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ASSESSMENT OF THE EFFICIENCY OF THE STABILIZATION TREATMENT FOR WATER OF VARIOUS MINERALIZATION

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Abstract

The work conducted and described investigates the impact of the antiscalant RT-2024-3 on the efficiency of water stabilization treatment. The research investigated the influence of antiscalant dosage and initial water hardness on stabilization and antiscaling effects. The stabilization effect ranges from 76.7 % to 80.0 %, while the antiscaling effect is between 97.40 % and 99.33 % at antiscalant doses of 20–30 mg/dm³ for treating water with a hardness of 4.5–5.0 mg-eq/ dm³. When the water hardness increased to 7.3 mg-eq/dm³, at antiscalant doses of 25–30 mg/dm³, a stabilization effect of 60 % and an antiscaling effect of 89 % were achieved. To obtain satisfactory results with higher hardness, the dosage should be increased to more than 30 mg/dm³. The study emphasizes the importance of considering the initial water parameters to select the optimal stabilization treatment regime, ensuring the economic and technological efficiency of the process. The findings can be beneficial for industrial and municipal water treatment systems operating with water of varying compositions.

Keywords: antiscalant; stabilization effect; antiscaling effect; mineralization; corrosion; efficiency.

ВИЗНАЧЕННЯ ЕФЕКТИВНОСТІ СТАБІЛІЗАЦІЙНОЇ ОБРОБКИ ВОДИ РІЗНОЇ МІНЕРАЛІЗАЦІЇ

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Анотація

Проведена та описана робота по дослідженню впливу на ефективність стабілізаційної обробки води антискаланту RT-2024-3. Вивчено вплив дозування антискаланту та початкової жорсткості води на стабілізаційний і протинакипний ефекти. Стабілізаційний ефект становить 76.7–80.0 %, а протинакипний ефект знаходиться в межах 97.40–99.33 % за дозування антискаланту 20–30 мг/дм³ для обробки води з жорсткістю 4.5–5.0 мг-екв/дм³. За умови підвищення жорсткості води до 7.3 мг-екв/дм³ за дозування антискаланту 25–30 мг/дм³ вдалось досягнути стабілізаційного ефекту на рівні 60 %, а протинакипного ефекту – 89 %. Для отримання задовільних результатів з вищою жорсткістю варто підвищувати дозування понад 30 мг/дм³. Дослідження підкреслює важливість врахування початкових параметрів води для вибору оптимального режиму стабілізаційної обробки, що забезпечить економічну та технологічну ефективність процесу. Отримані результати можуть бути корисними для промислових та комунальних систем водопідготовки, що працюють із водою різного складу.

Ключові слова: антискалант, стабілізаційний ефект, протинакипний ефект, мінералізація, корозія, ефективність.

Introduction

In the modern world, water is of high importance and is used for various purposes, including drinking water supply, industrial processes, and agriculture. The existing water scarcity crisis is currently intensifying. Therefore, the issue of rational use and protection of water resources is very relevant [1; 2]. To overcome the shortage of water resources in industry, water circulation cooling systems are widely used [3]. It is important to consider that water may contain various impurities, which can lead to scale formation and deposits on equipment surfaces. Continuous use of cooling water causes an increase in salt concentration, raising the likelihood of scale deposits on equipment surfaces, which leads to a reduction in heat transfer efficiency and an increase in operational and maintenance costs. Moreover, the adsorption of calcium deposits on equipment surfaces can cause corrosion and even shorten the equipment's lifespan. Therefore, research and improvement of effective methods for preventing or removing scale formation are relevant.

To prevent salt deposits, methods of preliminary water treatment such as reagent [4–7] or ion exchange [8–11] methods are used. However, their main disadvantages are the high cost of equipment, the need for expensive reagents, and the formation of precipitates or eluates that require further processing [12; 13].

To prevent the formation of scale and deposits on equipment surfaces, chemical substances such as antiscalants [14] are used. Their action is based on binding calcium and magnesium ions, which are the main components of scale, making them more soluble and less prone to deposition; antiscalants can also modify salt crystals [15; 16]. The use of antiscalants allows for increased efficiency of water treatment equipment and reduced maintenance and repair costs. Additionally, this helps conserve water resources and prevent environmental pollution from the discharge of spent mineralized waters.

Currently, the addition of chemical antiscalants to water circulation cooling systems is one of the most economical and effective methods [17; 18]. Their functions include inhibiting crystal formation and stopping their growth, thus achieving excellent scale protection performance [19–22].

When choosing an antiscalant, it is important to consider factors such as water characteristics, type of equipment, operating conditions, and economic feasibility.

In water cooling systems consisting of iron pipes, iron ions are washed out and precipitate due to corrosion. In the presence of these iron compounds, the required dosage level of the scale inhibitor is always high. If the antiscalant has a good ability to disperse iron ions and can keep them in the system, the water cooling system can be preserved from increased corrosion and rapid oxidation of soluble iron. Polymeric antiscalants, generally with carboxylic acid functional groups, provide high efficiency for calcium phosphate, iron oxide, etc. [23].

Widely used antiscalants are phosphorus-containing complexing agents-phosphonates – that prevent the formation of precipitates in supersaturated solutions of inorganic salts. Phosphonates are effective in preventing the formation of calcium carbonate, sulfate, and phosphate deposits. Phosphorus-containing antiscalants demonstrate high inhibitory properties, allowing the avoidance of $CaCO_3$ deposition. However, the use of phosphorus-containing antiscalants can lead to eutrophication of water bodies and the destruction of the ecological environment.

Sodium hexametaphosphate (SHMP) is used as an antiscalant to prevent the formation of scale such as metal sulfates and calcium carbonate. The wide usage of this antiscalant is explained by its high efficiency. It has been shown that polyacrylic acid (PAA) better inhibits scale formation compared to SHMP [24].

Sodium hexametaphosphate (SHMP), a polyphosphate, was the most common antiscalant until recently. However, its usage has been significantly limited due to its propensity for hydrolysis, which makes it ineffective [25].

Aminotrismethylene phosphonic acid (ATMP), is well known for preventing the formation of calcium salt scale at the early stages of the crystallization process. Therefore, phosphonates can be dosed stoichiometrically to alkaline earth ions [26]. As a result, the required concentration of phosphonate antiscalants is often lower compared to other antiscaling agents [27].

The effect of antiscalants on calcium carbonate scale formation was studied using ATMP (aminotrismethylene phosphonic acid) as a scale inhibitor. ATMP, commercially known as Hydrex 4102, is one of the widely used antiscalants for inhibiting calcium carbonate scale in water due to its excellent chelating ability with calcium ions and low threshold inhibitory dose [28].

Antiscalants based on polycarboxylic and polyacrylic acids (PAA) are among the most

common environmentally friendly antiscaling agents due to the absence of phosphorus [29–31].

It has also been shown that PAA-based antiscalants prevent scale formation through a combination of lattice distortion, complexation, and dispersion mechanisms [32].

Polyacrylic acid (PAA) is more effective in preventing gypsum scale formation [33].

Polyepoxysuccinic acid (PESA) is a phosphorus-free, nitrogen-free, and biodegradable corrosion inhibitor. It is a promising environmentally friendly inhibitor that has attracted significant research attention in many countries [34–43]. Although PESA has excellent inhibition performance for calcium carbonate scale, it can barely inhibit calcium phosphate and has poor performance against iron oxide. When used in highly hard and strongly alkaline water, its efficiency in inhibiting calcium carbonate scale is also unsatisfactory. To improve the comprehensive efficiency of PESA, researchers have conducted studies on modifying PESA by introducing other functional groups. In this study, an antiscalant was synthesized by introducing a sulfonic acid group, and its stabilization properties were investigated under static conditions [44].

Some studies in the literature have focused on polyepoxysuccinic acid (PESA) and polyaspartic acid (PASA) antiscalants as green scale inhibitors because they are nitrogen-free, phosphorus-free, non-toxic, and biodegradable. Experimental results [45] obtained under static conditions for inhibiting $CaCO_3$ demonstrated high efficiency of PESA [46]. However, its scale inhibition efficiency for $Ca_3(PO_4)_2$ is poor [47]. To improve the comprehensive scale inhibition efficiency, it is important to modify it by introducing functional groups into its side chain, such as hydroxyl groups, carboxyl groups, sulfo groups, and/or phosphonyl groups [48; 49].

To address the issue of mineral scaling, various chemicals and antiscalants have been used, including polyacrylic acid (PAA), polyacrylamide, hydrolyzed polymaleic anhydride (HPMA), 1-hydroxyethane-1,1-diphosphonic acid (HEDP), and polyphosphates [50; 56].

These scale inhibitors primarily control mineral scale through two mechanisms of scale inhibition: one involves the ability of scale inhibitors to sequester ions that form scale (e.g., Ca^{2+} and Mg^{2+}) in solution to prevent their precipitation as solids through complexation [57]; the other involves chemical scale inhibitors interacting with mineral species to disrupt the crystallization process and keep crystalline particles dispersed in a water suspension, making them less prone to sedimentation or adhesion to equipment surfaces [58; 59]. HEDP, HPA and PAC have been widely used as scale inhibitors, corrosion inhibitors, or dispersants. PAC exhibits a 'threshold effect'. Inhibiting $CaCO_3$ can hinder the formation of vaterite, aragonite, or calcite crystals, slowing their growth [60; 61]. HEDP can alter the structure of calcium carbonate by incorporating into the crystals, thereby reducing scale formation on heat exchange surfaces [62]. The effect of HPA on the growth of calcium carbonate particles on stainless steel surfaces has been studied; HPA can affect the growth of $CaCO_3$ crystals through the adsorption of carboxylate ions onto calcium carbonate nuclei [63]. Additionally, HPA has been synthesized and studied for its stabilizing properties under static conditions [64].

Mixtures of different types of scale inhibitors, when mixed in certain ratios, can have much greater scale inhibition efficiency. Experiments and process optimization are usually required to find the optimal mixing ratio. Data on optimizing the mixture ratio of HEDP, PAC, and HPA for calcium carbonate inhibition are scarce. The synergistic effect of HEDP, HPA, and PAC for inhibiting calcium carbonate is still lacking [65]. Polyphosphonate scale inhibitors, such as 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) or 1-hydroxyethane-1,1-diphosphonic acid (HEDP), easily lead to the formation of orthophosphate through their own hydrolysis or decomposition, and orthophosphate itself can react with calcium ions to form relatively insoluble calcium phosphate scale. Furthermore, polyphosphonates, by converting to orthophosphate, can potentially serve as nutrients for algae. Another class of modern scale inhibitors is polycarboxylates, such as polyacrylic acids (PAA) or poly(maleic anhydride) (PMA), which have low calcium tolerance and react with calcium ions to form insoluble calcium polymeric salts [66; 67].

Polyacrylic acid (PAA), polymaleic acid (PMA), polyaspartic acid (PAS), and polyepoxyantartic acid (PEAA) are carboxylates used as scale inhibitors. Additionally, copolymers such as maleic acid/acrylic acid (MA/AA) copolymer and terpolymers such as maleic acid/acrylic acid/acrylamide (MA/AA/AM) terpolymer are utilized. Typically, one of the monomers in terpolymers is non-ionic, such as acrylamide, aimed at enhancing the polymer's dispersing

properties by increasing steric hindrance between particles [68].

In recent decades, incorporating phosphorus-containing functional groups into polymer matrices has increasingly been employed to enhance scale inhibition effectiveness and corrosion resistance [69–71]. These products combine polymer properties with the advantages of higher thermal stability, greater calcium tolerance, and a broader pH tolerance range compared to other types of inhibitors [72; 73].

Phosphonates are effective in preventing the precipitation of calcium carbonates, sulfates, and phosphates [74]. Therefore, phosphorus-containing antiscalants demonstrate high inhibitory properties that help prevent $CaCO_3$ deposition. However, the use of phosphorus-containing antiscalants may lead to eutrophication of water bodies and environmental degradation [75; 76].

Due to increasing environmental concerns and emission restrictions, the development and application of new phosphate-free and low-toxicity green antiscalants are critically important. Another approach involves using phosphorus-containing antiscalants in closed-loop cooling systems to prevent their release into water bodies.

Therefore, applying antiscalants for water treatment in closed-loop industrial water cycles not only improves heat transfer conditions of heat exchange equipment and reduces energy consumption but also enhances equipment efficiency, productivity, and reliability. It reduces the need for fresh water makeup and nutrients, thereby lowering the anthropogenic load on water bodies and protecting the water basin from the discharge of mineralized effluents.

Thus, water stabilization treatment using antiscalants should aim not only at temporary scale and deposition problem resolution but also at implementing a comprehensive strategy that will lead to long-term cost savings, increased efficiency, and environmental responsibility.

This study aimed to determine the effectiveness of an antiscalant in waters of different mineralization to address the issue of protecting water circulation systems from scale formation.

The research objectives included:
- Evaluation of the effectiveness of stabilizing agents in tap, artesian, and simulated water;
- Establishing the dependency of water stabilizing treatment effectiveness on antiscalant dosage and process conditions.

Experimental part
Materials and methods
Water from the municipal supply (Hardness = 4.50 mg-eq/dm³; $[Ca^{2+}]$ = 3.50 mg-eq/dm³; $[Mg^{2+}]$ = 1.00 mg-eq/dm³; Alkalinity = 3.70 mg-eq/dm³; $[SO_4^{2-}]$ = 29.70 mg/dm³; $[NO_3^-]$ = 37.50 mg/dm³; $[Cl^-]$ = 23.90 mg/dm³; pH = 6.70; $[Fe^{2+/3+}]$ = 0.19 mg/dm³; Mineralization = 295,3 mg/dm³), water from the River Desna (Hardness = 5.00 mg-eq/dm³; $[Ca^{2+}]$ = 3.80 mg-eq/dm³; $[Mg^{2+}]$ = 1.20 mg-eq/dm³; Alkalinity = 4.40 mg-eq/dm³; $[SO_4^{2-}]$ = 25.50 mg/dm³; $[NO_3^-]$ = 3.37 mg/dm³; $[Cl^-]$ = 14.10 mg/dm³; pH = 8.09; $[Fe^{2+/3+}]$ = 0.57 mg/dm³; Mineralization = 315.00 mg/dm³) and model solutions with hardness of 7.33 (273.7 mg $NaHCO_3$, 147.5 mg Na_2CO_3, 295,4 mg $CaCl_2$ and 247.6 mg $MgSO_4 \cdot 7H_2O$ were added to 1 dm³ of deionized water) and 14.65 mg-eq/dm³ (547.5 mg $NaHCO_3$, 295.0 mg Na_2CO_3, 590,7 mg $CaCl_2$ and 495.2 mg $MgSO_4 \cdot 7H_2O$ were added to 1 dm³ of deionized water) were used to evaluate the effectiveness of the anti-scalant against scale formation.

Samples of 0.1 dm³ were held at a temperature of 80 °C for 2 hours.

To ensure data reproducibility, all experiments were conducted with three repetitions.

The inhibitor used was RT-2024-3. Its characteristics are provided in Table 1.

Table 1

Main characteristics of the antiscalant

Name	Composition	Water solubility	Aggregate state	Color	Density at 20 ⁰C, g/m³	pH
RT-2024-3	Phosphate mixtures – 20-40 %, phosphonates – 15–30 %, dispersants – 5–10 %, water	Completely	Liquid	Colorless	1.22	8.20

The doses of the antiscalant ranged from 2.50 to 30.00 mg/dm³. Samples were cooled, filtered, and the residual water hardness was measured. Water hardness was determined using the

titration method with Eriochrome Black T as the indicator.

The stabilizing effect was assessed by the reduction in water hardness upon heating the solution with the antiscalant relative to the initial

value. This parameter was calculated using the formula:

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

where SE is the stabilization effect, %; ΔH is the reduction in hardness in the blank experiment, mg-eq/dm^3; ΔH_i is the reduction in hardness in the scale inhibitor experiment, mg-eq/dm^3; H_i is the residual hardness in the sample with the stabilizer, mg-eq/dm^3

The reduction in hardness in the scale inhibitor experiment was determined by the formula:

$$\Delta H_i = H - H_i;$$

where H is the initial hardness of the solution, mg-eq/dm^3; H_i is the residual hardness in the sample with the stabilizer, mg-eq/dm^3.

The reduction in hardness in the blank experiment was determined by the formula:

$$\Delta H = H - H_{res.}$$

where H is the initial hardness of the solution, mg-eq/dm^3; $H_{res.}$ is the residual hardness in the blank sample, mg-eq/dm^3;

The anti-scaling effect was calculated using the formula:

$$ASE = \frac{H_i}{H} \cdot 100\%,$$
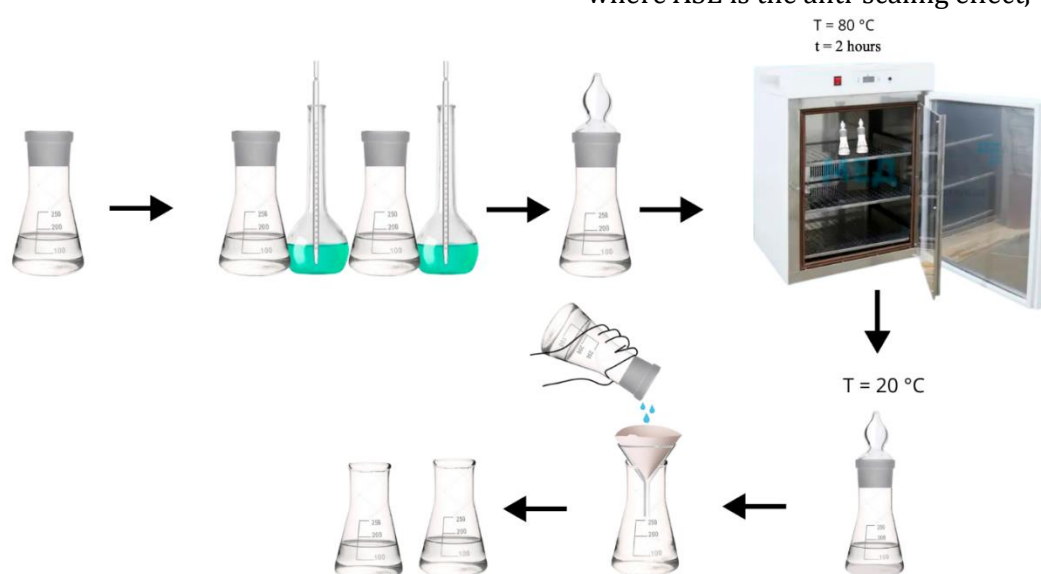
where ASE is the anti-scaling effect, %.

Fig. 1. Scheme of the water treatment process with antiscalant for scale removal

Results and Discussion

The study investigated the stabilizing effect of the antiscalant RT-2024-3. The influence of the dosage of this reagent on the stabilizing and anti-scaling effects of tap water from Kyiv city is shown in Figure 2, and natural water from the River Desna is shown in Figure 3.

With an increase in the dosage of the antiscalant in tap water with hardness ranging from 2.5 to 30.0 %, the stabilizing and anti-scaling effects increased from 8.67 to 80.00 % and from 96.96 to 99.33 %, respectively.

Increasing the reagent dosage from 10.00 to 30.00 mg/dm^3 allows for an increase in the stabilizing and anti-scaling effects of natural water

from a surface source from 30.00 to 76.67 % and from 95.80 to 98.60 %, respectively.

Thus, the application of RT-2024-3 is quite promising for treating water with hardness levels between 4.5 and 5.00 mg-eq/dm^3 at doses above 20 mg/dm^3, as in all cases the stabilizing effect exceeded 53 % and increased to 76.7–80.0 %. Additionally, the anti-scaling effect ranged from 97.40 to 99.33 %.

Gipan provided high stability of artesian water (hardness = 4.7 mg-eq/dm^3) in terms of sediment formation at a concentration above 10 mg/dm^3. At inhibitor doses of 1–20 mg/dm^3, SE varied from 58.8 % to 88.2 % [14]. This antiscalant has a higher efficiency compared to RT-2024-3.
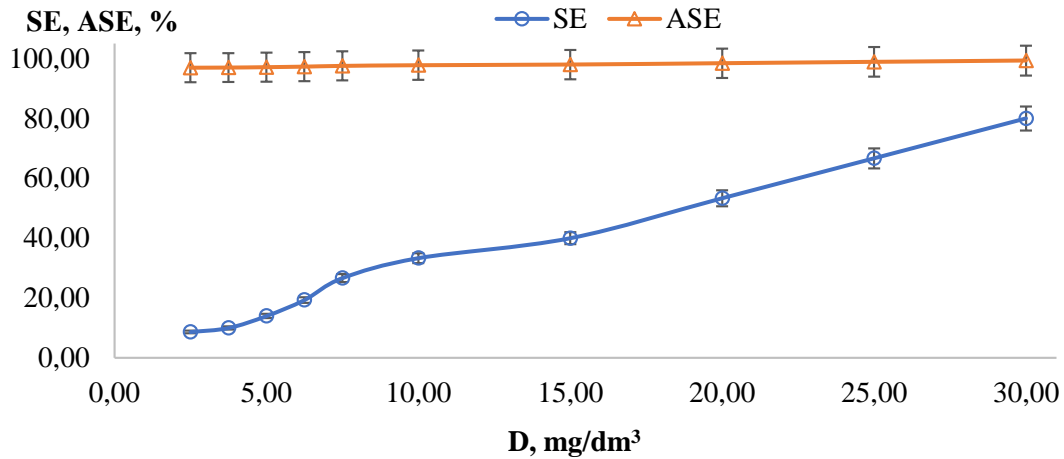
Fig. 2. The effect of the dosage of antiscalant RT-2024-3 at 80 °C on the stability of tap water in Kyiv with hardness (H) = 4.5 mg-eq/dm³
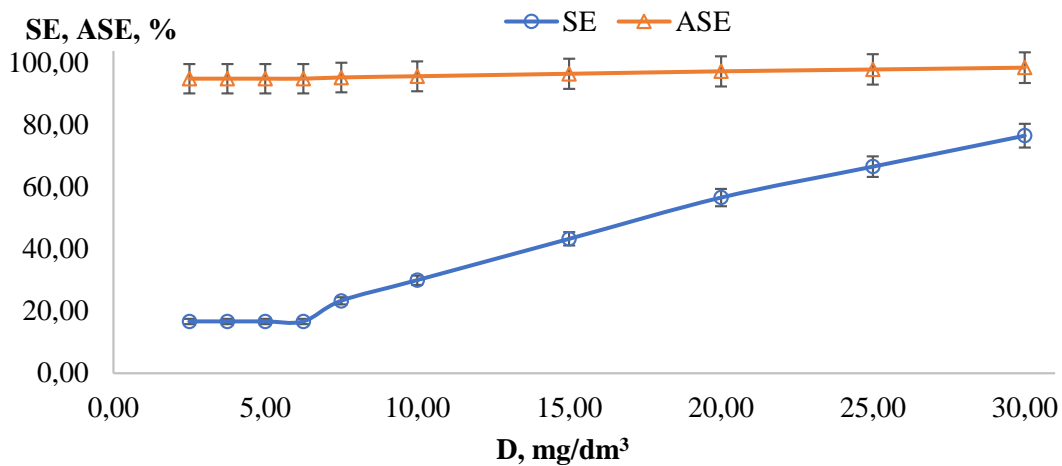

Fig. 3. The influence of the dosage of antiscalant RT-2024-3 at 80 °C on the stability of natural water from the River Desna at H = 5.0 mg-eq/dm³

Figure 4 presents data on the stabilizing and anti-scaling effects of water with a hardness of 7.3 mg-eq/dm³. The effectiveness of stabilizing treatment of water with a hardness of 14.65 mg-eq/dm³ can be inferred from the data provided in Figure 5.
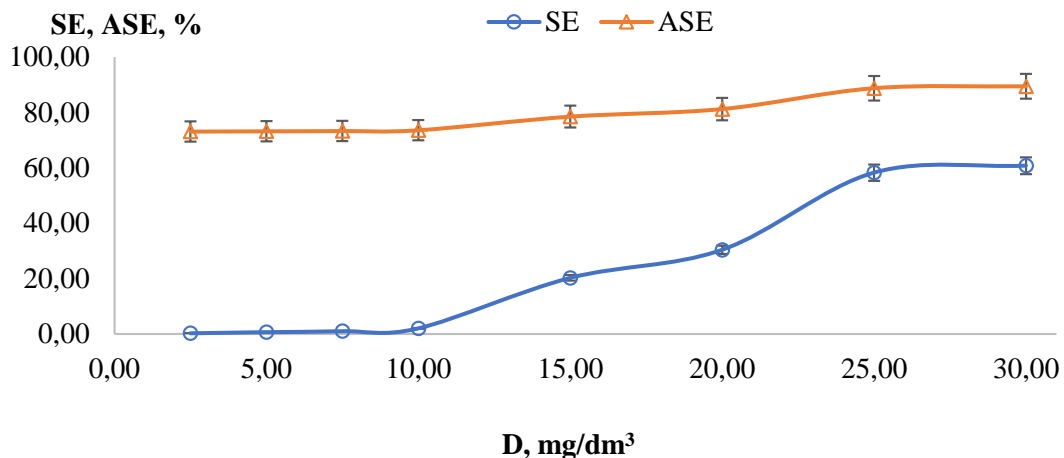

Fig. 4. The impact of RT-2024-3 antiscalant dosage at 80 °C on the stability of model solution with hardness (H) = 7.3 mg-eq/dm³
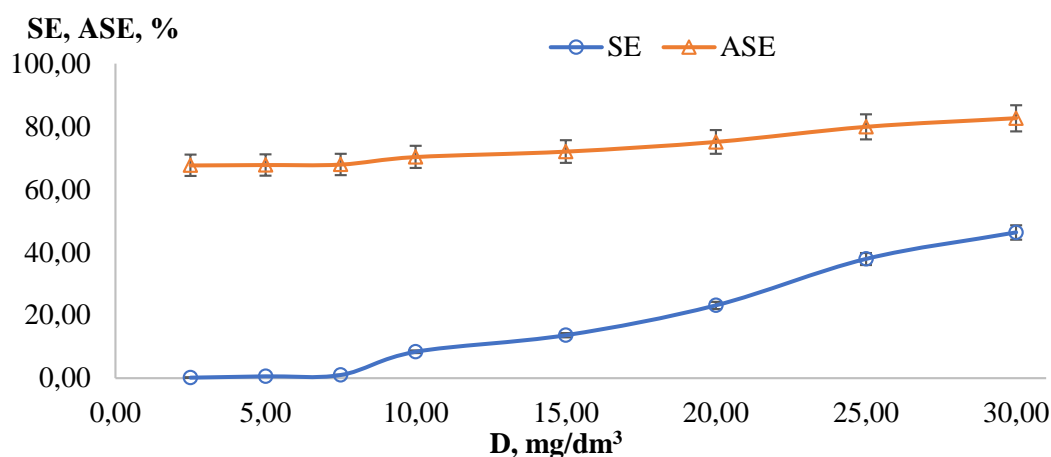
Fig. 5. The impact of RT-2024-3 antiscalant dosage at 80 °C on the stability of model solution with hardness (H) = 14.65 mg-eq/dm³

The reagent proved ineffective at doses up to 10 mg/dm³ when treating solutions with hardness greater than 7.33 mg-eq/dm³, with stabilization effects not exceeding 2 %. However, introducing the antiscalant into water with hardness of 7.33 mg-eq/dm3 at doses ranging from 15.00 to 30.00 mg/dm³ resulted in stabilization effects within 20.25–60.76 %. Using the antiscalant for water with higher hardness yielded slightly worse results, with stabilization efficiency at doses of 20.00 to 30.00 mg/dm³ ranging from 23.16 % to 46.32 %, which is unsatisfactory. This is likely due to low reagent doses, suggesting that further studies should explore similar experiments with doses exceeding 30 mg/dm³. The need for higher antiscalant doses compared to recommended levels may be associated with the formation of more complex salts in real water systems.

The application of antiscalants is one of the most effective methods to combat scaling. Antiscalants lead to the formation of small crystals in the water stream, thereby preventing deposits on equipment surfaces. The studies utilized model solutions with relatively high mineralization and hardness, making the water quite unstable in terms of scaling. This explains the insufficiently effective results of stabilization treatment for water with hardness above 7.3 mg-eq/dm³ when using antiscalants, as their effectiveness largely depends on water quality.

Conclusions

The effectiveness of the antiscalant significantly varies depending on the dosage, thus it should be applied in different concentrations depending on the water quality in the system. Applying the antiscalant at doses of 20–30 mg/dm³ is promising for treating water with hardness less than 5.0 mg-eq/dm³. The stabilization effect ranges from 76.7 % to 80.0 %, and the anti-scaling effect remains within 97.40–99.33 %.

The effectiveness of the antiscalant largely depends on water quality, hence satisfactory results were obtained with doses of the reagent exceeding 25–30 mg/dm³ for water hardness up to 7.3 mg-eq/dm³. The stabilization effect was at 60 %, and the anti-scaling effect was at 89 %. To achieve satisfactory results with higher hardness, it is advisable to increase the dosage beyond 30 mg/dm³.

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