 kHz, there was a change in the hydrogen index from 7.8 to 8.75 (artesian water) and from 5.9 to 6.3 (tap water).

The experimental points on the graph are given as the arithmetic mean.

This figure also shows changes in the pH value of water according to the literature data [10,12,14].

Changes in the pH value are reliable indicators of physical and chemical changes occurring during the sounding of water.

As can be seen from the graph, the change in the pH value of water, after the duration of ultrasonic treatment in 30 seconds, increases slightly.

The graph shows that the frequency of ultrasound affects the change in pH.

The increase in the pH value of water occurs during ultrasonic treatment with a frequency of 22 kHz.

The decrease in the pH of water occurs during ultrasonic treatment with a frequency of 1 MHz.

When ultrasonic treatment with a frequency of 8 kHz, the pH value of the water does not change.

Summary

1. The experimental data obtained confirm that ultrasound affects the pH change of water.
2. Changes in the pH of water depends on the frequency of ultrasonic vibrations.

Conclusion

1. It is known from the literature that in the ultrasonic field in the cavitation mode, active radicals are formed in the water, which affect the changes in the pH of the water.
2. Depending on the frequency of ultrasonic vibrations, hydroxyl radicals $OH^*$ are formed in water (22 kHz) - the pH of water increases or atomic hydrogen $H^*$ (1 MHz) - the pH of water decreases.
3. The conducted experimental researches allow to use the ultrasonic method of water treatment for intensification of processes of water treatment.
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