KAPITEL 4 / *CHAPTER 4* [4]
TECHNOLOGY AND EQUIPMENT FOR REDUCING WATER HARDNESS THROUGH EFFECTIVE REMOVAL OF CALCIUM HYDROCARBONATE

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Introduction

Reducing the hardness of water is an urgent problem both for municipal water supply systems and for industrial enterprises and thermal plants. This problem is especially noticeable where underground and ground water with a high hardness index due to the presence of mineral impurities, in particular calcium and magnesium hydrocarbonates, are used for domestic and drinking water supply. When such water is heated, calcium and magnesium ions, which cause water hardness, form sparingly soluble compounds. These compounds are deposited on the surfaces of heat exchangers, thermal power plants, and pipelines, which leads to decrease in their efficiency, excessive fuel consumption, frequent stops for cleaning, etc. Research into this area was carried out by many scientists and made it possible to solve the problem of removing hardness salts from water, but the problem of finding optimal ways of its implementation, aimed at reducing energy costs and intensifying the water softening process, is still relevant.

To reduce water hardness, methods of thermal, reagent, membrane, electrochemical and magnetic treatment, ion exchange, and their combination are used. In particular, classical methods of water softening (chemical, sedimentation inhibitors, electrochemical treatment, ion exchange and membrane separation) were analyzed in work [1-4].

Although the above methods have become widespread, they have a number of disadvantages related to the large consumption of reagents, the need for preliminary water preparation, wastewater treatment, and the difficulty of their disposal. This leads to the search for new technological solutions to intensify the process of reducing water hardness.

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One of the energy-efficient methods of impacting liquid heterogeneous media is the principle of discrete-pulse energy input (DPEI). This method makes it possible to intensify technological processes in the heat energy industry, utilities, food, chemical, and other industries [5-7].

The application of the DPEI principle to reduce water hardness should create conditions for intensifying the process of extracting calcium bicarbonate with lower energy costs for the process and obtaining a long-lasting effect after treatment. This could reduce the cost of water treatment and increase the productivity of the water softening process.

4.1. The aim and objectives of the study

The purpose of this study is to improve the efficiency of calcium bicarbonate removal and reduce water hardness due to the application of the DPEI principle. This could provide an opportunity to improve the technology of water purification for municipal water supply systems, for industrial enterprises, and thermal stations.

To achieve the goal, the following tasks were set:

– to determine the influence of the speed of the flow shift and the number of treatment cycles in the rotary-pulsation apparatus on the pH of the water and the concentration of calcium ions;

– to determine the effect of ammonia concentration and the number of processing cycles in the rotary-pulsation apparatus on the pH value of the aqueous solution at a constant speed of the flow shift;

– to determine the effect of ammonium hydroxide concentration and flow shear rate on the concentration of calcium ions in water;

– to determine the influence of the concentration of ammonium hydroxide in water and the number of processing cycles in the rotary-pulsation apparatus on the total hard- ness of water;

– to determine the influence of the concentration of ammonium hydroxide and the shear rate of the liquid flow on the total hardness of water.

4.2. The study materials and methods

4.2.1. The object and hypothesis of the study

The object of our research was water from an artesian well, which was treated on a rotary-pulsation apparatus with the DPEI principle in a rotary-type aeration-oxidizing unit. The water used had the following physical and chemical parameters: pH – 7,2; concentration of calcium ions – 77,1 mg/L; total hardness – 13,4 mmol/L.

To determine the chemical composition of water, the DSanPiN 2.2.4-171-10 procedure “Hygienic requirements for drinking water intended for human consumption” was used. The pH of aqueous solutions was measured with a pH meter “Expert-pH”, the total hardness was deter- mined by the trilonometric titration method according to DSTU 7525:2014 “Drinking water. Requirements and methods of quality control”, the concentration of calcium ions was determined by trilonometric titration according to the requirements of DSTU ISO 6058-2003 “Water quality. Determination of calcium. Titrometric method using ethylenediaminetetraacetic acid”.

The hypothesis of the study assumed that the set of physical effects that appear when applying the DPEI principle to liquid systems, in particular water, could allow intensifying the process of removing calcium bicarbonate and reducing its stiffness.

The study accepted the following assumptions:

- the decrease in the concentration of calcium hydrocarbonate occurs due to the removal of free carbon dioxide;
- removal of free carbon dioxide is associated with the transfer of carbon dioxide from the liquid to the gas phase;
- the intensification of the free carbon dioxide removal process occurs due to the increase in the contact surface of the phases;
- adding ammonia will speed up the process of lowering the concentration of

calcium bicarbonate.

The study adopted the following simplifications:

– extraction of free carbon dioxide was considered as mass transfer through the surface of phase separation with- out considering the extraction of free carbon dioxide due to the possible growth and coalescence of microbubbles of carbon dioxide in the liquid;

– the influence of the change in liquid temperature due to dissipative heat release on the kinetics of the process was not considered.

4.2.2. Experimental installation

Water purification from calcium bicarbonate was carried out on a rotary-type aeration oxidation unit (Fig. 1).

Figure 1 - Aeration and oxidation installation of the rotor type:

1 – reactor; 2 – rotary-pulsation apparatus; 3 – three-way faucet; 4 – recirculation circuit; 5 – filtration column; 6 – spray head; 7 – control unit

The installation consists of the following units: reactor, rotary-pulsation apparatus, recirculation circuit, heat exchange circuit, control unit, measuring equipment, filtration column.

The reactor is a tank with a usable volume of 60 liters and is intended for the liquid treatment process. To avoid heating of the liquid due to energy dissipation during the circulation of water through the rotary-pulsation apparatus, the reactor body is equipped with a heat exchange circuit, which was used to maintain the specified temperature of the liquid. A pipe for connecting the recirculation pipeline is mounted in the upper part of the reactor. In the lid of the reactor, technological nozzles are provided for the introduction of liquid into the working volume. In the bottom part of the reactor, a valve is provided for changing the volumetric flow rate.

The control unit is designed to control and regulate the operation of electrical equipment. The unit consists of a magnetic starter, a frequency converter, an ammeter, and an electricity meter.

The filtration column is a glass tube that is filled with filter material (balls of polystyrene foam, activated carbon, quartz sand, etc.) and is designed for oxidation and sediment removal.

The research-industrial plant works as follows. Water is supplied to the reactor (1) through a pipe. Then the rotary pulsation device (2) is turned on, the three-way valve (3) is in the position where the liquid circulates through the re- circulation pipeline (4) along the “reactor - rotary pulsation device - reactor” circuit.

During recirculation, a two-way valve is opened, through which air from the atmosphere enters due to the vacuum created in the suction pipeline. Thus, the liquid is saturated with air. The resulting mixture is sent to the working chamber of the rotary-pulsation apparatus where it is processed according to the DPEI principle. After the rotary-pulsation apparatus, the mixture of air bubbles dispersed in the liquid (gas emulsion) enters the pipeline and enters the lower part of the filtration column (5). Passing through the filter layer, the liquid leaves the column and is fed to the collector of finished products. In the case of insufficient purification, the liquid can be recirculated through the closed circuit «reactor - rotary pulsation apparatus - filtration column - reactor» the required number of times, after which it enters the collector of finished products.

During recirculation, the liquid enters back into the reactor, passing through the spray head (6). The process parameters are set through the control unit (7).

4.3. Effect of treatment parameters on pH, concentration of calcium ions, and water hardness.

4.3.1. The influence of the speed of the flow shift and the number of processing cycles in the rotary-pulsation apparatus on the pH of water and the concentration of calcium ions

Water purification was carried out at a temperature of 20°C, a flow shear rate of $(20–40)\cdot 10^3$ s^{-1} during 1–20 processing cycles.

The speed of the flow shift was determined by the formula:

$$\gamma = \frac{\omega \cdot R}{\delta},$$

where ω is the angular speed of rotation of the rotor, s^{-1}; *R* is the radius from the center of the electric motor shaft to the inner surface of the rotor, m; δ is the gap between the stator and the rotor, m.

One treatment cycle was considered the time during which the entire volume of treated water will pass through the rotary-pulsation apparatus.

During the research, changes in the concentration of calcium ions and pH were monitored in the water. Fig. 2 shows the dependence of water pH on the number of processing cycles and the shear rate acting on the liquid flow.

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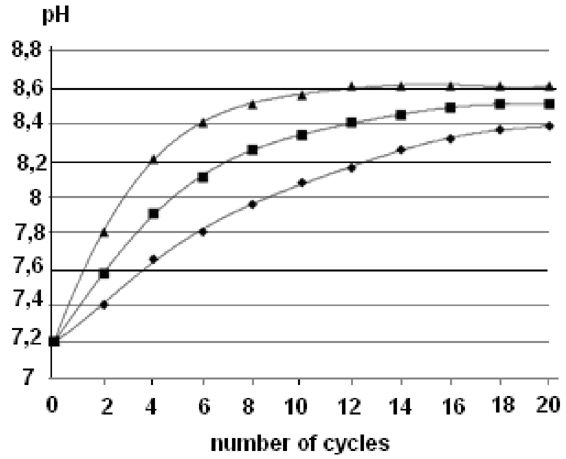

Figure 2 - The dependence of the change in water pH on the number of treatment cycles and the flow shear rate: ♦ – 20; ■ – 30; ▲ – 40 (10^3 s^{-1})

The most significant increase in pH was observed during water treatment with a flow shift rate of $40 \cdot 10^3$ s^{-1} during 11–12 treatment cycles. During further water treatment, the pH practically did not change.

Table 1 shows the change in the concentration of calcium ions (with an initial concentration of 71,7 mg/L) depending on the number of processing cycles and the speed of the liquid flow shift.

Table 1 - Change in the concentration of calcium ions (mg/L) depending on the number of treatment cycles and the displacement speed of the fluid flow γ (10^3 s^{-1})

Number of processing cycles	Calcium ion concentration, mg/L		
	$\gamma=20 \cdot 10^3$ s^{-1}	$\gamma=30 \cdot 10^3$ s^{-1}	$\gamma=40 \cdot 10^3$ s^{-1}
5	74,0	72,2	67,4
10	70,1	67,2	58,5
15	66,3	62,6	57,1
20	57,9	57,3	57,0

Our results show that water treatment in the rotary-pulsation apparatus can reduce the content of calcium ions by 28–30 %.

4.3.2. Influence of ammonia concentration and number of treatment cycles on pH at constant flow shear rate

A study was conducted on the alkalinization of the source water with an aqueous ammonia solution in the amount of 0,005–0,015 wt% with subsequent treatment of the mixture in a rotary-pulsation apparatus with the flow shear rate of $(20–40)\cdot10^3$ s^{-1} during 10–20 processing cycles. The results are shown in Fig. 3.

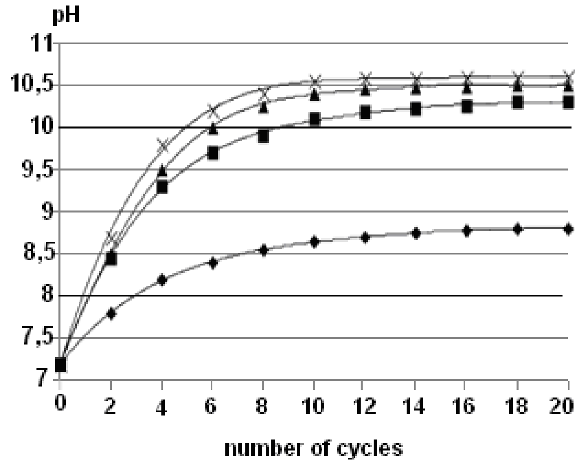

Figure 3 - The dependence of change in pH of an aqueous solution on the concentration of ammonia and the number of treatment cycles at the flow shift rate of $40\cdot10^3$ s^{-1}: ♦ – 0,00; ■ – 0,05; ▲ – 0,1; × – 0,15 (wt%).

As the ammonia concentration in water increases from 0,05 to 0,15 wt%, the pH value increases to a maximum during the first 10–12 treatment cycles for all ammonia concentration values.

4.3.3. Influence of ammonium hydroxide concentration and flow shear rate on calcium ion concentration in water

Table 2 gives experimental data on the change in the amount of calcium ions (mg/L) depending on the concentration of ammonium hydroxide in water and the shear rate acting on the liquid flow during treatment in a rotary-pulsation apparatus.

With an increase in the content of ammonium hydroxide in the solution from 0,0 to 0,15 mg/L without treatment, the concentration of calcium ions decreases by 64%. With an increase in the shear rate of the flow $(20, 30, 40)\cdot10^3$ s^{-1}, the concentration of calcium ions decreases by 98,5; 98,7; 99,3 % respectively.

Table 2 - Dependence of the change in the amount of calcium ions (mg/L) on the concentration of ammonium hydroxide in water and the shear rate acting on the liquid flow during treatment in a rotary-pulsation apparatus (γ)

Ammonium hydroxide content in solution, wt%	Calcium ion concentration, mg/L			
	0	$\gamma=20\cdot10^3$ s^{-1}	$\gamma=30\cdot10^3$ s^{-1}	$\gamma=40\cdot10^3$ s^{-1}
0	77,1	70,1	67,2	58,4
0,05	56,5	14,6	11,9	9,08
0,1	50,3	1,17	0,94	0,72
0,15	27,6	1,14	0,92	0,70

4.3.4 Influence of the concentration of ammonium hydroxide in water and the number of processing cycles in the rotary-pulsating apparatus on the total water hardness

Fig. 4 shows the dependence of change in the total hard- ness of water on the content of ammonium hydroxide and the number of treatment cycles in the rotary-pulsation apparatus at a constant shear rate. The initial water hardness was 13,4 mmol/L. Our results indicate that a decrease in water hardness to a value of less than 0,2 mmol/L is observed at a concentration of ammonium hydroxide of 0,1 –0,15% wt% after 9–10 treatment cycles.

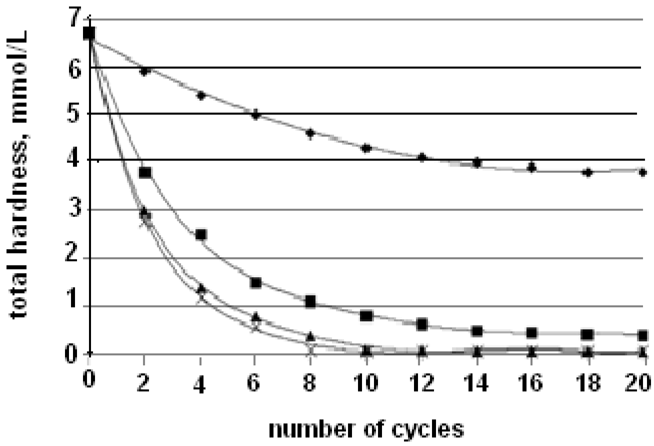

Figure 4 - The dependence of change in the total hardness of water on the content of ammonium hydroxide in the solution and the number of treatment cycles in the rotary-pulsation apparatus (flow shear rate, $40\cdot10^3$ s^{-1}): ♦ – 0,0; ■ – 0,05; ▲ – 0,1; × – 0,15 (wt%)

The content of ammonium hydroxide in the amount of 0,5 wt% makes it possible to reduce the hardness of water to 0,8 mmol/L after 10–12 treatment cycles. Without the addition of ammonium hydroxide, water hardness decreases to 7,6 mmol/L after 10–11 treatment cycles.

4.3.5. Influence of ammonium hydroxide concentration and fluid flow shear rate on total water hardness

Table 3 gives the results of measuring the total hardness of water depending on the content of ammonium hydroxide in it and the speed of the flow shift after treatment in a rotary-pulsation apparatus.

Table 3 - The dependence of decrease in the total hardness of water (mmol/L) on the content of ammonium hydroxide in it and the speed of the flow shift (γ) after treatment in a rotary- pulsation apparatus

Ammonium hydroxide content in solution, wt%	Total water hardness, mmol/L			
	0	$\gamma=20\cdot10^3$ s^{-1}	$\gamma=30\cdot10^3$ s^{-1}	$\gamma=40\cdot10^3$ s^{-1}
0	13,4	11,0	9,4	7,6
0,05	6,0	3,8	1,6	0,8
0,1	4,6	1,6	0,2	0,16
0,15	4,4	0,28	0,18	0,14

According to the data in Table 3, achieving an indicator of total hardness of water less than 0,2 mmol/L is observed when the concentration of ammonium hydroxide in the solution is higher than 0.1 wt% and the shear rate of the flow is higher than $30\cdot10^3$ s^{-1}.

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Conclusions

1. It was established that an increase in the shear rate of the liquid flow when it passes through the rotary-pulsation apparatus and an increase in the number of treatment cycles leads to an increase in the pH of water from 7,2 to 8,6 at a shear rate of $40\cdot10^3$ s^{-1} after 10–12 treatment cycles. A similar pattern was also observed when determining the concentration of calcium ions, which decreased from 77,1 to 57,1 mg/L during 15 treatment cycles at the same flow shear rate. These changes are caused by the breaking of hydrogen bonds in water as a result of its mechanoactivation, the extraction of absorbed carbon dioxide, and the formation of insoluble calcium carbonate. A decrease in the content of calcium ions by 28–30 %, however, is not enough for the use of such water in thermal power generation.

2. It was determined that with an increase in the concentration of ammonia and the number of treatment cycles in the rotary-pulsation apparatus at a constant shear rate of $40\cdot10^3$ s^{-1}, an increase in water pH is observed. With an ammonia concentration of 0,05 to 0,15 wt%, after 10 cycles of treatment, the pH of the water exceeds 10. Without the addition of ammonia, the pH of the water increases to 8,6.

3. With an increase in the concentration of ammonium hydroxide in the solution from 0 to 0,15 mg/L without treatment, the concentration of calcium ions decreases by 64 %, but at flow shear rates $(20, 30, 40)\cdot10^3$ s^{-1}, the concentration of calcium ions decreases by 98,5; 987; 99,3 %, respectively.

4. It was established that the reduction of water hardness to a value of less than 0,2 mmol/L occurs at a concentration of ammonium hydroxide of 0,1 – 0,15 wt% after 9–10 treatment cycles. This meets the water quality requirements for water heating boilers, while without the addition of ammonium hydroxide, water hardness is reduced to a maximum of 7,6 mmol/L.

5. It was determined that in order to ensure a water hardness of 0,16 mmol/L, the optimal content of ammonium hydroxide in the solution should be 0,1 wt% at a shear rate of the liquid flow of $40\cdot10^3$ s^{-1}. This is consistent with generally accepted requirements for water quality for water heating boilers, according to which water hardness should not exceed 0,1–0,2 mmol/L.