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## STUDY OF THE EFFICIENCY OF APPLICATION OF SCALE INHIBITORS FOR WATER

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## STUDY OF THE EFFICIENCY OF APPLICATION OF SCALE INHIBITORS FOR WATER

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**Abstract.** Scale formation in pipelines and on equipment surfaces is a serious problem in many branches of industry. Different scales are formed in cooling water systems and caused heat transfer problems. A common method for controlling scale deposition is the use of chemicals which act as antiscalants. This study focuses on the selection of antiscalant and the parameters of the process for the creation of resource-saving technologies for the use of water in industry. To inhibit the scale formation in cooling water systems, antiscalant RT-2024-4 was used, characterised and the ability of the reagent to mitigate the scale formation was tested. Artesian, tap water and water from the Desna River and model solutions with a hardness of 7.33–14.65 mg-eq/L were used as test objects. The conducted studies show that the temperature increase in the range of 80–90°C and the time of thermostating in the range of 2–5 hours have practically no effect on the stabilisation and anti-scale effects. The statistical data processing method was used to analyse the experimental data. High stability of water with respect to scale formation was established. The expediency of using the scale stabilizer RT-2024-4 for mineralised and highly mineralized waters was shown.

**Keywords:** antiscalant, water, scaling, hardness ion.

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### Introduction

Water is one of the most important resources for industrial processes, both for the production of products and for the maintenance of materials and equipment. Water management is critical in manufacturing, regardless of industry [1-4]. The main part of water is used for: production of products, transportation of various substances, production of electricity and most of all in cooling systems [5-7]. The main problems involving the use of water in cooling systems are related to the presence of certain impurities such as hardening salts due to calcium and magnesium compounds [8], which can cause scale formation in the pipes and on the surface of the equipment. On the other hand, soft water can cause pipe corrosion and other problems [9-12].

The scale damage is mainly reflected in the following aspects [13,14]:

- the pipeline will be blocked, which reduces the cross-sectional area of water circulation and increases the flow resistance, which will lead to an increase in the cost of electricity transmission;

- the heat transfer resistance of the heat exchanger pipe wall increases significantly, which leads to an increase in energy consumption;
- cracking under scale will easily lead to corrosion and cause pipe perforation.

Therefore, stabilisation of water quality is the key to ensuring safe and stable operation of heat exchange systems [15].

As a rule, corrosion, scale and biofouling problems increase with increasing water use cycles, resulting in higher concentrations of soluble components in the water [16]. These problems have a large economic impact because they cause deterioration of the metal surface and loss of heat exchange capacity [17,18]. Therefore, water cooling systems are usually chemically treated to avoid corrosion, scaling and contamination. Many inhibitors and biocides have been used in water cooling systems to solve these problems [19,20]. To maintain the chemical composition of water in order to reduce scale formation, stabilisation treatment of cooling water with sulfuric acid is used. The negative sides of this

approach are that the presence of acid causes equipment corrosion and secondary water pollution [21]. Sometimes, other chemical methods of water treatment to change the salt composition, such as ion exchange or reverse osmosis, are used to prevent scale formation processes [22]. However, ion exchange treatment and reverse osmosis are quite expensive and energy-consuming technologies.

To increase the efficiency of water use in water circulation systems, corrosion and scale inhibitors can be regarded as promising approach. Scale inhibitors such as phosphates, polyphosphates and organophosphonates are commonly used, as well as corrosion inhibitors such as zinc sulphate and azoles. As a rule, chlorine and/or sodium hypochlorite are most widely used as antifouling biocides in cooling systems [23]. Inhibitors and chlorine are added continuously, while non-oxidizing biocides such as quaternary ammonium compounds are usually added once a week.

The action of inorganic scale inhibitors is based on the principle of creating a protective film on the metal surface. However, some of them, in particular nitrates and chromates, despite their effectiveness, are toxic to the environment. Therefore, new research is aimed at developing effective and safe inhibitors based on molybdates, silicates and phosphates, which protect metal from corrosion no less effectively. The use of some organic inhibitors is also quite effective. However, one of the problems of using such inhibitors is their limited solubility, which negatively affects the effectiveness of their protection. Organic natural and synthetic polymer inhibitors are usually used as dispersants in the inhibition process. Basically, low-molecular polymers based on acrylate and organophosphorus substances are used to inhibit scale [24].

Modern anti-scale products usually contain proprietary blends of polymers such as polycarboxylates, polyacrylates and polyphosphates. However, due to some limitations of polyphosphates, they are increasingly replaced by more stable polymers based on carboxylic acids (polyacrylic acid, polymaleic acid, etc.), which work effectively in conditions of high temperatures and aggressive environments [25]. Recently, much research has focused on the creation and use of green antiscalants. Despite significant advantages, such as low toxicity and biodegradability, green/natural antiscalants (*e.g.*, based on plant extracts, modified polysaccharides, tannins, lignosulfonates, *etc.*) have a number of potential drawbacks. Many natural compounds are less

stable at high temperatures and in aggressive chemical environments characteristic of industrial cooling systems or steam boilers. They can decompose, losing their inhibitory ability [26]. Some natural inhibitors may be effective against certain types of scale (*e.g.*, calcium carbonate), but less effective against others (*e.g.*, calcium sulphate, silicates) [27,28]. Compatibility issues may also arise between green antiscalants and other chemical reagents used for water treatment (*e.g.*, biocides, corrosion inhibitors) [29].

However, for effective protection of water circulation systems against scale formation, a detailed selection of reagents and process conditions when introducing antiscalant is quite important and necessary [30,31].

The novelty and significance of such research lie in the creation of these new, safe, and effective chemical solutions or the establishment of scientifically validated, optimized application protocols. Successfully achieving these objectives would overcome the limitations of current methods, significantly reduce the economic losses associated with scale and corrosion [17,18], ensure the stable and safe operation of vital industrial cooling systems [15], and promote environmentally responsible water treatment practices.

Therefore, the purpose of the work was to conduct research on the selection of antiscalant and the parameters of the process for the creation of resource-saving technologies for the use of water in industry, which allows the transition to closed water circulation systems.

## Experimental

### Materials

The research was carried out using water of different origin in particular from the river Desna, tap water, artesian water and model solution. Total hardness was: water from the Desna river - 5.00 mg-eq/L ( $C(\text{Ca}^{2+}) = 3.80$  mg-eq/L;  $C(\text{Mg}^{2+}) = 1.20$  mg-eq/L); tap water - 4.50 mg-eq/L ( $C(\text{Ca}^{2+}) = 3.50$  mg-eq/L;  $C(\text{Mg}^{2+}) = 1.00$  mg-eq/L); artesian water - 4.90 mg-eq/L ( $C(\text{Ca}^{2+}) =$  mg-eq/L;  $C(\text{Mg}^{2+}) =$  mg-eq/L); model solution I - 7.33 mg-eq/L ( $C(\text{Ca}^{2+}) = 5.33$  mg-eq/L;  $C(\text{Mg}^{2+}) = 2.00$  mg-eq/L), model solution II - 14.65 mg-eq/L ( $C(\text{Ca}^{2+}) = 10.66$  mg-eq/L;  $C(\text{Mg}^{2+}) = 4.00$  mg-eq/L). The concentration of  $\text{SO}_4^{2-}$  was: water from the river Desna – 0.53 mg-eq/L; tap water – 0.62 mg-eq/L; artesian water - 0.71 mg-eq/L; model solution I - 1.05 mg-eq/L, model solution II - 2.66 mg-eq/L. The concentration of  $\text{Cl}^-$  was: water from the river Desna - 0.40 mg-eq/L; tap water - 0.67 mg-eq/L;

artesian water - 0.90 mg-eq/L; model solution I - 2.01 mg-eq/L, model solution II - 5.32 mg-eq/L. RT-2024-4 antiscalant was used to protect against scale (Table 1).

#### Instruments

A water thermostat was used to ensure the required temperature regime. Ashless Blue Ribbon paper filters were used to separate sediment from water. The titrimetric method (with Trilon B) was used to determine water hardness before and after antiscalant treatment.

#### Water treatment procedure

Antiscalant was added to 0.5 L samples of water. Antiscalant doses were 2.5–100.0 mg-eq/L. The samples were kept at a temperature of 80°C for 2.0 to 5.0 hours. Then it was cooled and filtered, and the residual hardness of the water was determined. To ensure reproducibility of experimental data, all water stabilisation experiments were performed in 3-fold replication. Stabilizing (SE) and anti-scale (ASE) effects were calculated using Eqs.(1,2) [32].

$$SE = \left(1 - \frac{H - H_i}{H - H_r}\right) \cdot 100\%. \quad (1)$$

$$ASE = \frac{H_i}{H} \cdot 100\%, \quad (2)$$

where,  $H_i$  - residual hardness with antiscalant RT-2024-4 mg-eq/L;  
 $H$  - initial hardness, mg-eq/L;  
 $H_r$  - residual hardness in comparison sample, mg-eq/L.

The scheme of the water stabilisation treatment process is presented in Figure 1.

#### Statistical analysis procedure

Water treatment with antiscalant RT-2024-4 was carried out in laboratory conditions according to a statistical  $2^3$ -factorial design, the implementation conditions of which are presented in Table 2. The variables studied were the temperature ( $X_1$ ) and the thermostating time ( $X_2$ ), and the SE ( $Y_1$ ), ASE ( $Y_2$ ) were investigated.

Experimental studies were performed to investigate the effect of the individual and combined effects of  $X_1$  and  $X_2$ . A second-order polynomial model was used to mathematically describe the process of water treatment with antiscalant RT-2024-4 according to Eq.(3).

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_1X_2 + a_4X_1^2 + a_5X_2^2 \quad (3)$$

where,  $Y$  - a response factor;  
 $a_0$ - $a_{1,2,3}$  - regression coefficients.

The coefficients of the second-order mathematical model were calculated by regression analysis. The variance analysis was carried out using the MINITAB 17 software. Based on the obtained regression Eqs.(4,5), response surfaces were constructed using the MATLAB software.

The research conducted using Axis ANG 220C electronic balance, MICROMed TC-80 dry-air thermostat, HORIBA LAQUAtwin NO3-11 portable nitrometer, YD300 portable water hardness meter, AE - 10 aqua distiller, pHTEST 3 pH meter. All reagent used in this research were A.R.

$$Y_1 = +70.31 + 0.74856 \cdot X_1 - 1.4295 \cdot X_2 - 0.004882 \cdot X_1^2 + 0.016484 \cdot X_1 \cdot X_2 - 0.065156 \cdot X_2^2 \quad (4)$$

$$Y_2 = +99.462 + 0.016785 \cdot X_1 - 0.098865 \cdot X_2 - 0.00012267 \cdot X_1^2 + 0.00067667 \cdot X_1 \cdot X_2 + 0.0030815 \cdot X_2^2 \quad (5)$$

Table 1

| Characteristics of antiscalant. |  |                        |        |
|---------------------------------|--|------------------------|--------|
| Name                            | Composition  | Specific gravity, g/mL | pH     |
| RT-2024-4                       | A mixture of phosphates (30–35%), phosphonic carboxylates (13–17%) of polymeric dispersants (3–4%) | 1.05–1.15              | > 12.0 |

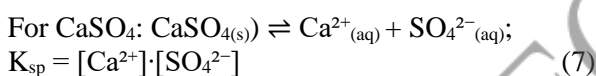
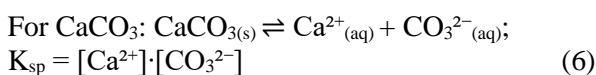


Figure 1. Scheme of the water treatment process with antiscalant RT-2024-4 for scale removal.

## Results and discussion

The process of scale formation on the surface of the equipment depends on a number of factors, such as hardness, surface material, temperature of the medium, flow rate and concentration of salts in the water. Ions of salts soluble in aqueous solutions approach the surface and interact with it due to electromagnetic forces. This leads to the formation of crystal nuclei on the surface, which develop over time, forming layers of scale. An increase in temperature contributes to an increase in the activation energy of the salt deposition reaction and accelerates the transport of scale particles from the volume of water to the surface.

Unlike most solid salts, the solubility of which increases with temperature, calcium carbonate ( $\text{CaCO}_3$ ) and calcium sulphate ( $\text{CaSO}_4$ ) exhibit inverse (or retrograde) solubility. This means that their solubility in water is reduced when heated. The solubility product ( $K_{sp}$ ) is the equilibrium constant for the dissolution process of sparingly soluble salts, according to Eqs. (6,7).



where,  $K_{sp}$  shows the maximum product of ion concentrations that can exist in a saturated solution at a certain temperature. If the actual product of the ion concentrations in water exceeds  $K_{sp}$ , the salt precipitation process begins. For salts with inverse solubility, such as  $\text{CaCO}_3$  and  $\text{CaSO}_4$ , the  $K_{sp}$  value decreases with increasing temperature, leading to supersaturation of the solution.

In addition, increasing the temperature gives the ions in the solution more kinetic energy. This helps them overcome the energy barrier (activation energy) for the formation of crystal nuclei (nucleation) and the subsequent growth of these crystals on the surfaces. That is, even if the solution has become supersaturated (due to a decrease in  $K_{sp}$ ), the higher temperature accelerates the deposition process itself. At the same time, the higher temperature increases the diffusion rate of ions and small particles in the water. This means that the  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}/\text{SO}_4^{2-}$  ions, as well as scale microcrystals that have already formed in the water volume, reach the heating surfaces faster, where further deposition and growth of the scale layer can occur.

The scale inhibition mechanism primarily depends on the chemical nature of the inhibitors. Scale and corrosion inhibitors are chemical compounds that slow down the rate of scale formation. They usually contain substances consisting of many active functional groups of similar or different types that have the ability to bond with growing scale crystals or particles, thus holding them in an aqueous solution.

Calcium carbonate  $\text{CaCO}_3$  is one of the most common deposits formed by the dissociation of  $\text{HCO}_3^-$  ions. The degree of scale inhibition primarily depends on the amount of  $\text{Ca}^{2+}$  ions and the presence of bicarbonates in the source water. As the temperature and pH of the solution medium increase, the rate of decomposition of bicarbonate increases. Also, the rate of decomposition is affected by the total dissolved solids (TDS) content in the water. Calcium sulphate dehydrate (gypsum) is a fairly common form of sulphate scale at ambient temperatures.

Previous studies of water stabilisation treatment [33,34] showed that each type of water requires a careful selection of the dose of reagents, depending on its composition. That is why this work is devoted to determining the effectiveness of water stabilisation treatment of water of different origin and different mineralization.

The results of using the scale stabilizer are shown in Figures 2-7.

Inhibitor was added to aqueous solutions in concentrations of 2.5–50 mg-eq/L and heated for 2 hours at a temperature of 80°C using a water thermostat. As can be seen from Figure 2, scale inhibitor RT-2024-4 is quite effective in the treatment of water from the Desna River at doses above 10 mg/L. At the inhibitor dose of 10.0 mg/L, the stabilisation and anti-scale effects reached 23.33 and 95.40%, respectively. At an inhibitor dose of 40 mg/L, these indicators reached 94.33 and 99.66%, respectively.

When treating tap water, the antiscalant RT-2024-4 was quite effective in stabilizing scale formation at doses of 10-50 mg/L (Figure 3). CE is 94.0 - 98.0% at doses of 40.0–50.0 mg/L.

Figure 4 shows that the proposed inhibitor provides high stability of artesian water with respect to sediments under these conditions. As can be seen from Figure 5, at an inhibitor concentration of 15.0 mg/L, the stabilisation effect reached 40.67%. With an increase in the consumption of this inhibitor to 40.0–50.0 mg/L, the stabilisation effect was 95.5–98.5%. At doses above 2.5 mg/L, high values of the anti-scale effect were recorded, which in all cases is greater than SE.

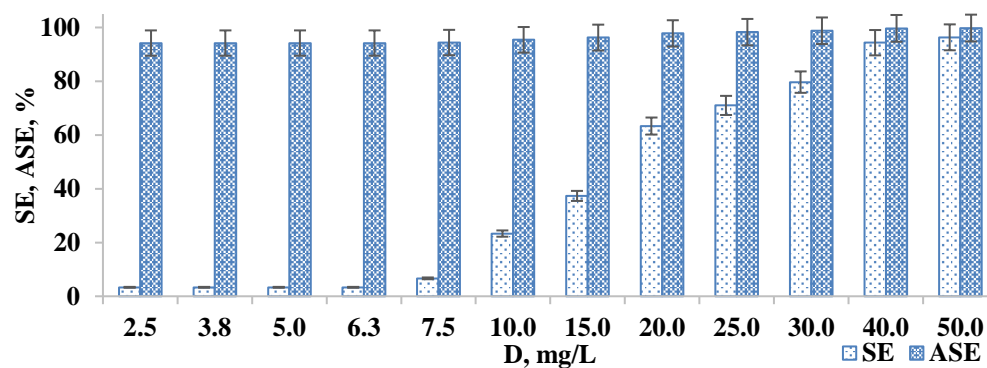


Figure 2. Dependence of the SE and ASE in water from the river Desna on dose when using RT-2024-4.

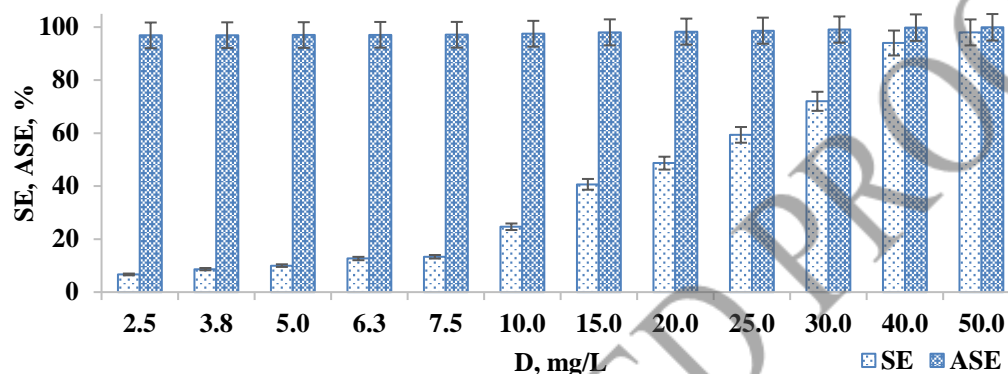


Figure 3. Dependence of the SE and ASE in tap water on dose when using RT-2024-4.

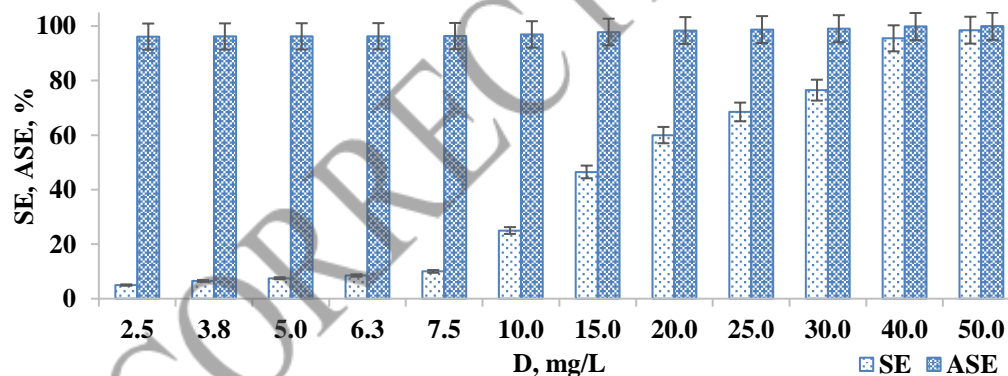


Figure 4. Dependence of the SE and ASE in artesian water on dose when using RT-2024-4.

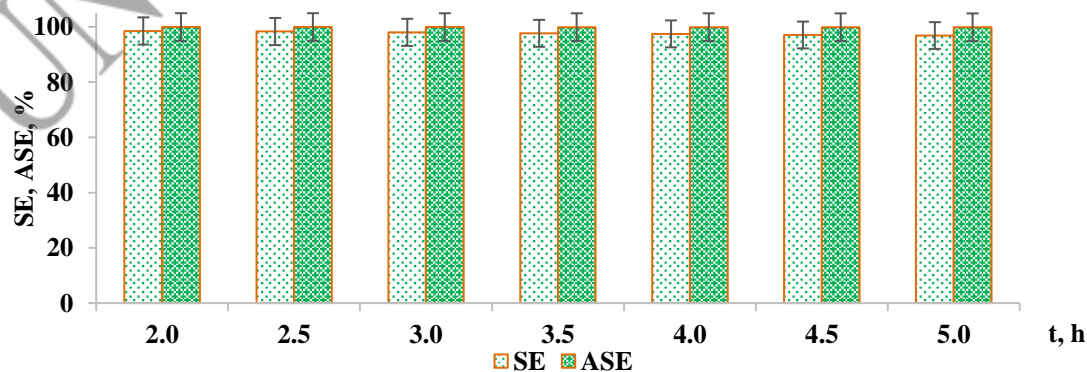


Figure 5. Dependence of the SE and ASE in artesian water on time when using RT-2024-4.



Artesian water, compared to tap water and water from the Desna river, contains a higher value of total mineralization, which included increased concentrations of bicarbonates, sulphates and chlorides. Higher initial sulphate concentration in artesian water directly increases the risk of sulphate scale formation, requiring a higher dose of antiscalant to inhibit it. Higher concentration of chlorides significantly increases the total mineralization and ionic strength of the solution. This can reduce the solubility of other salts (*e.g.* calcium carbonate) and thus indirectly contribute to scale formation [35].

In water-scarce industrial regions, mineralized and highly mineralized water with high hardness can be used in cooling systems, the carbonate index can exceed 50–70 (mg-eq/L)<sup>2</sup>. It is very difficult to solve the problem of stabilisation of such waters to prevent sedimentation. The effectiveness of the sedimentation inhibitor was evaluated based on the change in water hardness when it was heated to a temperature of 80°C in the presence of the inhibitor. The results of the research are shown in Figures 6,7.

As can be seen from Figures 6, 7, the efficiency of water stabilisation depends on the consumption of the inhibitor RT-2024-4. Despite the fact that the hardness of the water was 7.33–14.65 mg-eq/L with alkalinity 4.85–9.70 mg-eq/L, with an antiscalant dose of 30 mg-eq/L, the stabilisation effect reached 58.95–76.96%.

The stabilisation effect depends on the water characteristics and varied from 40.51 to 96.20% and from 37.89 to 90.32% at inhibitor doses of 20.0–50.0 mg/L for water with a hardness of 7.33 and 14.65 mg-eq/L. Therefore, the selection of the optimal dose of the inhibitor ensures a significant increase in the efficiency of equipment protection against sediment deposits.

Figure 6 shows that treatment of water with a carbonate index > 27 (mg-eq/L)<sup>2</sup> stabilizer is effective at a dose > 30 mg/L. In the case when the carbonate index exceeds 100 (mg-eq/L)<sup>2</sup> (Figure 7), the dose of RT-2024-4 must be increased to 50–100 mg/L. Another option for using such waters in cooling systems is their preliminary special treatment, for example by reagent or ion exchange methods, which will ensure their effective softening.

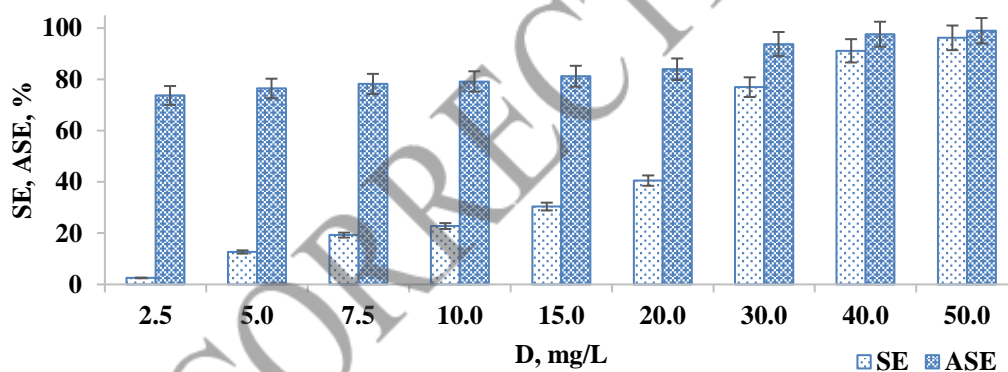


Figure 6. Dependence of the SE and ASE in model solution with hardness 7.33 mg-eq/L ( $[Ca^{2+}] = 5.57$  mg-eq/L,  $A = 4.85$  mg-eq/L) on dose when using RT-2024-4.

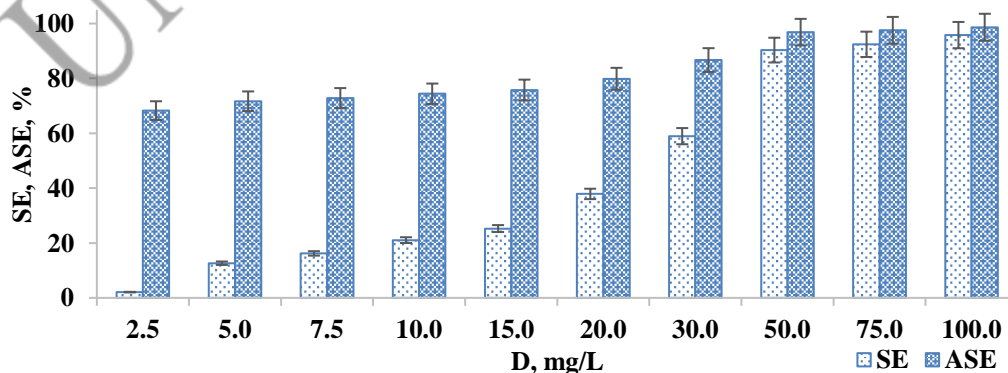


Figure 7. Dependence of the SE and ASE in model solution with hardness 14.65 mg-eq/L ( $[Ca^{2+}] = 11.14$  mg-eq/L,  $A = 9.70$  mg-eq/L) on dose when using RT-2024-4.

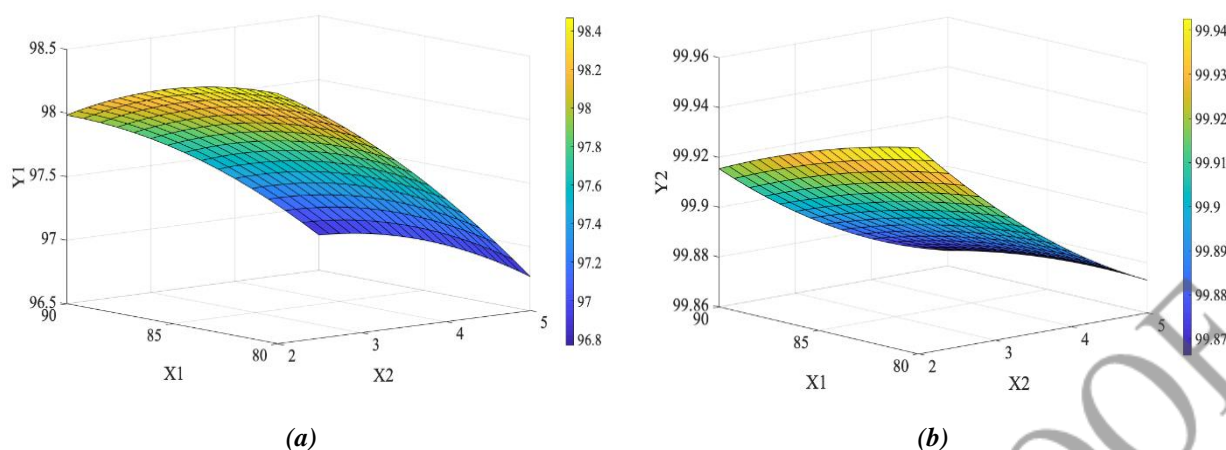


Figure 8. 3D-surface responses: SE (a); ASE (b).

Table 2

| 2 <sup>3</sup> -factorial design for water treatment antiscalant RT-2024-4 |                |                |
|--|----------------|----------------|
| Factor   | Low level (-1) | High level (1) |
| The temperature (X <sub>1</sub> ) and the thermostating time (°C)          | 80.0           | 90.0           |
| The thermostating time X <sub>2</sub> (h)                                  | 2.0            | 5.0            |

Table 3

List of some conventional and green scale inhibitors and their effectiveness as antiscalants.

| Antiscalant  | Dose, mg/L | SE, % | Scalant/ Type water | Ref.    |
|--------------|------------|-------|---------------------|---------|
| AA-APEM      | 16.0       | ~ 77  | CaCO <sub>3</sub>   | [36]    |
| AA-APEM-APTA | 16.0       | ~ 75  | CaCO <sub>3</sub>   | [36]    |
| HPMA         | 16.0       | ~ 48  | CaCO <sub>3</sub>   | [36]    |
| PAA          | 16.0       | ~ 47  | CaCO <sub>3</sub>   | [36]    |
| PESA         | 16.0       | ~ 41  | CaCO <sub>3</sub>   | [36]    |
| HPMA         | 2          | 79    | CaSO <sub>4</sub>   | [37 39] |
| PAA          | 2          | 38    | CaSO <sub>4</sub>   | [37,39] |
| PESA         | 10         | 90    | CaSO <sub>4</sub>   | [25,38] |
| RT-2024-3    | 30         | 80    | tap water           | [39]    |
| Rape extract | 10         | ~ 60  | tap water           | [40]    |

A statistical 2<sup>3</sup>-factorial design with treatment conditions or factors is given on Table 2.

Both an increase in temperature in the range of 80–90°C, and a thermostating time in the range of 2–5 hours have practically no effect on the stabilisation and anti-scale effects (Figure 8).

So, with an antiscalant dose of 50 mg/L, the treatment of artesian water is effective at a temperature of 80–90°C, which allows us to recommend this reagent for use in real heat supply systems.

Growing environmental concerns stimulate the development of eco-friendly antiscalants with enhanced biodegradability. Significant efforts have been made to create new, more stable, and sustainable alternatives to traditional scale inhibitors. Examples of these antiscalants are presented in Table 3.

As can be seen from the data, some natural inhibitors are effective against certain types of scale (*e.g.*, calcium carbonate) but less effective against others (*e.g.*, calcium sulphate).

### Conclusions

In this paper, modern methods of water conditioning for water circulation systems when using a scale stabilizer are considered. The proposed scale stabilizer provides water stability with respect to sediments at the level of 72.00–98.00% in tap water, 76.50–98.50% in artesian water, 79.67–96.33% in water from the Desna River, at reagent doses of 30–50 mg/L.

The effectiveness of the scale stabilizer RT-2024-4 for mineralized and highly mineralized waters was evaluated. The stability of water with a hardness of 7.33 mg-eq/dm<sup>3</sup> relative



to sediments is 40.51–96.2 at reagent doses of 20–50 mg/L. The stability of water with a hardness of 14.65 mg-eq/L relative to sediments is 37.89–95.79% at reagent doses of 20–100 mg/L.

The conducted research and mathematical processing of the obtained experimental data showed that both the temperature increase in the range of 80–90°C and the time of thermostating in the range of 2–5 hours have practically no effect on the stabilisation and anti-scale effects.

The novelty of the results consists in the comprehensive assessment of the effectiveness of the scale stabilizer RT-2024-4 for different types of natural water and waters with different levels of mineralization, which indicates its versatility and adaptability to operating conditions. The proposed reagent demonstrates an effective stabilizing effect even in highly mineralized waters, which expands the possibilities of its use in industrial water circulation systems with increased load. The analysis showed thermal stability and resistance to chemical action of the reagent under operating conditions, which is important given the high-temperature operating modes of heat exchange equipment.

Future research will be directed to the synthesis of an antiscalant, which is an effective reagent at lower concentrations. Therefore, it is crucial to develop a new generation of scale inhibitors that not only demonstrate high efficiency in preventing scale formation but also comply with health and environmental standards, ensuring minimal ecological impact.

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