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MODIFICATION OF COMPOSITION OF SALINITY INHIBITORS BASED ON ORGANOPHOSPHONATES AND ACRYLIC ACID

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Abstract: *Chemical and mineralogical compositions of mineral deposits and acidic precipitations have been studied, and synergistically effective compositions of inhibitors of salt deposits have been selected based on -PO_3H_2 and COOH containing organic compounds. The article proposes a formulation of a mineral salts deposit inhibitor corresponding to regulatory indicators (not less than 90%) for the protection of municipal boiler houses and industrial equipment, comparative results of the industrial preparation Komperex-710. The obtained compositions were found to be effective inhibitors in concentrations of 8-12 mg/l in waters with calcium and magnesium chlorides Chimbaia, Turtkulia and Biruni with hardness of 7.9-9.6 mg·eq/l and in concentrations of 10-14 mg/l in waters with calcium and magnesium carbonates Nukus and Shukmanay.*

Key words: *acrylic acid, organophosphonates, water hardness, mineral salt deposits inhibitors, inhibition efficiency, Komperex-710.*

Introduction. Currently, in our republic, as in all developed countries of the world, pays great attention to the rational use of natural resources, the development of waste-free, resource-saving technology for the production of practically important products based on local raw materials and industrial waste.

The government of the Republic of Uzbekistan pays great attention to organization of production of new products of domestic chemical industry, including production of chemical means of plant protection, medicines, dyes, estrogens for extraction of rare ions, inhibitors of corrosion, salt and nonferrous metals, etc.

Application of effective means of struggle against salting - antiscalants - gives the chance to create the circulating, closed and drainless systems corresponding to requirements of modern manufacture and ecology. Salt-ladle inhibitors when added to water from 2.0 to 10 g/m3 by 90% or more prevent scale formation on the surface of heat exchangers, steam boilers, pipelines, etc.

The solution to the problem of protection of equipment against scaling is also relevant for the mining and metallurgical industry of the Republic of Uzbekistan. At Navoi Mining and Metallurgical Plant by protection from intense salt formation and corrosion of equipment in the process of neutralization of acidic effluents, including increasing the efficiency of extraction of

gold from hard ores by bio-oxidation method is used imported antiscalant called " Komperex - 710".

One of the top priorities in the production of inhibitors of salt deposits is the preparation of effective compositions.

There are data in the literature that ATMP compositions with Zn^{2+} and various additives are used as synergistic fragments as inhibitors of salt deposits and corrosion [1]. The following are used as additives to *Zn*-ATMP: N-cetyl-N_1N_1N-thrimethylammonium bromide (STAB) [2]; EDPA, aminoethylenediphosphonic acid [3]; phthalic anhydride [4, 5].

Glycine Zn^{2+}, an environmentally friendly inhibitor system, was investigated by weight reduction [6]. A synergistic effect exists between glycine and the Zn^{2+} system. The composition consists of 250 h/mln glycine and 50 h/mln. Zn^{2+} provides a good inhibition efficiency of 82%. A polarization study shows that this composition acts as an anode inhibitor. The research of IR spectra allows to conclude that the Fe^{2+}-Gly complex formed on the anode sections of metal surface controlled the anode reaction, and $Zn(OH)_2$ formed on the cathode sections of metal surface controlled the cathode reaction. The surface morphology and metal surface roughness were analyzed by atomic force microscopy. A suitable mechanism for corrosion inhibition was proposed based on the results obtained from the study of weight loss and surface analysis techniques. Ecological system of glycine inhibitor Zn^{2+} can find application in water cooling system.

It is proposed to use as a synergistic composition for protection against corrosion and inhibition of salinity: phosphonosuccinate is an oligomer with sulfomethylated acrylamide with acrylates [7]; producing ATMP with amides and polymers in the series of acrylic acid derivatives with amido- and sulfonic groups [8]; hydroxyphosphinucleic acid and its salts [9]; ATMP, EDPA, DTPPA, diphosphonomethyl glycine (DPMG), as well as polymers in the series of sulfonic acrylates, etc. [10]; a water-soluble molybdenum salt, a stabilizing agent - a thermopolymer of acrylic acid, methacrylic acid and N-secretariat of butylacrylamide, as well as zinc or nickel salts of orthophosphates [11]; copolymer of acrylic acid with hydroxypropyl acrylate [12]; alkyl polycarboxylates, hydroxyphosphone-acetic acid, aminophosphonates with polymers of acrylic, maleic and epoxy-succinic acids [13].

The researchers' attention in recent years has been focused on the creation of composite compounds based on polymers. So, it is proposed a salt sediment inhibitor, which includes simultaneously inhibitors of salt deposits (polyacrylates, phosphorylated polymaleic anhydride, OEF: OEDF, ATMP, DTPPA, PBTC) and corrosion (amino acids: glycine, lysine, etc.) [14, 15].

Discussion of results. Comparative tests of samples were carried out on two types of NGMK's technological solutions with high alkalinity (pH>10.0) containing rhodanides, carbonates and metal ions - Au, Ca, K, Cu. The efficiency of salt sedimentation was determined at the temperature range of 60 - 80 °C and concentrations of 2, 4, 6 mg/l.

Three types of inhibitors were selected for the analysis: reference inhibitor Komperex-710, oxyethylene diphosphonic acid (ODEF) and composition prepared on the basis of OEDF, acrylic emulsion (produced by JSC "Navoiazot") and the condensation product of urea with acetic aldehyde of linear structure, in the ratio 29:1:70 % (conventional name - UAK-1).

It is necessary to mention that during the whole period of laboratory tests the high efficiency of industrial salt sludge inhibitor Komperex-710 is observed. The maximum efficiency of the

anticaking effect of the preparation at 80°C, minimum doses of 2 mg/l is 90.0 %, and at a dose of 4 mg/l - 96.0 %.

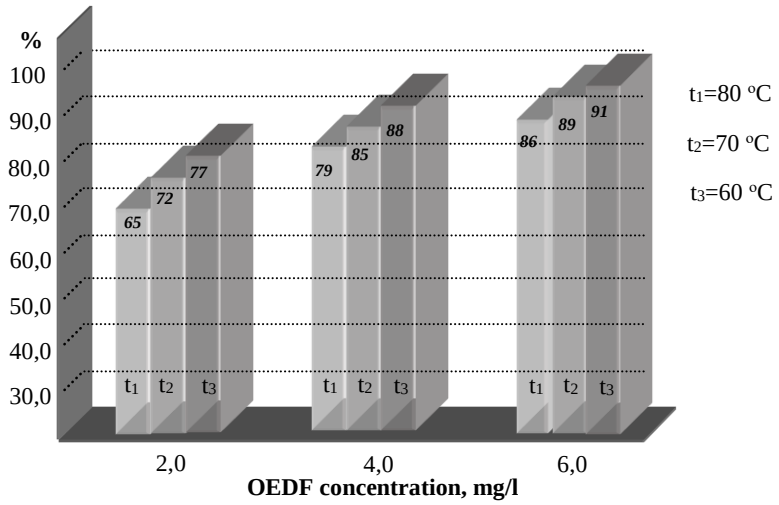

Fig.1. Efficiency of OEDF as a function of temperature.

It has been determined during the OEDF test (Fig.1) that the efficiency of inhibition of salt precipitate fallout increases with increasing dose of the preparation, but with increasing temperature the efficiency decreases, reaching the maximum dosage of 6 mg/l (MPC - OEDF) at 60° C - 91,0 %, 70° C - 89,0 % and 80° C - 86,0 %.

As noted above, the efficiency of inhibition of the precipitation of saline, a multi-component mixture of UAK-1, is also compared.

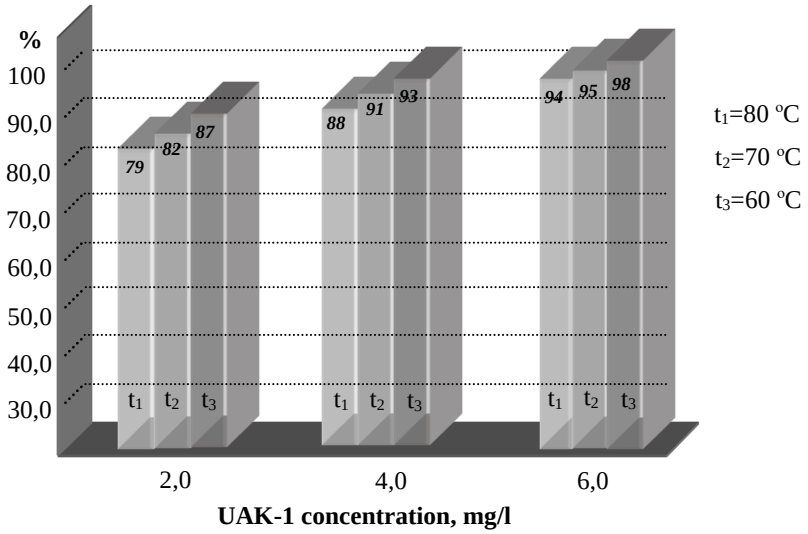

Fig.2. Efficiency of UAK-1 as a function of temperature.

As one can observe from the data of Fig.2, the efficiency of UAK-1 increases with increasing dose and at 6 g/t provides high protection: at 60° C - 98,0 %, 70° C - 95,0 % and at 80° C - 94,0 %.

It follows from the above that replacing the industrial benchmark Komperex-710 with the proposed composition UAK-1, consisting of 29% OEDF + 1% acrylic emulsion + 70% of the condensation product of urea with acetic aldehyde (multi-tonnage products of local production of

JSC "Navoiazot"), the synergetic effect of which has been proven by experimental data, as inhibitors of salt sedimentation, can reduce the cost of this drug several times.

Table 1

Comparative performance indicators of salt sediment inhibitor from its concentration at 80° C in five regions of the Karakalpakstan Republic

№	Inhibitor	Dose of inhibitor, mg/l	Efficiency %				
			Water hardness test, mg*eq/L				
			Nukus	Sukmanay	Turtkul	Biruniy	Chimbay
			17,0	**12,8**	**8,0**	**7,9**	**9,6**
1.	MSDI-1	4,0	79	82	87	87	84
		6,0	80	83	88	89	86
		8,0	82	85	89	89	88
		10,0	83	88	90	90	89
		12,0	85	90	91	91	90
		14,0	85	90	91	91	90
2.	Option	4,0	83	84	89	90	88
		6,0	84	86	91	92	89
		8,0	86	87	93	93	90
		10,0	88	89	94	94	91
		12,0	89	90	95	95	92
		14,0	89	90	95	95	93
3.	Zn-OEDF	4,0	81	84	86	87	87
		6,0	82	85	88	88	88
		8,0	84	86	89	89	89
		10,0	86	88	90	91	90
		12,0	87	89	91	92	91
		14,0	87	90	92	93	91
4.	“Nalco-2000”	4,0	87	89	91	92	89
		6,0	88	90	92	93	90
		8,0	89	91	94	94	90
		10,0	90	92	94	95	91

		12,0	91	93	95	95	92
		14,0	91	93	95	95	93
5.	Proposed composition	4,0	85	86	90	90	87
		6,0	86	88	92	91	89
		8,0	87	89	93	93	89
		10,0	89	90	94	94	91
		12,0	90	92	95	95	92
		14,0	91	92	95	95	93

This study also compares the efficiency of industrial inhibitors MSDI -1, Option, Zn-OEDF, "Nalco-2000" with our proposed composition of polymeric acrylic acid and ATMP with the addition of cube residue of vacuum distillation of monoethanolamine (VOCPM) in a ratio of 1 : 1 : 1.

Inhibitor concentrations for preventing salt deposits in the range of 4 - 14 mg/l have been studied. As shown in Table 1, the most effective inhibitors to prevent inorganic salt deposits are Option, Nalco-2000 and the proposed composition. The highest efficiency of these drugs in preventing salt deposits is 95 %, 94 % and 95 % respectively. If used in water, the maximum hardness of Nukus, their efficiency reaches 90 % in concentrations of 12 mg / l, it should be noted that the content of imported - an expensive reagent in the composition of the proposed drug is one third.

As the increase in the efficiency of salt deposits inhibition is insignificant at the concentration above 14 mg/l, further studies were conducted with the concentration of salt deposits inhibitors of 12 mg/l.

According to table 1 can be seen that among industrial inhibitors of salt deposits in concentrations up to 14 mg/l have the highest efficiency: MSDI -1 and OEDF to prevent the formation of calcium and magnesium chloride deposits in Chimbay, Turtkul and Biruniy waters, Zn-OEDF and Option in Sukmanay and Nukus waters to prevent the formation of calcium sulfate, Option and Nalco-2000 for calcium and magnesium chloride deposits. MSDI -1 and Zn-OEDF inhibitors have low efficiency in the waters of the predominant chloride anions.

Temperature is one of the most important parameters influencing salt deposits during oil production. It is well known that changes in temperature have a significant impact on the solubility of inorganic salts, which in turn affects the intensity of formation of deposits of salts and their effectiveness inhibition.

The research was conducted in the temperature range from 60 to 90° C under dynamic conditions. Research results are presented in Fig.3.

As illustrated in Fig. 3, an increase in temperature has a negative effect on the inhibition process of sediment formation. As the temperature rises, the efficiency of inhibitors to prevent the formation of calcium carbonate and magnesium sulfate decreases, as the solubility of these salts decreases with temperature rise. However, the decrease in efficiency of the applied preparation at temperature increase is insignificant, the efficiency remains more than 90 %. At the same time, the temperature increase increases the efficiency of inhibition as the solubility of calcium and magnesium chlorides increases with temperature increase.

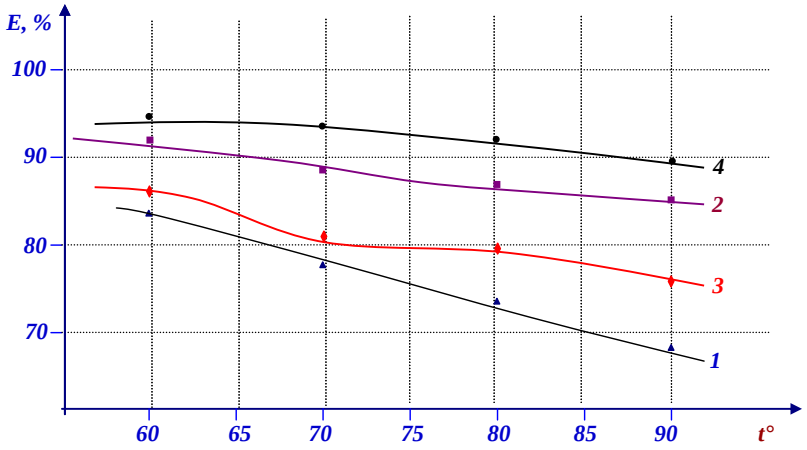

Fig.3. Dependence of efficiency of the salt sediment inhibitor on temperature at 12 mg/l: 1- MSDI -1; 2- Option; 3- Zn- OEDF; 4- proposed composition

Besides changing the solubility of salts with increasing temperature, there are other factors that can explain the change in the efficiency of inhibition of salts depending on the temperature. With increasing water temperature, microcrystalline salt particles move faster and the speed of colliding particles increases, resulting in faster precipitation.

Adsorption of scale inhibitors on the surface of microparticles of salts is exothermic. Therefore, as the system temperature increases, the degree of adsorption of inhibitors weakens. The kinetics of the deposition of salt crystals is one of the factors influencing the efficiency of the inhibitors of salt deposits. The study assumed that the degree of saturation of solutions with ions is constant at all temperatures. The temperature also influences the rate of deposition of salt crystals and the degree of saturation, since the saturation of solutions with ions is considered to be the driving force of salt deposition.

Consequently, the influence of changes in the specified parameters is mutually compensated. Therefore, with increasing temperature there is a decrease in the efficiency of inhibition of calcium carbonate and calcium sulfate deposits.

The aqueous solution of polyacrylic acid (BP-PAK) in pure form and in composition with MSDI and OEDF, was also used as antiscalants in artificially prepared inlets by composition approaching to JSC "UzKORGAZ" in dynamic conditions. Compositions of BP-PAC : OEDF, BP-PAC : OEDF : ATMP and BP-PAC : ATMP have been prepared. The data are presented in Table 2.

According to the data of table 2 shows that the prepared compositions are able to effectively suppress the processes of scale formation in environments with different initial corrosion activity, at the same time compositions of BP-PAC : OEDF : ATMP (maximum efficiency - 97.0 %) is much more effective than the composition of BP-PAC : OEDF and BP-PAC : ATMP (maximum efficiency - 95.0 - 96.0 % respectively). It should be noted that the preparation of composition with OEDF due to several complications: in the preparation of high concentrations of precipitate falls out.

Table 2

Study of inhibitory activity. Temperature 40 - 50° C

№	Inhibitor components	Concentration of inhibitor components, mg/l	Efficiency, %

Temperature 40 °C			
1	BP-PAK	0,5	87
		1,0	89
		1,5	90
		2,0	91
2	BP-PAK: OEDF	1,0 + 1,0	92
		1,5 + 1,5	94
		2,0 + 2,0	95
3	BP-PAK: ATMP	0,5 + 0,5	91
		1,0 + 1,0	93
		1,5 + 1,5	95
		2,0 + 2,0	96
4	BP-PAK: OEDF: ATMP	0,4 + 0,3 + 0,3	92
		0,8 + 0,6 + 0,6	94
		1,0 + 1,0 + 1,0	95
		1,6 + 1,2 + 1,2	97
Temperature 50 °C			
1	BP-PAK	0,5	86
		1,0	89
		1,5	89
		2,0	90
2	BP-PAK: OEDF	0,5 + 0,5	87
		1,0 + 1,0	90
		1,5 + 1,5	90
		2,0 + 2,0	91
3	BP-PAK : ATMP	0,5 + 0,5	88
		1,0 + 1,0	90
		1,5 + 1,5	91
		2,0 + 2,0	92
4	BP-PAK: OEDF: ATMP	0,4 + 0,3 + 0,3	90
		0,8 + 0,6 + 0,6	92
		1,0 + 1,0 + 1,0	93

		1,6 + 1,2 + 1,2	95

Further experiments to determine the efficiency of scale prevention were carried out in the laboratory of district boilers RK-1 (Nukus) and RK-2 (Sukmanay) of JSC "Kommunallik Issylik Oyi" of the Republic of Karakalpakstan. Laboratory comparison tests of antiscalant samples were carried out in the volume of 400 ml and steamed up to 200 ml. The evaporation temperature was 80 C. The results of the experiments are presented in Table 3.

Table 3

Comparative results of laboratory antiscalant testing

Name of samples	pH	Reagent type	Calcium hardness, mg/l	Total hardness, mg/l
Initial sample, RK-1 collector	9,80		770	910
Steamed sample of RK-1 collector	8,02	Reagent-free	890	1005
RK-1 sample + 2 g/m^3 reagent	9,05	Komperex-710	1020	1080
RK-1 sample + 4 g/m^3 reagent	9,00	Komperex-710	1050	1900
RK-1 sample + 2 g/m^3 reagent	9,10	BP-PAK : ATMP	950	1730
RK-1 sample + 4 g/m^3 reagent	9,08	BP-PAK : ATMP	1010	1750
Initial sample, collector RK-2	10,50		990	2060
Steamed sample of collector №47	7,00	Reagent-free	800	900
RK-2 sample + 2 g/m^3 reagent	7,01	Komperex-710	1200	1920
RK-2 sample + 4 g/m3 reagent	7,05	Komperex-710	1250	1940
RK-2 sample + 2 g/m^3 reagent	7,03	BP-PAK : ATMP	770	850
RK-2 sample + 4 g/m^3 reagent	7,07	BP-PAK : ATMP	1110	1690

As it can be seen from the data of the table, the reagent BP-PAK : ATMP at pH ≥9,5 - 10,0 of technological solutions and dosing of 2-4 g/m^3 effectively restrains sediment formation.

Conclusions. The analysis of literature data on synthesis and application of inhibitors of mineral salt deposits shows that numerous organic compounds of different composition and structure in compositions with oligomers and polymers containing carboxylic groups have been proposed as inhibitors of salt deposits. Inhibiting properties of -PO_3H_2 and -COOH containing organic compounds have been investigated. It has been experimentally proved that by preparing compositions in equimolecular relations using acrylic acid oligomer with MSDI -1, OEDF can obtain an inhibitor with highly effective inhibiting properties, the effectiveness of which meets the requirements of these regulations.

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