

# Research on inhibiting properties of new schale deposition reagents

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**Abstract.** New compositions for inhibiting scale deposits on oil-field equipment and pipelines have been developed based on a nitrogen-containing compound, inhibited hydrochloric acid, anionic polymer and water. The efficiency of inhibiting scale deposits was assessed using artificially prepared mineral waters of carbonate and sulfate types, simulating formation waters. It was found that the introduction of the prepared compositions into calcium sulfate and calcium carbonate solutions at a rate of 50 mg/l provides a high protective effect compared to an inhibitor consumption of 30 mg/l. The content of the active substance in the compositions is 14.5 – 18.5%.

**Keywords:** scale deposition inhibitor, inhibition efficiency, mineral deposits, calcium sulfate, calcium carbonate, active substance.

## 1 Introduction

Mineral deposits are formed in various zones of oil production systems. Due to changes in the partial pressure of carbon dioxide, chemical composition of water or temperature, the chemical equilibrium is disturbed. Salt deposits are found in wells, at various depths along the wellbore, in oil gathering system (OGS) pipelines, in oil treatment unit equipment, in oil transportation pipelines, in formation pressure maintenance system (RPMS) equipment and pipelines. Salt deposits cause significant complications during oil production. Salt deposits reduce the internal diameter of the tubing and, as a result, reduce the amount of liquid extracted from the wells. They also lead to failure of deep-well pumps during mechanized oil production, failure of measuring equipment, reduced performance of heaters-cleaners, intensive corrosion of the internal surfaces of pump-compressor pipes, oil and gas pipelines and reservoir pressure maintenance systems, where local stratification and subsurface corrosion occur [1]. Salt deposits are not 100% pure salts. Mineral deposits always contain iron compounds (oxides, carbonates) and insoluble substances (mechanical impurities such as sand or clay). Mechanical impurities such as iron oxides act as crystallization centers on which salt crystals grow, which leads to the inclusion of impurities in the structures of mineral deposits. The main method for preventing scale formation is the use of scale inhibitors. To effectively prevent precipitation of poorly soluble salts from supersaturated solutions, the

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inhibitor must be adsorbed on more than 16% of the surface of all crystals.

Since scale inhibitors influence the crystallization process through adsorption rather than chemical reactions, the concentrations required for inhibiting precipitate formation are relatively low – typically from 5 to 40 mg/l for commercial products, which are 10-50% solutions of individual substances (or their mixtures) in aqueous or aqueous-alcoholic mixtures [2].

Three mechanisms are distinguished in how scale inhibitors affect the crystallization process of poorly soluble salts from supersaturated aqueous solutions [3-5]: The inhibitor, by adsorbing on the surface of the crystal nucleus, prevents further growth (this is called the threshold mechanism) or stabilization of the supersaturated solution; The inhibitor, adsorbing on the actively growing crystal surface and lattice defects, halts or slows crystal growth and can also alter the crystal lattice (this is the crystal growth inhibition mechanism); The inhibitor, adsorbing on crystal surfaces, prevents the crystals from interacting and aggregating into uniform deposits (this is the dispersion mechanism).

Scale inhibitors exhibit all three mechanisms simultaneously, but one effect is predominant.

**Objective.** The goal of this work is to develop new scale inhibitors to protect oilfield equipment and pipelines from mineral deposits and to study their inhibiting properties, thereby protecting the environment from contamination.

## 2 Practical section

The most effective and technologically advanced method to prevent inorganic salt deposition is the use of chemical reagents – scale inhibitors. Strict requirements are imposed on these inhibitors [6]:

- They must prevent inorganic salt deposition at low reagent concentrations.
- They must be compatible with reservoir, produced, and injected waters of various compositions and dissolve well in them.
- They must be stable during storage and transportation.
- They must not negatively impact oil production, collection, transport, and processing technology, including in cases where chemical products are used for other purposes.
- They must not negatively affect oil refining processes or degrade the quality of refined products.
- They must not increase the corrosive activity of the environment in which they are dissolved.
- They must not promote the stability of water-oil emulsions.
- They must be safe for personnel and environmentally friendly.
- The residual content of inhibitors in different water compositions must be analytically detectable under field conditions.
- Each inhibitor must have a technological application characteristic, a maximum permissible concentration in water and air, and safe work recommendations.

New scale deposition inhibiting compositions for oilfield equipment and pipelines were developed based on nitrogen-containing compounds, inhibited hydrochloric acid, an anionic polymer, and water. For the preparation of these inhibitors, nitrogen-containing compounds such as ammonium phosphate, monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and urea were used, while carboxymethylcellulose (CMC) and polyacrylamide (PAA) were employed as anionic polymers.

The preparation of mineral scale inhibitors is carried out as follows: a nitrogen-containing compound and water are loaded into a reactor. A mechanical stirrer is activated, and the contents of the reactor are heated to 40-45°C. Inhibited hydrochloric acid (20%) is loaded into a separating funnel and gradually added to the reactor. Then, an anionic polymer is

introduced into the reactor, and the stirring continues at the specified temperature until a homogeneous mass is formed. The density of the prepared compositions at 20°C is 1050-1100 kg/m<sup>3</sup>, kinematic viscosity at 20°C is 30-40 mm<sup>2</sup>/s, freezing temperature is minus 15-20°C, and the pH is 3-6. The compositions are transparent liquids, ranging from light to slightly yellow in color.

One of the main requirements for scale inhibitors is their adsorption-desorption properties. It is known that oil- and gas-bearing formations have different wettability and adsorption capacities [6]. Therefore, to improve the adsorption-desorption characteristics of the scale inhibitor, reagents that reduce interfacial tension at the "oil-inhibiting solution" boundary should be used. This allows increasing the contact surface with both silicate and aluminosilicate minerals and the carbonate component of the cement composition. Due to their adsorption-desorption characteristics, the prepared reagents act as long-term salt inhibitors and show high efficiency. Treating the surface of productive formations with an inhibiting composition containing hydrochloric acid reduces the surface tension at the "rock-oil-inhibiting solution" boundary, which helps to better prepare the rock surface for adsorption by displacing oil films and hydrophilizing the surface [7]. Additionally, the roughness of the rock increases due to the chemical interaction of hydrochloric acid with carbonate minerals. Moreover, hydrochloric acid can clean the rock surface from oil films, changing its wettability and thus ensuring uniform and complete adsorption of the scale inhibitor.

**Table 1.** Results of Scale Inhibitor Preparation.

№	The quantity of substances in the inhibitor composition, in mass %								
	Nitrogen-containing compound					Anionic polymer		Inhibited hydrochloric acid	Water
	MEA	DEA	TEA	Ammonium phosphate	Urea	KMS	PAA		
1	10	-	-	-	-	2.75	-	2	85.25
2	-	10	-	-	-	2.50	-	2	85.50
3	-	-	10	-	-	2.75	-	2	85.25
4	-	-	-	10	-	2.50	-	2	85.50
5	-	-	-	-	10	2.75	-	2	85.25
6	15	-	-	-	-	2.25	-	1	81.75
7	-	15	-	-	-	2.50	-	1	81.50
8	-	-	15	-	-	2.25	-	1	81.75
9	-	-	-	15	-	2.50	-	1	81.50
10	-	-	-	-	15	2.50	-	1	81.50
11	10	-	-	-	-	-	2.75	2	85.25
12	-	10	-	-	-	-	2.50	2	85.50
13	-	-	10	-	-	-	2.75	2	85.25
14	-	-	-	10	-	-	2.50	2	85.50
15	-	-	-	-	10	-	2.75	2	85.25
16	15	-	-	-	-	-	2.25	1	81.75
17	-	15	-	-	-	-	2.50	1	81.50
18	-	-	15	-	-	-	2.25	1	81.75
19	-	-	-	15	-	-	2.50	1	81.50
20	-	-	-	-	15	-	2.50	1	81.50
21	8	-	-	-	-	2.25	-	2	87.75
22	-	6	-	-	-	2.5	-	2	89.50
23	-	-	4	-	-	2.75	-	2	91.25
24	-	-	-	17	-	-	2.25	1	79.75
25	-	-	-	-	20	-	2.5	1	76.50

The aqueous solution of the amine-containing compound reduces interfacial tension between phases, negatively affecting the formation of salt layers. The anionic polymer, by blocking calcium ions, helps prevent the formation of calcium sulfate and calcium carbonates.

From Table 1, it can be seen that the nitrogen-containing compound in the scale inhibitor compositions constitutes 10–15%, the anionic polymer 2.25–2.75%, and the inhibited hydrochloric acid 1–2% (which corresponds to a 5–10% acid solution).

The effectiveness of scale inhibition was evaluated using a standardized methodology, based on the reagent's ability to retain  $\text{Ca}^{2+}$  cations in artificially prepared mineral waters of carbonate and sulfate types, simulating reservoir waters from oil fields. The artificial waters were prepared as follows [8]:

Carbonated water	Sulfate water
Solution 1, g/dm <sup>3</sup> :	Solution 1, g/dm <sup>3</sup> :
NaHCO <sub>3</sub> – 2.3	Na <sub>2</sub> SO <sub>4</sub> – 13.0
Solution 2, g/dm <sup>3</sup> :	NaCl – 18.8
CaCO <sub>3</sub> – 2.92	MgCl <sub>2</sub> · 6H <sub>2</sub> O – 1.24
MgCl <sub>2</sub> · 6H <sub>2</sub> O – 4.26	Solution 2, g/dm <sup>3</sup> :
NaCl – 40.4	CaCl <sub>2</sub> – 13.6

**The testing methodology consisted of the following:** In a 100 ml flask, a specified amount of 1% solution of the test composition was added using a pipette. Then, 50 ml of artificially prepared carbonate or sulfate water was added. The products were mixed, and then another 50 ml of carbonate or sulfate water was added. After thorough mixing, the sample was kept at 80°C for 6 hours. At the same time, a control sample without the addition of the reagent was prepared. The samples were filtered while hot, and the calcium ion content was determined in the filtrates using a titrimetric method. Each experiment was conducted in duplicate. The protective effect of inorganic salt inhibition was determined by the formula:

$$E = (C_x - C_0)/(C_i - C_0)$$

where:  $E$ , % - protective effect;  $C_x$ , mg/dm<sup>3</sup> - content of precipitating ions in the solution in the presence of the inhibiting composition, determined after the experiment;  $C_0$ , mg/dm<sup>3</sup> - content of precipitating ions in the solution without the inhibiting composition, determined after the experiment;  $C_i$ , mg/dm<sup>3</sup> - content of precipitating ions in the original solution, determined before the experiment. The results of the experiments to determine the protective effect of the prepared inhibitors are presented in Table 2.

**Table 2.** Results of the Work on Determining the Protective Effect of Inhibitors.

№ of sample	Composition of the inhibitor	Inhibitor dosage, mg/L	Protective effect of the inhibitor	
			CaSO <sub>4</sub> · 2 H <sub>2</sub> O	CaCO <sub>3</sub>
1	2	3	4	5
1	14.75 % Active substance. 85.25 % water	30	89.6	91.3
		50	98.8	99.4
2	14.5 % Active substance. 85.5 % water	30	89.2	90.5
		50	98.2	99.1
3	14.75 % Active substance. 85.25 % water	30	90.6	91.5
		50	99.2	99.8
4	14.5 % Active substance. 85.5% water	30	90.4	92.3
		50	99.2	99.7
5	14.75 % Active substance. 85.25 % water	30	90.8	92.8
		50	99.8	99.9
6	18.25 % Active substance. 81.75 % water	30	92.3	93.3
		50	99.8	99.7

Continuation of table 2.

№ of sample	Composition of the inhibitor	Inhibitor dosage, mg/L	Protective effect of the inhibitor	
			CaSO <sub>4</sub> · 2 H <sub>2</sub> O	CaCO <sub>3</sub>
1	2	3	4	5
6	18.25 % Active substance.	30	92.3	93.3
	81.75 % water	50	99.8	99.7
7	18.5 % Active substance.	30	92.4	93.2
	81.5 % water	50	99.7	99.8
8	18.25 % Active substance.	30	92.1	92.8
	81.75 % water	50	99.4	99.7
9	18.5 % Active substance.	30	93.5	93.7
	81.5 % water	50	99.8	100.0
10	18.5 % Active substance.	30	92.4	93.0
	81.5 % water	50	99.4	99.6
11	14.75 % Active substance.	30	90.5	91.3
	85.25 % water	50	99.2	99.3
12	14.5 % Active substance.	30	89.8	90.8
	85.5 % water	50	98.9	99.1
13	14.75 % Active substance.	30	90.7	91.6
	85.25 % water	50	99.4	99.7
14	14.5 % Active substance.	30	91.3	92.7
	85.5 % water	50	99.8	100.0
15	14.75 % Active substance.	30	90.4	92.3
	85.25 % water	50	99.7	99.8
16	18.25 % Active substance.	30	92.7	92.1
	81.75 % water	50	99.5	99.7
17	18.5 % Active substance.	30	90.8	91.7
	81.5 % water	50	98.9	99.3
18	18.25 % Active substance.	30	91.0	91.6
	81.75 % water	50	99.7	99.8
19	18.5 % Active substance.	30	92.7	92.3
	81.5 % water	50	99.6	99.8
20	18.5 % Active substance.	30	91.5	93.7
	81.5 % water	50	99.2	99.8
21	12.25 % Active substance.	30	79.8	80.4
	87.75 % water	50	82.3	83.6
22	10.5 % Active substance.	30	75.3	77.4
	89.5 % water	50	80.7	81.5
23	8.75 % Active substance.	30	70.2	71.8
	91.25 % water	50	75.4	76.8
24	20.25 % Active substance.	30	77.4	78.4
	79.75 % water	50	81.3	80.9
25	23.5 % Active substance.	30	69.8	70.3
	76.5 % water	50	75.3	76.8

From Table 2, it is clear that the introduction of the prepared compositions into solutions of calcium sulfate and calcium carbonate at a dosage of 50 mg/L results in a high protective effect compared to cases where the inhibitor dosage was 30 mg/L. The active substance in the compositions ranges from 14.5% to 18.5%.

Compositions for inhibiting mineral scale deposits have been prepared, where the amount of nitrogen-containing substances is slightly lower or higher compared to the compositions obtained earlier. The results of the conducted work are presented in Table 1.

The effectiveness of inhibiting scale deposition by the prepared compositions was studied, where the amount of nitrogen-containing compound was taken in lower (4%, 6%, and 8% mass) and higher (17% and 20% mass) quantities compared to the nitrogen-containing compounds in the compositions prepared earlier (Table 1). The results of the studies to determine the protective effect of the latter compositions in the medium of carbonate and sulfate-type mineral waters, simulating formation waters, are presented in Table 2.

From Table 2, it is evident that the active substance in the compositions is 8.75%. The active substance in the compositions is 12.25% in the case of a lower amount of nitrogen-containing compound in the composition, and 20.25% to 23.5% in the case of a higher amount. These results indicate that a smaller amount of nitrogen-containing compound in the composition (less than 10% mass) leads to a weakening of the inhibiting properties of the scale inhibitors. The presence of a larger amount (more than 15% mass) of nitrogen-containing compound in the composition appears to contribute to incompatibility with highly mineralized waters.

### 3 Conclusion

Thus, the compositions for inhibiting scale deposits occurring on oil-field equipment and pipelines have been developed, based on nitrogen-containing compounds, inhibited hydrochloric acid, anionic polymer and water. The efficiency of inhibiting scale deposits was assessed using artificially prepared mineral waters of carbonate and sulfate types simulating formation waters. It was found that the introduction of the prepared compositions into calcium sulfate and calcium carbonate solutions at a dosage of 50 mg/l leads to a high protective effect compared to cases where the inhibitor dosage was 30 mg/l. The content of the active substance in the compositions ranges from 14.5% to 18.5%. A smaller amount of nitrogen-containing compound in the composition (less than 10% by weight) leads to a weakening of the inhibiting properties of scale inhibitors. The presence of a larger amount (more than 15% by weight) of nitrogen-containing compound in the composition apparently contributes to incompatibility with highly mineralized waters.

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