Application of reagent-free methods to eliminate the causes of salt deposition in thermal systems on geothermal sources

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Abstract. The article deals with the problems associated with the formation of scale on equipment and communications in greenhouse complexes with geothermal heat sources. To prevent scale on the equipment and communications in greenhouse complexes, double-circuit geothermal heat supply systems with intermediate heat exchangers are used, in which fresh softened water is heated with geothermal heat, which is then supplied to consumer needs. In the existing system, the heat exchanger and primary circuit communications in contact with the geothermal coolant are subjected to scale formation. Currently, physical, chemical, biological and combined methods of descaling are used. The article presents the results of the research work on the use of reagent-free methods of treatment of geothermal waters at the enterprise CJSC “Raduga”. As a result of the conducted research work, it was decided to install an acoustic-magnetic apparatus. A significant reduction in salt deposition was achieved by acoustic-magnetic treatment of geothermal water using an acoustic-magnetic apparatus. The greatest efficiency of water treatment is achieved by combining ultrasound with a magnetic rotating field. Studies have shown that the acoustic-magnetic treatment of water allows one not only to protect effectively the metal from corrosion, but also to remove salt deposits and corrosion products in a heat supply system. Patents of the Russian Federation were obtained for the method of water treatment presented in the article.

1. Introduction

The agricultural technology of growing vegetables in a greenhouse requires the maintenance of a strict temperature regime. Geothermal sources can be used for heat supply of greenhouse complexes. The main drawback of these systems is the increased formation of scale on the inner surface of the coolant pipes. To prevent scale on equipment and communications in greenhouse complexes, double-circuit geothermal heat supply systems with intermediate heat exchangers are used, in which fresh softened water is heated with geothermal heat, which is supplied to consumer needs in the future. However, the heat exchanger and the primary circuit communications in contact with the geothermal coolant are subjected to scale formation in this system. It is known that in the process of salt deposition, thermal characteristics are worsened, hydraulic resistance of pipelines increases; their complete blockage and system failure are possible.

We analyze the existing methods to reduce salt deposition in thermal systems. There are a number of chemical reagents produced in Russia: IOMS, OEDF, AFON, PAF, NTF, etc. complexons based on salts of organophosphorous acids, recommended for use in the circuits of hot water boilers and heat
networks for binding of some hardness ions in soluble compounds. Without examining the chemical nature of these reagents in detail, it is possible to say that they only inhibit the growth of crystals of slightly soluble salts on internal surfaces of components without affecting the pH of the extraction water and the content of corrosive dissolved gases. The zinc complex of oxyethylenediphosphonic acid, Na2Zn OEDF, was positioned as a chemical reagent combining the action of a film-forming corrosion inhibitor and an anti-boiling action. However, recent results of research [1] show that the effectiveness of this reagent is very low. The use of this reagent is due to several restrictions, including operating temperature, which makes it hardly probable the effective use of Na2Zn OEDF acid at the operating temperature of the heating above +60°C. In addition, when planning the operating conditions of the heating system, you should consider certain toxicity of chemical compounds in these reagents. As indicated in [2], the widespread use of complexons based on phosphonates often leads to negative consequences, for example, clogging the passages in the bundles of heat exchange tubes of network heaters with calcium and magnesium carbonates. The reason of this phenomenon is the change in the concentration of the active component in the complexon from batch to batch, which does not allow one to maintain an effective dosage of the reagent. The applied reagent methods do not allow to prevent scaling, but operate due to scale forming.

Currently, research is being conducted in the field of electrochemical treatment of oil-water emulsion. The authors of the article [3] believe that electrochemical methods of wastewater treatment are promising, since they have the advantages of reagent-free technologies and provide a higher degree of wastewater treatment due to a feasible combination of electrocoagulation and electrooxidation processes.

Magnetic treatment is the easiest way to limit salt deposition. The principle of the method is that under the action of a magnetic field, ferromagnetic water impurities are enlarged and adsorb carbonate crystals on their surface, as a result of which the formation of the solid phase of CaCO3 occurs in the water column, and not on the heating surface. The sludge formed during magnetic treatment is fine (the particles have a diameter of less than 0.5 microns) and do not get consolidated quickly. Magnetic technology of influence on the coolant is a reagent-free method of combating scale and deposits, while providing a change in the properties of water for the intensification of water treatment processes. The wide spread of magnetic technology in heat power industry is due to the comparative simplicity of the devices used, the minimum requirements for their maintenance, low operating costs and environmental safety of the technology [4]. Electrodialysis is made using titanium membranes. The system of removal of scale of oxide of iron from feed water of the boiler with use of the superconducting magnet which can be used at thermal power plants is considered in the work [6]. The authors argue that the removal of scale can prevent a decrease in the efficiency of electricity production and contribute to the reduction of carbon dioxide emissions. Special hydromagnetic devices with permanent magnets or electromagnets are used for magnetic treatment of water. At the same time, they generate a magnetic field affecting the water flowing in the working channel of the apparatus. Magnetic devices can have both internal and external (relative to the working channel) arrangement of the magnetizing system. With low flow rates of treated water, the most common devices are permanent magnets made of ferrite-barium alloys and with electromagnets on a common core. Hydromagnetic devices with electromagnets are used at high coolant consumption in heat supply systems, as well as in hot-water boilers, where the contaminating component is iron oxides [4]. The research is being conducted in this area (Malkin V.P., Yamamoto J.). In his work [5] the author considers various methods of industrial wastewater treatment, explores the possibility of combining electrodialysis and magnetic methods of wastewater treatment.

Works in the field of reagent-free water treatment in electromagnetic fields were carried out by a group of authors [7]. It was found that the method of reagent-free treatment of water in electromagnetic fields is determined by multifactorial criteria that make up the process of magnetization of water in heating systems. It is shown that the electromagnetic interaction of water magnetization technology is carried out through the feedback mechanism, and the quantitative indicators of the integrated control system determine the processes of water magnetization.
Significant reduction of salt deposition is achieved by ultrasonic treatment of geothermal water. Under the influence of ultrasound, crystals are formed not on the surface of the metal, but in the water column and subsequently pass into the sludge. There are different methods of obtaining elastic vibrations of the sound and ultrasonic frequency range. Generators on electronic lamps, transistors and thyristors operating in pulsed or continuous mode are often used for this purpose. The first have found the greatest application in heat power engineering for prevention of scale, dewaxing of fuel oil pipelines, the second are successfully applied in ultrasonic purification of products from various pollutions, and also in welding, dispersing, emulsifying for intensification of mass exchange in chemical and food technology, etc. [8].

Paper [9] considers biological methods of water supply for fire departments to firefight peat fires by bio-energy activation of drinking water are considered. The article shows the methods of reagent-free water purification and their comparative analysis. The article provides a detailed analysis of theoretical foundations for further improvement of the water supply scheme.

In the work [10] there were the systems of industrial water supply, water objects in which biocenoses were formed. The developed new biotechnology of reagent-free prevention of biological fouling of technological equipment is based on the induction of biofilm formation on an aqueous insoluble fibrous packet, which has a more developed surface compared to the surface of the heat exchanger and is placed in a separate apparatus-bio bonding material.

The considered methods require high energy costs and the use of an additional reagent. The disadvantage of all reagent methods is that their implementation requires the creation of special facilities for storage and dosing of the reagent, control of its action, qualified service personnel, etc. The considered reagent-free methods allow solving a separate group of problems, and their effectiveness requires close attention. Taking into account the fact that the existing methods eliminate the effects of scale formation or have low efficiency in the volumes of enterprises, the above gives grounds for hypothesizing the possibility of applying the joint influence of acoustic and magnetic fields on the process of scale formation by means of an acoustic-magnetic apparatus.

2. Methods
The closest analogue to acoustic-magnetic device is a device for protection against corrosion and formation of deposits on functional surfaces of pipelines and equipment of heat supply systems [11]. This device is composed of a circulation pump, communicated through a connecting pipeline to the boiler, a water supply pipeline, a hydraulically interconnected bypass pipeline of heating network, a liquid treatment unit and a generator unit, electrically and independently connected to a circulation pump, a liquid treatment unit, a boiler. The disadvantage of the prototype is the complexity of the treatment process and a relatively low degree of water stability. The technical result of the proposed improved device is to simplify the processing and increase of water stability for heat supply systems.

In the new apparatus as a generator unit there was the source of three-phase alternating voltage which creates alternating voltage in the resonant sound frequency range of 32-35 kHz, and the connecting pipeline has a unit processing liquid in the form of a cylindrical non-magnetic body having inside a magnetic striction source of ultrasonic vibrations, and outside – an extra body with an axial through hole of diamagnetic material with a magnetic system (made of several ferrite rings mounted apart at a distance that does not allow overlapping the rotating magnetic field, wherein each of the ferrite rings has a coil, containing at least three windings to outlets, united in the “star” scheme, the coils are connected in parallel and connected to the generator unit). The body with the electromagnetic system is filled with a compound, for example, epoxy resin. The additional body has a groove and a connector for linking the coil terminals to the generator block.

The patented device [12, 13] for protection against formation of deposits on surfaces of pipelines of heat supply systems is applied in preparation of geothermal water to application in the heating system of a greenhouse complex of CJSC “Raduga” (the Republic of Adygea). The procedure of preparing water before installing the acoustic-magnetic device was as follows: thermal water with temperature of 86 °C enters the tank, where due to a decrease in pressure from the wellhead to the atmospheric, there
is a sharp degassing of the geothermal solution and a shift of the carbonate equilibrium towards the formation of CaCO₃. The storage tank is also a settling tank for mineral sludge that falls out of the water after degassing. There are two parallel lines in the diagram. To facilitate the release of CaCO₃ and intensify the crystallization process, wooden gratings are inserted inside the tank. Almost all calcium carbonate is released on the tank walls and grates. After 15-20 days, water was switched to another tank. The scaled tank and grates were manually cleaned and prepared to the new cycle.

When one line is operating, the second is cleaned from accumulated sludge. Water from the storage tank is sent to the heat exchanger, where it transfers heat to fresh softened water, which is then sent to the heat supply system. Waste thermal water is sent to the surface for discharge, and if there are components in it that prevent such discharge, it is pumped back into the layer. This method of removing calcium carbonate is associated with some loss of low temperature potential of thermal water.

Titanium coated heat exchangers are used to prevent corrosion in heat exchangers. Due to the high cost of titanium, the use of such heat exchangers at the enterprise is not profitable. In recent years, plastic pipes of different brands that can withstand high pressures and temperatures are produced. The use of such pipes in geothermal power supply systems at the enterprise CJSC “Raduga” has not completely removed the problem of corrosion in communications during transportation of primary geothermal coolant.

The corrosive effect of geothermal waters on the metal is due to the following factors: mineralization, gas content (hydrogen sulfide, carbon dioxide, oxygen), pressure, temperature (the highest corrosion rate is observed at temperature of 60-90 °C), value of pH solutions. Hydrogen sulfide (H2S) increases the corrosion rate by 40%, the maximum corrosion occurs at its concentration in water 4-5 mg/l. Corrosion caused by carbon dioxide is minimal compared to oxygen and hydrogen sulfide. Chlorine ions combined with hydrogen sulfide and carbon dioxide have a corrosive effect on the metal. When oxygen enters the thermal water, hydrogen sulfide corrosion is intensified 2 times, carbon dioxide – 1.5 times, and chlorine-ionic – 3-4 times. Salt deposition occurs when the thermal or dynamic equilibrium is disturbed in a thermal solution, and more strongly it manifests itself the more sharply disturbance has occurred. Calcium carbonate deposition is the most common type of salt deposition. A slight shift in equilibrium is required, which can be expressed in changes in pressure, temperature, and salinity of the solution in order to release calcite into the solid phase.

If thermal carbon dioxide water is saturated with calcium carbonate in reservoir conditions, it comes to the surface and the pressure gradually decreases, carbon dioxide degassing occurs from the thermal solution and we obtain its multiple saturation with calcites occurs. The saturated solution precipitates on the surface with a further decrease in pressure (after the wellhead valve, the transition of water from a smaller diameter pipe to a larger one, etc.). In the process of salt deposition, thermal characteristics are deteriorated, hydraulic resistances of pipelines increase, their complete blockage and system failure are possible.

The choice of the experimental scheme for reagent-free treatment of thermal waters was made on the basis of hydrogeothermal, thermal, thermodynamic and technical and economic calculations, taking into account the chemical composition and mineralization of hydrotherms, most of which are prone to corrosion and salt deposition on the contact surfaces. When choosing the scheme of the experiment, it was found that thermal water should be directly supplied to the heat supply system, the water is not subjected (at peak temperatures) to additional heating in boilers or heat exchangers.

The process of scale formation on the walls of heat exchangers is a complex process of separation of salts from water treated with physical fields. Optimization of such a process can be carried out in conditions when the analytical form of the function linking the optimization parameter with the factors determining the process is unknown. The optimization parameter is chosen as the type of the system model - the anti-boiling effect of reagent-free water treatment, which is a function of a large number of factors:

$$\theta = f_{1}(\pi_{i1}, \pi_{i2}, \pi_{i3}, \pi_{i4}, \pi_{i5}, \pi_{i6}, \pi_{i7}, \pi_{i8})$$  \hspace{1cm} (1)
The influence of the following criteria on the process of descaling reduction was studied at the laboratory facility:

- $\pi_{11}$ – relation of the internal diameter to the basic size;
- $\pi_{12}$ – relation of the width of the ring to the basic size;
- $\pi_{13}$ – value of the coefficient of filling the window with winding;
- $\pi_{14}$ – relation of losses in the core to losses in the winding;
- $\pi_{15}$ – criteria equation of geothermal parameters of different types and constructions of acoustic – magnetic apparatus;
- $\pi_{16}$ – relation of areas of the apparatus and magnetic conductor;
- $\pi_{17}$ – relation of results of the apparatus’s tests with theoretical data;
- $\pi_{18}$ – process of heat emission.

Efficiency of reagent-free treatment was defined from the ratio:

$$\theta = \frac{M_0 - M_m}{M_0},$$

where $M_0$ - mass of scale deposited on the surface of the heat exchanger for the period $\tau$ without water treatment; $M_m$ - mass of scale deposited on the surface of the heat exchanger for the period $\tau$ after water treatment.

To obtain a linear mathematical model of the process, 1/8 replicas of factor experiment $2^7$ were implemented. The main levels and intervals of variation of factors were chosen based on a priori information about the process. Let us denote conditionally upper, lower and main levels with signs "+", "-" and "0" respectively. The planning matrix and the results of the experiments are given in Table 1. The experiments were conducted in randomized. We will carry out statistical processing of the results obtained during the experiment. In order to determine the point estimates of the distribution law, it is necessary to exclude gross errors or misses in the measurement results, for which the Charlier criterion was used, the number of observations in a series is (10<n<20).

| Table 1. Matrix of planning and results of experiments’ realization |
|---------------------------------------------------------------|
| Main level          | 0.605 | 0.44  | 0.000485 | 5.29 | 0.07 | 0.73 |
| Variation interval  | 0.29  | 0.12  | 0.00029  | 0.56 | 0.12 | 0.12 |
| Upper level         | 0.46  | 0.38  | 0.00063  | 5.01 | 0.13 | 0.79 |
| Low level           | 0.75  | 0.5   | 0.00034  | 5.57 | 0.01 | 0.67 |
| Codified symbols    | $\pi^1$ | $\pi^2$ | $\pi^3$ | $\pi^4$ | $\pi^5$ | $y$ |

In accordance with the planning matrix, there were the experiments (calculations) defined by the criterion regression equation for the acoustic-magnetic treatment of thermal waters in the form of:

$$\xi = 38,079 + 0,262\pi^1 + 0,0053\pi^2 - 78,552\pi^3 + 0,1\pi^4 + 0,308\pi^5.$$  

The statistical analysis of the results of the experiment revealed homogeneity of the variance of the experiments, the variance of the reproducibility of the experiment. Testing the hypothesis about the adequacy of the model, $RS=3.52$ characterizes the normal distribution, since $3.12<3.52<4.12$. The average relative error of the approximation: $e = 2.93\%$.

3. Results

Devices of acoustic-magnetic water treatment were tested on geothermal deposits of Maikop district of the Republic of Adygea. During the technical regulations on pipes and assemblies, salt deposition was not detected, which confirms the high efficiency of the method. The device of acoustic-magnetic water
treatment is successfully used in CJSC "Raduga" and has the following characteristics: the amount of treated water is up to 0.25 m\(^3\)/s, power consumption is about 150 Wt.

Experimental studies on geothermal sources of JSC "Raduga" for the protection of equipment metal from corrosion and salt deposits conducted in 2016-2019 showed that acoustic-magnetic water treatment allowed not only effectively to protect the metal from corrosion, but also to remove existing salt deposits and corrosion products in the heat supply system. Acoustic-magnetic technology is a reagent-free method of combating scale and deposits, providing changes in the physical and chemical properties of water for the intensification of water treatment processes.

Taking into account the observations made, according to the method of the experiment, it was decided to install an acoustic-magnetic apparatus together with an automation system immediately after the geothermal water exit from the ground (Figure 1).

Due to intensive salt deposition, the geothermal heat supply system ceased to function at the enterprise CJSC "Raduga" for one year. Salt deposits in the pipes of geothermal systems have an expressed crystalline character. The degree of adhesion and the size of crystals depend on temperature and pressure at which the deposition was formed. Let us consider the patterns of salt deposition in the system prior to the installation of an acoustic-magnetic apparatus for reagent-free water treatment. At first the deposits in the tube are insular, then a continuous ring of deposits is formed, on which new layers are formed (Figure 2).

Under the action of acoustic-magnetic field, crystals are formed not on the surface of the metal, but in the water column, and subsequently pass into the sludge. Devices of acoustic-magnetic water treatment were tested on geothermal deposits of Maikop district of the Republic of Adygea. No salt
deposition was detected on pipes and assemblies during the technical inspection, which confirms the high efficiency of the method. Observations of the processes of calcium carbonate deposition in the geothermal system in water deposits of different chemical composition, mineralization, temperature and pressure at the wellhead, the presence of suspended particles showed that the deposition of calcium carbonate for the waters of various wells occurs in a strictly defined place along the route of water transportation. This place, other things being equal, is characterized by pressure and temperature values, which are different for different waters. Most often the deposition of calcium carbonate occurred behind the valves, in places of a sharp drop in pressure and elbows of the pipes. Figure 3 shows a valve in which the water treated by the apparatus flowed.

Figure 3. Valve the treated water flowed in

Ultrasound enters the system in waves on both sides of the device. The efficiency of acoustic energy is manifested in the prevention of the formation of primary crystals on the pipes. Magnetic treatment consists in the fact that under the action of a rotating magnetic field, ferromagnetic water impurities are enlarged and adsorb carbonate crystals on their surface, as a result of which the formation of the solid phase CaCO$_3$ occurs in the water column, and not on the surface of the pipes. The sludge formed during magnetic treatment is fine-dispersed.

4. Discussion
The proposed hypothesis about the possibility of combining acoustic and magnetic fields in the working zone of one acoustic-magnetic apparatus was implemented at the industrial enterprise CJSC "Rainbow". As a result of implementation of research work on one of the wells of geothermal sources there was the decision on installation of the acoustic-magnetic device on all systems of geothermal heat supply. During the acoustic-magnetic treatment of geothermal water with the help of an acoustic-magnetic apparatus, a significant reduction in salt deposition was achieved. The greatest efficiency of water treatment is achieved by combining ultrasound with a magnetic rotating field. There were the patents of the RF on this method [12, 13].

5. Conclusion
1. Acoustic-magnetic reagent-free technology of scale and sediment control provides change of physical and chemical properties of water for the purpose of intensification of water treatment processes.
2. Studies have shown that the acoustic-magnetic treatment of water allows one not only to protect effectively the metal from corrosion, but also to remove salt deposits and corrosion products in the heat supply system.
3. The proposed hypothesis about the possibility of combining acoustic and magnetic fields in the working zone of one acoustic-magnetic apparatus was implemented at the industrial enterprise.
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