E A Ananeva and D Y Feklistov
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe sh. 31, 115409, Moscow, Russia.

E-mail: fateev@isp.nsc.ru

Abstract. Methods of water treatment were developed using activators, which lead to decrease of scale formation due to the conversion of hardness salts into aragonite crystal form. The installation was created on the base of conducted research, which can be used in systems of circulating water supply and allows to provide the decrease of scale formation.

1. Introduction
Precipitate formation process of calcium carbonate precipitation is a major process of scale formation during water usage in thermal engineering. The aim of the work is to create mobile installation, using water treatment methods. Water treatment methods allow decreasing scale formation on the walls of heat exchanger. Preparatory experiments had been put in the base of installation development. Using possibility of such ways of water treatment leads to the decrease of scale formation without water softening.

Crystalline form of hardness salts, size distribution of crystals, and other properties of nascent scale depends on different factors. For example, with the help of synchrotron emission it was detected that at temperatures $7–25\,\text{°C}$ fast dehydration of nanoparticles of amorphous calcium carbonate and its crystallization as vaterite takes place on the first stage; on the second stage vaterite transforms into calcite [1].

Well-known nonreagent magnetic water treatment [2] facilitates to directional crystallization of calcium carbonate in the form of needle aragonite. These crystals have bad adhesion to the support, poor grip with each other and can be located in solution for a long time. In this case magnesium and calcium salts, contained in water, don’t form solid deposit on the walls of heat exchanger pipes. However, decrease effect of scale formation by magnetic field is unstable and in some cases is lost with time. Magnetic and electrochemical water treatment unequally influence on the shape, size, and crystals precipitation rate of calcium carbonate. Transformation effect of electrochemically formed calcium carbonate crystals influenced by magnetic field into sheaf-like crystals of aragonite was detected [3].

It was established, that filtration of earth water through microporous materials influences on the shape of calcium carbonate crystals, formed at water heating.

2. Main text
Research of microfiltration influence on scale formation process and on the shape of hardness salts of crystals was carried out, using filtration unit «Millipore» with membrane, which channel size is
0.45 μm. Model hardness solutions were mixed solutions of calcium chloride and sodium bicarbonate in tap water. Hardness of water was determined on the inlet and outlet of solutions from installations using method of complexometric titration with trilon B. The presence of scale reducing effect was detected by the value of carbonate hardness in supernatant fluid, and also by scale formation on glasses, which had been contacted with treated and untreated water on the evaporation stage. If the hardness in supernatant fluid after boiling of already treated water was higher, than in case of analogue experiment with untreated water, this fact circumstantially detects the presence of the effect of scale decrease. In this case, micro particles of calcium carbonate are in suspension state.

Relative amount of scale, formed on glasses at their immersion to initial evaporated and filtered water, was evaluated by the change of optical density (D) using spectrophotometer Specol 1300. Glasses were immersed into vessels, filled with test water samples. Water was boiled and evaporated to half in order to create the supersaturation to calcium carbonate. Effect was interpreted as scale reducing, if glasses optical density, which were boiled in treated water samples was lower, than glasses optical density in analogue experiments with initial water samples. The shape of nascent calcium carbonate crystals was evaluated using microscope METAM PB-21-1.

Verification results of «quasi-softening» effect presence in model solution, using filtration unit “Millipore” with membrane 0.45 μm are presented in table 1 and fig.1

**Table 1. Verification results of «quasi-softening» effect**

| Indicator name, unit of measurement | Initial water (hydrocarbonate water with high value of hardness) | Water after treatment | Notation                                      |
|-------------------------------------|---------------------------------------------------------------|----------------------|-----------------------------------------------|
| pH                                 | 7.3                                                           | 7.3                  | «Quasi-softening» effect was detected          |
| Hydrocarbonates, mg/l               | 520                                                           | 500                  |                                               |
| Water hardness before boiling, "H" | 7.3                                                           | 7.3                  |                                               |
| Supernatant fluid hardness after boiling, "H" | 4.6                                                           | 4.8                  |                                               |
| Scale formation on glasses, increment of optical density, ΔD | 0.035                                                         | 0.005                | Effect of scale decrease was detected          |
| Crystal shape                       | Calcite crystals                                              | Aragonite crystals   | Aragonite crystals prevail fig.1              |

Conducted researches show, that microfiltration doesn't lead to water hardness changing, but post heating of this water doesn’t lead to scale formation. Detected effect of «quasi-softening», earlier was mentioned at filtration through polymer with space-globular structure. (SGS) [4].

![Figure 1. Shape of calcium carbonate crystals, formed at water boiling: a) initial water – calcite; b) after filtration though nylon membrane 0.45 μm – aragonite.](image-url)
For the creation of stable «quasi-softening» effect at installation designing activating additives in the form of ions of ferric iron and hydrocarbonate. Ions $\text{Fe}^{(+3)}$ promotes crystallization of calcium carbonate in the form of aragonite. Photos of calcium carbonate crystals, formed at initial water boiling and water with the addition of ferric chloride, was shown in fig. 2.

**Figure 2.** Calcium carbonate crystals shape, formed at water boiling: a) initial water – calcite; b) initial water with activating additive of ferrous ions (+3) – aragonite.

Activating additive of sodium hydrocarbonate allows to regulate $\text{pH}$ of initial water and accelerates the process of hydrolysis of ferric chloride. Hydrolysis takes place with the forming of ferric chloride, which coagulates and gives a precipitate with high developed surface. On the surface of the precipitate $\text{Fe(OH)}_3$, adsorption of calcium and magnesium ions occurs and partly reduces the hardness of initial water.

Suspended particles, including calcite microcrystals as the most thermodynamically stable modification of calcium carbonate are removed from the water on the stage of microfiltration. As the result, conditions for for aragonite crystals formation are created, as aragonite crystals are less resistant to supersaturation and precipitate faster. [5]. It corresponds to known "steps rule" of Ostwald (at system transformation from one state to another, firstly less stable form segregates) [6]. Available energy of phase transformation of aragonite into calcite approximately is 1.1 kJ/mol. The energy barrier for such a transformation is big enough, that's why unstable form of aragonite can be maintained indefinitely long.

Nowadays, creation of circulating and closed circuit systems of water supply in order to reduce the consumption for technological purposes of pure water and to decrease environmental impact is an actual problem. The use of circulating water supply allows reducing the consumption of natural water in ten times, with significantly lower operating and capital costs. The proportion of circulating water is continuously increasing in all industries. Basically, circulating water is used in heat-exchange facilities for excess heat removing, while it is repeatedly heated to 40 - 45 °C and then cooled in cooling tower. Considerable part in the result of evaporation and entrainment is lost, besides, it is polluted to a certain limit while passing through pipelines of heat-exchange equipment. On the inner surfaces of heat exchanger tubes and the calcium carbonate is deposited, whose solubility decreases with increasing temperature. The deposition of calcium carbonate on the surface occurs even at relatively low heating 30 - 35 °C. The rate of deposition of calcium carbonate and other salts according to the technical standards should not exceed 0.25 g/(m$^3$·h). In order to prevent corrosion, fouling and scaling of the recycled water is removed from the system, replacing it with fresh water from a source or purified waste water [7].

In the result of conducted research, installation was designed. It allows to provide the decrease of scale formation in the systems of circulating water supply. Principal scheme of installation is shown in the Fig. 3.
Figure 3. Principal installation scheme of scale formation decrease.

Installation works according to principal scheme. Contaminated circulating water, going through inlet strainer 1 of preliminary mechanical purification, with the help of the pump 2 this water enters to the block 3 of reagent treatment, thus it is treated successively with sodium hydrocarbonate and ferric chloride. Input of reagents is carried out using water-watered ejectors 4 and 5, operating in mixing mode. Efficiency of treatment by reagent increases due to intensive mixing of the reagents and their uniform distribution in the treated water, which leads to lower costs of reagents. Due to the fact that the input of the reagents into purified water is carried out by ejectors without the use of special metering devices (metering pump), a reduction in energy consumption and reduction in material costs of water treatment takes place. On the next step, the water flow mixed with reagents is directed to reaction chamber 6 of the reagent treatment module 3. Effective mixing of reagents with treated water and their uniform distribution in the water volume takes place in reaction chamber 6. From the reaction chamber 6 water enters the coagulation chamber 7, where the formation of coagulated sludge takes place in sludge removal zone 8, and water is directed to clarified water chamber 9. Water, already containing no flakes and slurries with the help of water pump 10, enters into the microfiltration unit 11. Microfiltration unit operates on the principle of tangential flow with a pore size of the filter element is 0.5 µm. Tangential flow of feed water provides a continuous washout of detained contaminants from the surface of the filter element, preventing the formation of a layer of filtered sludge on the surface of the filter element. Pure water is returned to the working cycle of circulating water supply system and the water flow, not passed through the filter element enters the crystallization unit 12.

Conclusion
Calcium carbonate, obtained in crystallization unit in the form of aragonite, can be used as additives in the production of various construction materials: refractory materials, cements and fillers.

Acknowledgements.
The work was financially supported by the Ministry of Education and Science, agreement № 14.575.21.0086. Unique project identifier RFMEFI57514X0086.
References
[1] Rodriguez-Blanco J D, Shaw S and Benning L G 2011 Nanoscale 3 265-71.
[2] Mosin O and Ignatov I 2014 Nanotechnol. Research Practice 4 187-200.
[3] Goncharuk V V, Bagrij V A and Bashtan S Yu 2012 J. Water Chem. Technol. 34 226-31.
[4] Fridkin A M et al 2004 Voda i Ekologija: Problemy i Reshenija 3 22-8 (in Russian).
[5] Gas'kova O L, Solotchina Je P and Skljarova O A 2011 Geology Geophys. 52 704-11.
[6] Stromberg A G and Semchenko D P 2009 Fizicheskaja himija: uchebnik dlja vuzov (Moskva: Vysshaja shkola) p 527 (in Russian).
[7] Rodionov A I, Klushin V N and Sister V G 2000 Tehnologicheskie processy jekologicheskoy bezopasnosti: uchebnik dlja studentov tehnicheskikh i tehnologicheskikh special'nostej (Kaluga: Izdatel'stvo N Bochkarevoj) p 800 (in Russian).