



# STUDY OF THE POSSIBILITY OF USING NEW TYPES OF REAGENTS TO INCREASE THE EFFICIENCY OF CLOSED WATER CIRCULATION CYCLES

<sup>1</sup>Allayorov N.B., <sup>1</sup>Vapoev X.M., <sup>1</sup>Aliyev T.B.  
<sup>1</sup>Navoi State University of Mining and Technology

One of the biggest environmental problems in the world in the XXI century is the problem of water. The decrease in water reserves increases the need for water purification in the mining, chemical, petrochemical, textile and food industries. A million cubic meters of water from such large industrial zones are used. The concentration of anions and cations in the water used increases by 3-4 times.

Today, wastewater discharge from mining and chemical industrial zones in the Navoi region affects freshwater resources in nearby areas. To prevent this, methods of precipitation of anions and cations should be studied. At the industrial level, an important step is the implementation of measures for the reuse of purified water.

To ensure the efficient and environmentally friendly functioning of circulating systems at high values of the evaporation coefficient, special treatment of cooling water is necessary. In this regard, an urgent task is to develop and implement new methods of stabilizing water treatment in the cooling circulating cycles of enterprises.

Methods of stabilization treatment of cooling water in circulating water supply systems can be divided into two groups [1,2]:

- Physical (water treatment with ultrasound, magnetic field, etc.);
- Chemical (acidification, recarbonization, phosphating, phosphate-acid treatment, etc)

The authors of the works [3-6] proposed methods of cooling water treatment based on the use of installations emitting ultrasonic vibrations. In [7], the authors assume that when ultrasonic vibrations are applied to water, a large number of constantly shifting crystallization centers are formed, which complicates the growth and deposition of crystals of scale-forming compounds on the heat exchange surfaces of equipment.

The authors [8-11], who propose the use of a magnetic field for stabilizing water treatment, believe that the possible mechanism of the influence of a magnetic field on sedimentation processes is based on the polarization of sedimentation ions and water molecules.

In [12, 13], researchers conclude that the effect of radiation is observed only in a limited area of action of magnetic or ultrasonic emitters, as a rule, directly at the place of their installation.

In general, non-reagent methods of stabilizing water treatment are characterized by low efficiency and often do not show stable results, therefore they are not an alternative to chemical methods and can be recommended as auxiliary measures for reagent treatment of cooling water.

To date, one of the most widely used methods of processing recycled water at a number of domestic enterprises is acidic [14-16].

When using the acid method, it is more advisable to use weak organic acids. Thus, compositions based on citric acid or its salts are known [17], di- and monocarboxylic acids [18], homo- or copolymers of acrylic acid [19], an alkaline salt of polyethersulfonic and/or polymaleic acid [20]. However, the use of organic acids is effective only with a high content of them in the system, based on the stoichiometric interaction of carboxyl groups with calcium ions [21,22].

Initially, inorganic polyphosphates (hexametaphosphate, tripolyphosphate, etc.) were used as hardness stabilizers, which made it possible to reduce the degree of calcium scale formation, maintain a given alkalinity of recycled water and partially provide anticorrosive protection of the metal [23-24].

The purpose of this work is to study scale formation in water and their elimination with useful various reagents.

## EXPERIMENTAL METHODOLOGY

During the research, calcium chloride of the "bda" brand, six-way magnesium chloride of the "bda" brand, sodium bicarbonate of the "bda" brand were used as starting materials for the creation of model systems. The pH value was adjusted using 0.1 N sodium hydroxide solution and 0.1 n hydrochloric acid solution.

Chemicals produced by the company "Solenis Industries Sweden AB" were used as sedimentation inhibitors: Performax DC5000-EU, Performax 3S-600, amino trimethylene phosphonic acid ATMP (CAS 6419-19-8), phosphonobutantricarboxylic acid 50% (PBTC) (CAS 37971-36-1), with different molecular weight values (500, 1000).

The particle size distribution of calcium carbonate formed without additives and in the presence of inhibitors was determined using a photometric sedimentometer FSH-4. The principle of operation of the device is based on the sedimentation law of Stokes and the law of extinction of light in a turbid medium (the Boogler-Lambert-Behr law).



Measurement of the induction period of crystal formation in the  $\text{CaCl}_2\text{-NaHCO}_3\text{-H}_2\text{O}$  system in the presence of sedimentation inhibitors. To study the effect of additives of inhibitors of various classes on the duration of the induction period of crystal formation in the model system  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}/\text{CO}_3^{2-} - \text{H}_2\text{O}$ , a spectrophotometric method was used.

The beginning of the formation of a crystalline precipitate of carbonates was recorded using a Cary WinUV 50 spectrophotometer based on a break in the graph of the dependence of light transmission in the system on time.

The calculated amount of 0.1 M  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions and bidistilled water was mixed in a glass beaker using a magnetic stirrer and heated to a temperature of  $25^\circ\text{C}$ , after which the resulting solution was transferred to a thermostatically controlled glass cell of a spectrophotometer. The required amount of  $\text{NaHCO}_3$  solution heated to  $25^\circ\text{C}$  with a concentration of 0.1 M was added to the cuvette using a dispenser, after which the light transmission in the system was measured.

After each experiment, the cuvette was washed with 0.1 M HCl solution to completely remove the crystalline precipitate.

The carbonates were precipitated at a constant molar ratio of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  equal to 3.7. A mixture of calcium and magnesium chloride salts, as well as calcium carbonate, was stirred, heated and thermostated ( $80 \pm 5^\circ\text{C}$ , 3 hours), then the resulting precipitate was filtered and dried to a constant weight at room temperature.

Carbonate dispersions were prepared as follows: sample samples (fraction with a particle diameter of 10 microns) weighing 1.0 g were placed in glasses with a capacity of 150 ml, filled with distilled water or a solution (weighing 99.0 g) containing inhibitors of a given concentration, and dispersed using a magnetic stirrer at a speed of 600 rpm for 1 hour at a temperature of  $(293 \pm 1)\text{K}$ , after which a given volume of dispersion was taken from the glass from the same depth, transferred to a measuring flask and brought to 100 ml of distilled water. The pH value of the

dispersion was monitored using a pH meter and adjusted by adding a sodium hydroxide solution.

To select the wavelength, the prepared suspension was photometric relative to the reference solution (distilled water) at a wavelength from 315 to 990 nm. The wavelength corresponding to the highest absorption of the studied dispersion (450 nm) was chosen for the studies, which allowed the determination to be carried out with the greatest sensitivity and less error.

Measurements of the light transmission of the samples were carried out every 30 minutes at a wavelength of 450 nm, in a glass cuvette, 30 mm thick.

The error of the measurement results was:

- within the series of about  $\pm 1.6\%$
- between series of studies  $\pm 6.4\%$ .

## RESULTS AND THEIR DISCUSSION

Investigation of the effectiveness of scale formation inhibitor reagents under dynamic conditions on a model laboratory installation RMAS SCL-30P-2A (UK), which allows for a comparative analysis of various inhibitors under conditions of temperature changes, pH values and the composition of scale-forming solutions.

When conducting research on a PMAC model installation, solutions of calcium chloride, magnesium, and sodium bicarbonate are injected into the capillary at a constant volume and flow rate.

During the measurement, information about the differential pressure in the capillaries is automatically recorded at set intervals. The time interval during which a scale layer forms in the capillary, leading to an increase in differential pressure from zero to a certain value, is used as an indicator characterizing the effectiveness of preventing or slowing down (inhibiting) sedimentation. This indicator is a relative value – it characterizes the process of slowing the formation of sediment in the capillary compared to the control non-reactive variant. The less the pressure in the capillary increases over a certain period of time, the more effective the reagent is and the optimal dose used.

### Results of the Analysis of the Inhibitor "Performax 3-S600"

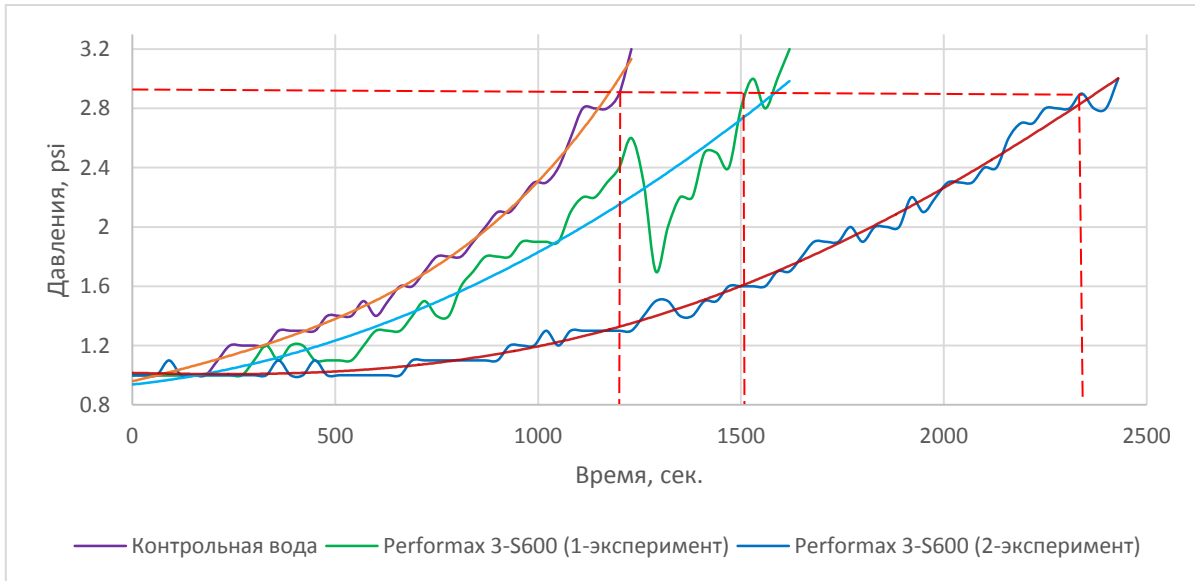


Figure 1 - Effects of a salt formation inhibitor Performax 3-S600 (0.1 mg/L) for differential pressure

### The results of the analysis of the inhibitor "ATMP 50%".

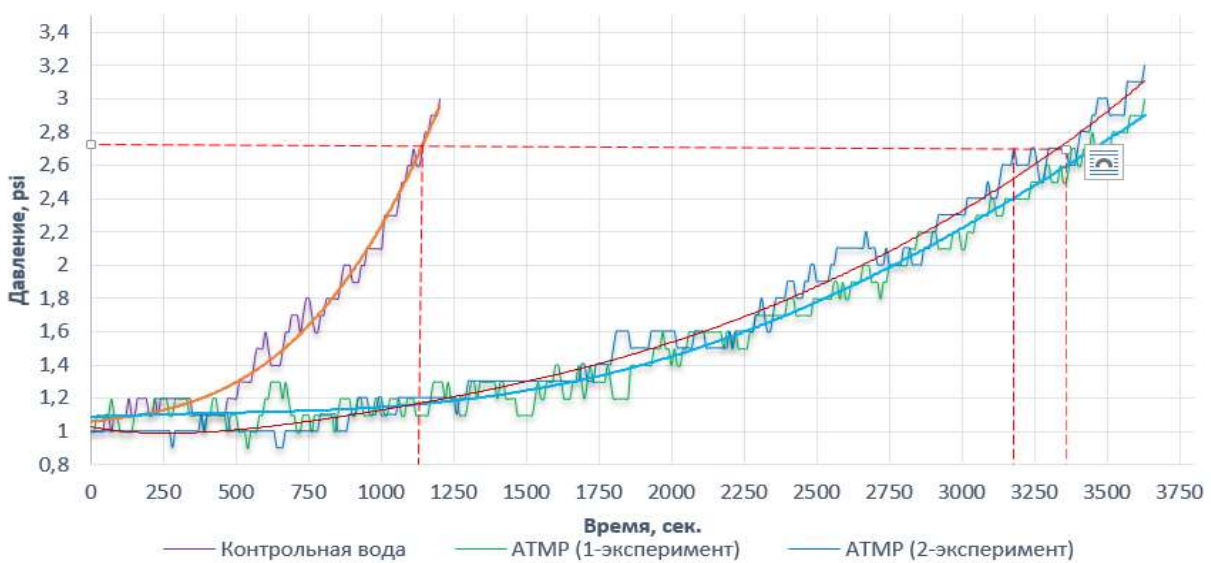


Figure 2 - Effects of a salt formation inhibitor ATMP 50% (0.1 mg/l) for differential pressure

### The results of the analysis of the PBTC inhibitor 50%.

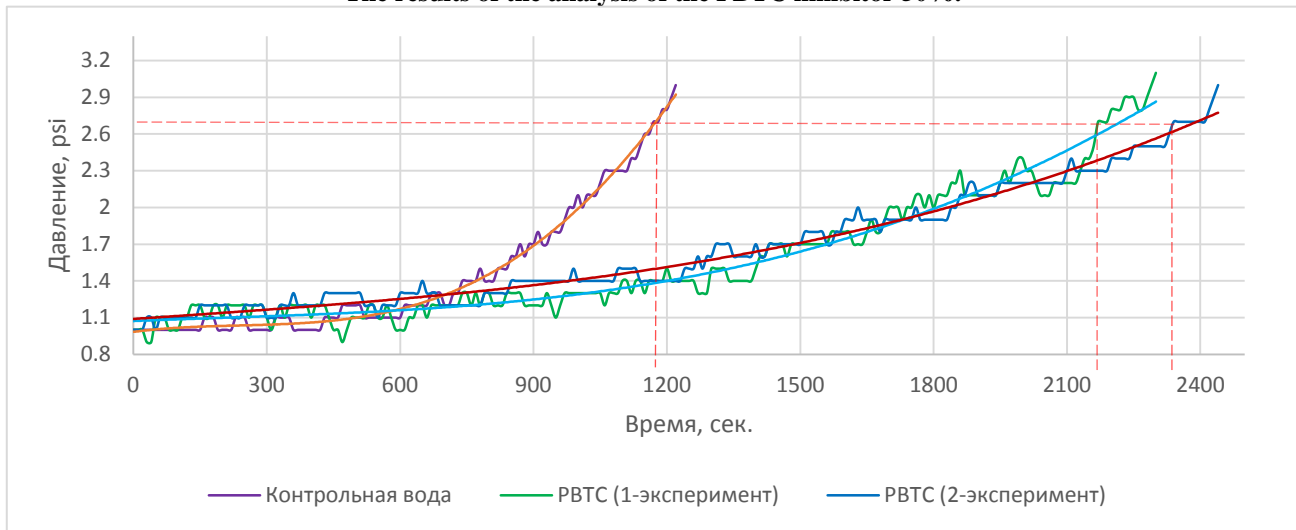


Figure 3 - Effects of a salt formation inhibitor PBTC 50% (0.1 mg/l) for differential pressure

### The results of the analysis of the PERFORMAX DC5000-EU inhibitor.

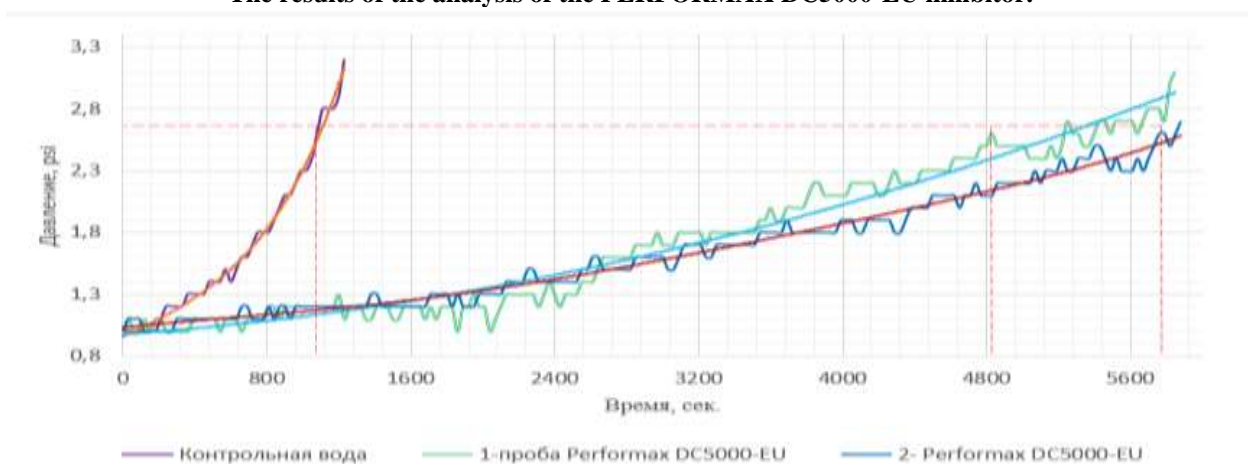


Figure 4 - Effects of the salt formation inhibitor PERFORMAX DC5000-EU (0.1 mg/L) on differential pressure

The analysis of the kinetic curves presented above allows us to draw the following conclusions. All the studied types of inhibitors slow down the process of salt formation and thereby increase the multiplicity of circulation. At the same time, these types of inhibitors differ significantly in their effectiveness. So if for the inhibitor "Performax 3-S600" the time to reach the control pressure in the capillary (reduction of salt formation) was 2.5 times, then for the inhibitor of the brand "ATMR 50%" this value was 3.5 times (from 1100 sec. for control experience up to 3200-3350 sec.). The best indicators for the effectiveness of salt formation inhibition were established for the PERFORMAX DC5000-EU brand inhibitor. For this inhibitor, the increase in the duration of reaching the control pressure in the capillary was 6.5 times (Figure 1-4).

Thus, it has been established that the use of salt formation inhibitors can be recommended as an effective way to increase the multiplicity of circulation of pure and conditionally pure water cycles that do not have direct contact with impurities (heat exchange, cooling and crystallization systems).

To improve the accuracy of measurements, the initial conditions were selected in such a way that the induction period was at least 5 minutes. Initiation of the nucleation process by foreign particles somehow present in the volume of the system was not observed, since the results obtained are characterized by high reproducibility of measurements (error <3%). The close values of the induction period when using two different cuvettes allowed us to conclude that the influence of the surface factor of the glass cuvette and the course of heterogeneous nucleation is insignificant.



Evaluation of the dispersing abilities of substances of various classes in relation to crystalline carbonate-containing precipitates. To determine the dispersing ability of inhibitors, the method of relative dispersion capacity was used. The relative dispersion capacity is a parameter that allows a comparative analysis of the dispersing ability of reagents with respect to water-insoluble particles in water systems. The concentration of calcium carbonate used in this method was 15-50 ppm, which exceeds the concentration of insoluble suspended solids present in water cycles. The concentration of the inhibitor used, on the contrary, was within the values proposed for use in practice.

The method of photometry based on the proportional relationship between light absorption and the concentration of the absorbing substance was chosen as the research method. The higher the dispersing ability of the compound, the better the carbonate particles are suspended in the aqueous dispersion and the lower the light transmission. The experimental value shows what percentage of calcium carbonate is in the suspended state after certain time intervals at a pH value of 8.

## CONCLUSION

The analysis of the kinetic curves obtained during the studies allows us to conclude that all the studied types of inhibitors slow down the process of salt formation and thereby increase the multiplicity of circulation. At the same time, these types of inhibitors differ significantly in their effectiveness. So if for the inhibitor "Performax 3-S600" the time to reach the control pressure in the capillary was 2.5 times, then for the inhibitor of the brand "ATMR 50%" this value was 3.5 times. The best indicators for the effectiveness of salt formation inhibition were established for the PERFORMAX DC5000-EU brand inhibitor. For this inhibitor, the increase in the duration of reaching the control pressure in the capillary was 6.5 times. Thus, the use of salt formation inhibitors can be recommended as an effective way to increase the multiplicity of circulation of pure and conditionally pure water circulation cycles that do not have direct contact with the admixture.

## REFERENCES

1. *Technical reference book on water treatment Degremont / M.I. Alekseev [et al.] ; under total. edited by M.I. Alekseev. - St. Petersburg : Novy zhurnal, 2007. - 1696 p.*
2. *Ryabchikov B.E. Modern methods of water preparation for industrial and domestic use / B.E. Ryabchikov - M. : Delhi print, 2004. - 328 p.*
3. *Goncharuk, V.V. The use of ultrasound in water purification / V.V. Goncharuk, V.V. Malyarenko, V.A. Yaremenko // Chemistry and technology of water. - 2008. - Vol. 30, No. 3. - pp. 253-277.*
4. *Mityuryaev, A.N. Ultrasonic method of preventing scale formation / A.N. Mityuryaev // Industrial power engineering. - 2004. - No. 4. - pp. 30-32.*
5. *Nikolaevsky, N.N. Ultrasonic method of preventing scale formation / N.N. Nikolaevsky // Heat supply news. - 2002. - Vol. 10, No. 26. - C. 44-45.*
6. *Antropov, G.V., Trushina I.V. The use of ultrasound to prevent scale formation / Antropov G.V., Trushina I.V. // Bulletin of SSTU. - 2007. - T. 3, No. 27. - C. 3.*
7. *Balichenko, O.I. Research on reagentless ultrasonic water treatment / O.I. Balichenko, V.I. Nezdoimov, A.A. Zalugin // Bulletin of the Donbass National Academy of Construction and Architecture. - 2009. - T. 2, No. 76. - C. 48-55.*
8. *Dushkin, S.S. Magnetic water treatment at chemical enterprises / S.S. Dushkin, V.N. Evstratov. - M. : Chemistry, 1986. - 142 p.*
9. *Coey, J. Magnetic water treatment / J. Coey, S. Cass // J. of Magnetism and Magnetic Materials. - 2000. - T. 209 № 1. - C. 71-74.*
10. *Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate / A. Fathi [et al.] // Water Research. - 2006. - T. 40, № 10. - C. 1941-1950.*
11. *Magnetic water treatment for scale prevention / C. Gabrielli [et al.] // Water Research. - 2001. - T. 35, № 13. - C. 3249-3259.*
12. *Sokolsky, Yu.M. Magnetized water: truth and fiction / Yu.M. Sokolsky - L. : Chemistry, 1990. - 144 p.*
13. *Points, V.F. Water and magnet / V.F. Points // Water treatment, Water treatment, Water Supply. - 2011. - No. 10. - C. 36-45.*
14. *Vikhrev, V. F. Water treatment / V.F. Vikhrev, M.S. Shkrob; edited by M.S. Shkrob. - M. : Energiya, 1973. - 416 p.*
15. *Solutions of peracids for hardness stabilization and the method of their preparation and use: pat. 945405 A2 EP, MPC6 With 02 F 1/72, With 02 F 1/50 / Reinold Andreas, Walzer Egon; applicant Degussa - Huels Aktiengesellschaft. - No. 99103500; application 24.02.1999; publ. 29.09.1999 // ISM. - 2000. - issue 38. - No. 9.*
16. *Composition based on maleic acid for the removal of lime scale: pat. 6001792 A US, IPC6 C 02 F 5/10 / Vos Eddy; applicant The Procter & Gamble Comp. - No. 090073; application. 19.07.1993; publ. 14.12.1999 // ISM. - 2000. - issue 38. - No. 12.*
17. *Composition for softening water: pat. 2001128332 A1 GB, MPK7 C 02 F 5/00, C 02 F 5/10 / M. Bosco, R. Casonati; applicant Reckitt Benckiser N.V. - No. 200128332; application No. 27.11.2001; publ. 28.05.2003 // ISM. - 2004. - issue 38. - No. 5.*
18. *Tablets for softening water: pat. 2382342 A1 GB, MPK7 C 02 F 5/08, C 02 F 5/00, C 02 F 5/10 / M. Bosco, R. Casonati; applicant Reckitt Benckiser N.V. - No. 200128321; application 27.11.2001; publ. 28.05.2003 // ISM. - 2004. - issue. 38. - No. 5.*
19. *Inhibitor of precipitation of calcium carbonate and phosphate in the form of scale: pat. 1346957 A2 EP, MPC7 C 02 F 5/10 / Austin Anne-Marie B., Ward Eric C.; applicant National Starch And Chemical Investment Holding Corporation. - No. 3005404; application 13.03.2003; publ. 24.09.2003 // ISM. - 2004. - issue 38. - No. 9.*
20. *Method of preventing scale formation: pat. 6146538 A US, IPC7 C 02 F 1/76 / Martin Roy; applicant United States Filter Corporation. - No. 378232; application No. 19.08.1999; publ. 14.11.2000 // ISM. - 2001. - issue 38. - No. 11.*
21. *Freidlin G.N. Aliphatic dicarboxylic acids / G.N. Freidlin. - M. : Chemistry. - 1978. - 263 p.*
22. *Wada, N. Effects of Carboxylic Acids on Calcite Formation in the Presence of Mg<sup>2+</sup> Ions / N. Wada, K. Yamashita, T. Umegaki // J. of colloid and interface science. - 1999. - Vol. 212, № 2. - P. 357-364.*
23. *Elliot M. N. Scale control by threshold treatment / M.N. Elliot // Desalination. - 1970. - Vol. 8, № 2. - P. 221-236.*
24. *Dove, P.M. Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observations by Scanning Force Microscopy / P.M. Dove, M.F. Hochella Jr // Geochimica et Cosmochimica Acta. - 1993. - Vol. 57, № 3. - C. 705-714.*