USE OF SULFAMIC ACID TO REMOVE CARBONATE DEPOSITS

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We study the use of sulfamic acid to remove scale deposits from the heat exchange equipment of stationary distillation-type desalination plants, in which from 5 to 15 tonnes of alkaline deposits may be generated. We determine the treatment technological parameters: maximal temperature 50°C, sulfamic acid concentration less than 10%. We study the influence of the depolarizer ions (Cu^{2+} and Fe^{3+}) on the corrosion rate of the structural materials and also the possibility of reducing the corrosion of the equipment with the aid of corrosion inhibitors: captax and PKU-3. A pilot-scale verification is made of the recommended technique for scale removal with the use of sulfamic acid.

The alkali deposits are usually removed from the heat-transfer surfaces of the evaporators and preheaters of distillation desalination plants (DDP) by a hydrochloric acid solution with corrosion inhibitor additives. The primary advantage of hydrochloric acid treatment is the high rate of dissolution of the alkaline deposits, and also the capability for partial dissolution of the hydroxide and oxide deposits. However, the high corrosivity of hydrochloric acid in relation to the construction materials of the DDP equipment and the serious difficulties that arise in storage and transportation (particularly by sea or highway transport) force us to seek more convenient and less hazardous reagents.

The most convenient reagent for scale removal in such cases is sulfamic acid. Its basic advantages lie in the fact that it is a crystalline substance that is safe in transportation and storage and can be conveyed by all forms of transport. Sulfamic acid has found use for the removal of deposits from marine desalination plants [1], milk plant equipment [2], and also industrial plants [3,4].

In recent years the question has been examined of the use of sulfamic acid for removing deposits from the heat transfer equipment of stationary DDPs, in which from 5 to 15 tonnes of alkaline deposits may be generated. Here the increased costs of sulfamic acid acquisition (in comparison, for example, with hydrochloric acid) will be compensated by the convenience of its storage, transportation, and usage.

We should note that the data on the regimes of acid treatment with the use of sulfamic acid are somewhat contradictory: some authors [4] propose that treatment be performed at elevated temperatures of the washing solution (from 50 to 80°C), others [3] recommend that the wash solution temperature not exceed 50°C. For the marine desalination plants it is recommended that treatment be terminated upon reduction of the acid mass fraction to 1% [1], which is irrational because of the increased reagent consumption.

Also contradictory are the data on the corrosivity of the solutions in relation to the construction materials. Thus, according to the data of [5], the corrosion rate of carbon steel in a sulfamic acid solution with mass fraction 3% at 25°C is 10 $mg/(m^2 \cdot hr)$, while according to the data of [6] the rate is 75 $g(m^2 \cdot hr)$.

Thus, it is practically impossible to select on the basis of the literature data the technological parameters for the conduct of acidic scale removal with sulfamic acid solutions in application to the stationary DDP.

We shall attempt to determine the basic treatment technological parameters. We determine the rates of scale dissolution in the sulfamic acid solution, the influence of the temperature of the acid solution on its hydrolysis, and we also determine the corrosion resistance of the primary construction materials that are used in the fabrication of stationary DDP.

The rate of scale dissolution by sulfamic acid was determined by the method described in [7]. The specimens were scale chips from the inner surfaces of the heat exchange pipes of DDP evaporators (Shevchenko). These scale chips were 95% (by mass) calcium carbonate. The washing solution of the specified concentration and

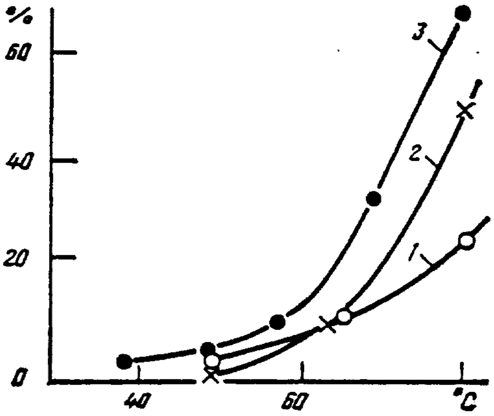

Fig. 2. Degree of sulfamic acid hydrolysis as a function of temperature with hydrolysis time six hours and acid concentration 50 (1), 100 (2), and 100 mg/*l* (3) from [3].

treatment technology is the corrosional aggressivity of the sulfaminic washing solution in relation to the construction materials of the DDP equipment.

We studied the corrosion of the construction materials that are most widely used in the fabrication of DDP heat-exchange equipment - brass LAMSh 77-2-0.05 (GOST [All-Union State Standard] 15527-70), carbon steel VSt.3sp (GOST 380-71), and the corrosion-resistant steel 12Kh18N10T (GOST 5632-72). The tests were made on a setup with rotating cylindrical specimens [8]. For the tests we used specimens, cut from commercially produced pipes of diameter 38 × 2 mm and height 10 mm. The solution flow velocity (1 m/sec) was modeled using the technique described in [9].

In the investigation of the proneness of the corrosion-resistant steel 12Kh18N10T to local corrosion the studies were made under static conditions in an autoclave, and the specimens were stressed welded rings of diameter 60 × 5 mm and height 10 mm [10].

To evaluate the influence of variable-valence metal ions on the corrosion of the materials, in several experiments we added to the sulfamic acid solution depolarizer-ions of divalent copper and trivalent iron, which under actual conditions of acid treatment enter the solution during dissolution of the scale deposits and corrosion products, and also in the process of corrosion of the construction materials. The concentration of the Cu^{2+} and Fe^{3+} that were introduced to the acid solution was selected with account for their maximal concentrations in the cleaning of DDP equipment.

The corrosion penetration rate was evaluated on the basis of the specimen mass loss. The error of the determination of the rate of corrosion penetration of the structural materials in the studies does not exceed ±25%.

It follows from the data of Table 1 that the corrosivity of the sulfamic acid solutions in relation to the carbon steel and brass depends on the acid concentration in the solution, the temperature, and the presence in the solution of the depolarizer-ions Fe^{3+} and Cu^{2+}. The corrosion of the austenitic steel 12Kh18N10T under the studied conditions is very slight, which agrees with the data presented in [6].

It is well known that the austenitic steel shows the highest tendency toward local corrosion under static conditions [11]. Therefore the tests of the welded ring specimens of steel 12Kh18N10T in the sulfamic acid solution with mass concentration 50 g/*l* were made under static conditions for 150 hr at 60°C. The tests showed that under these conditions the steel 12Kh18N10T did not have a tendency toward local corrosion.

The corrosion of the construction materials can be reduced with the aid of inhibitors [12]. We studied the influence of the commercially produced corrosion inhibitors captax and PKU-E on the corrosion of carbon steel and brass. The concentration of the inhibitors introduced to the sulfamic acid solution was chosen in accordance with their recommended protective concentration during their application in hydrochloric acid treatment to remove scale from the heat transfer equipment. The results of these tests are presented in Table 2.

Thus, the use of sulfamic acid together with the corrosion inhibitors captax or PKU-E significantly reduces the corrosive properties of the washing solution. However, in each specific case the selection of the corrosion inhibitor should be made with account for the peculiarities of acid treatment with the sulfamic acid solution: the composition of the scale (presence in the scale of Fe^{3+}, Cu^{2+}); the construction materials that are used in the fabrication of equipment and the concentration, temperature, and velocity of the washing solution. For practical

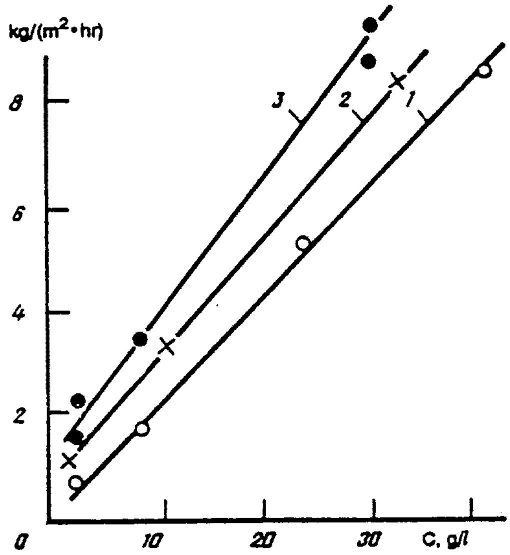

Fig. 1. Rate of carbonate scale dissolution versus sulfamic acid concentration at 20 (1), 40 (2) and 60°C (3).

temperature was circulated at a velocity of 1 m/sec through the cell with the scale specimen. At definite intervals of time we took samples, which were analyzed for their Ca^{2+}, Mg^{2+} content and acidity. The scale dissolution rate was calculated from the analysis results, and also from the specimen mass loss. The data obtained are shown in Fig. 1.

As we would expect, the scale dissolution rate increases with increase of the acid concentration and the temperature: with increase of the acid concentration by a factor of two the scale dissolution rate increases on the average by a factor of two, and with increase of the temperature by 10°C the dissolution rate increases by 1.1-1.2 times. These data indicate indirectly that the limiting stage of the dissolution process is the feeding of the reagent or the removal of the reaction products, i.e., the dissolution process is controlled by diffusion. Therefore carbonate scale dissolution must be performed with turbulent flow over the surface of the scale and, preferably, at elevated temperature of the washing solution.

However, the literature data [3] indicate that hydrolysis of the sulfamic acid takes place upon increase of the temperature >40°C. Hydrolysis takes place in two stages

$$NH_2SO_3H + H_2O \xrightarrow{t} NH_4SO_4H,$$

$$NH_4SO_4H + H_2O \xrightarrow{t} NH_4OH + H_2SO_4.$$

The accumulation of SO_4^{2-} in the washing solution, particularly in the boundary layer near the surface of the carbonate scale, may lead to the generation of the secondary sulfate scale $CaSO_4$, which can block reagent access to the scale that is being dissolved. Therefore we determined the kinetics of sulfamic acid hydrolysis as a function of temperature. The sulfamic acid solution with initial mass concentration 50 and 100 g/dm^3 was held at the specified temperature for six hours. The degree of sulfamic acid hydrolysis was determined on the basis of the amount of acid remaining in the solution.

The sulfamic acid determination technique was based on its reduction properties [3]

$$NH_2SO_3H + NaNO_2 \rightarrow NaHSO_4 + N_2 + H_2O.$$

The obtained data, shown in Fig. 2, agree quite well with the results of [3] and indicate that for prevention of the formation of secondary sulfate deposits the scale dissolution process should be conducted at a temperature not exceeding 50°C.

Another and no less important technological parameter that may also introduce corrections to the transfer surfaces after cleaning showed complete removal of the scale.

Sulfuric acid is added to the spent sulfamic acid solution in the amount necessary for binding of the dissolved calcium into calcium sulfate. After removal of the precipitate and addition of the new portion of sulfamic acid (usually up to 30% of the original amount) the solution can be reused for scale dissolution. This regeneration technology is described in considerable detail in [5].

These studies made it possible to determine the technological parameters for the conduct of acid cleaning of the heat transfer surfaces of DDP with sulfamic acid. The experimental-commercial removal of scale from the DDP confirmed the possibility and effectiveness of the use of sulfamic acid.

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Table 1

Corrosion of Construction Materials in Sulfamic Acid Solution with Agitation, Solution Velocity 1 m/sec for 24 hr

T, °C	Acid concentration, g/dm^3	Corrosion penetration rate, mm/year		
		brass LAMsh 77-2-0.05	carbon steel VSt3sp	corrosion-resistant steel 12Kh18N10T
25	10	0,48	3,98	0,03
25	30	1,22	6,17	0,03
25	50	5,77	38,78	0,03
50	30	6,57	21,21	0,03
25	30*	10,37	36,27	0,04

*Addition of depolarizer-ions at the rate of 0.45 g/dm^3 CU^{2+} and Fe^{3+}.

Table 2

Corrosion of Materials and Protective Action of Corrosion Inhibitors Captax and PKU-E in Sulfamic Acid Solution (30 g/*l*) at 50°C, Velocity 1 m/sec for 24 hr

Material	Depolarizer-ion mass concentration in solution, g/*l*	Corrosion inhibitor mass concentration, g/*l*		
		without inhibitor	captax; 3	PKU-3; 1
Carbon steel VSt3sp	—	21,21	$\frac{2,19}{89,67}$	$\frac{4,28}{79,77}$
Same	Cu^{2+} 0,45 Fe^{3+} 0,45	32,68	$\frac{1,72}{94,74}$	$\frac{11,98}{63,37}$
Brass LAMsh 77-2-0.05	Cu^{2+} 0,45 Fe^{3+} 0,45	10,17	$\frac{0,23}{97,73}$	$\frac{9,15}{10,03}$
Same	—	6,57	$\frac{0,28}{96,00}$	$\frac{0,59}{91,02}$

Note. Numerator) corrosion penetration rate, mm/yr, denominator) protective action, %.

verification of the results of the laboratory studies we performed experimental-commercial treatment of the heat transfer surface to remove the scale that is formed during evaporation of Caspian Sea water.

The scale was"deposited" on the heat exchange tubes of an evaporator with heat transfer area F = 6.5 m^2. The sea water evaporation temperature was 100°C. The scale thickness after seven days of evaporator operation varied from 03.5 mm at the entrance ends to 0.65 mm at the exit ends of the heat transfer tubes. It was found by chemical analysis that the scale consists of calcium carbonate (85% mass fraction) and magnesium hydroxide (15%).

The treatment was performed using a sulfamic acid solution with initial mass concentration of the acid 7 g/*l*. The washing solution was prepared directly in the loop being cleaned. During treatment the washing solution, heated to 25-28°C, circulated in the loop being cleaned with velocity 1.2 m/sec. The treatment continued for about two hours, and the average rate of scale dissolution after the first hour of cleaning, determined from the results of chemical analysis of the samples taken during cleaning, was 0.42 kg/(m^2·hr). Visual examination of the heat