Original Article

RESEARCH PHYSICO-CHEMICAL PROPERTIES OF WASTEWATER AND MECHANICAL IMPURITIES

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DOI: 10.47750/pnr.2022.13.S06.493

Abstract

The article presents the results of a study on the study of the physical and chemical properties of circulating industrial waters and mechanical impurities of their composition. In order to reduce the hardness of circulating water, various reagents were used, i.e. a mixture of Na_3PO_4+sulfonal; Na_2PO_4; Na_2PO_4+sulfonal; $Ca(OH)_2$ are unsuitable for reducing the hardness of circulating waters (Fig. 3.3), because the reduction in water hardness is not achieved to the limit using these reagents. To reduce the hardness of circulating industrial waters, the optimal reagent is recommended.

Key words: process water, mixture, hardness, softeners, suspension, reagent, filter, mechanical impurities.

INTRODUCTION

Solid particles of mechanical impurities in the composition of industrial waters of an oil refinery are considered to be a colloidal dispersed system, their sizes range from $0{,}25\cdot10^{-6}$-$50\cdot10^{-6}$ m. Such particles no longer settle for any duration of settling of the dispersed system. Colloidal particles, making a Brownian motion, can approach so much when colliding that van der Waals forces begin to manifest themselves between them. As a result, the particles begin to stick together, the particles of the dispersed phase become larger. In this case, for the most part, such large flakes are formed (flocculation process) that they precipitate (sedimentation process) [1-5].

Mechanical impurities consist mainly of highly dispersed particles of sand, clay and other formation hard rocks suspended in them, salt crystals. Solid particles not only stabilize the water emulsion, they reduce the performance of apparatus and pipelines, as a result of salt and sedimentation, increase fuel consumption due to a decrease in the heat transfer coefficient in heat exchangers, but also create conditions for the localization of corrosion processes, and sometimes they contribute to erosive wear of parts of centrifugal pumps , fittings, fittings and valves. Mechanical impurities form with process water also a dispersed system - "liquid-solid", the separation of which is carried out by settling in separators and settling tanks in the fields. [6-11].

LITERARY RIVIEW

Purification of circulating waters of an oil refinery is an urgent problem. Based on the above, the concentrations of mechanical impurities and their dispersity were determined by the sieve method. The traditional method for controlling the homogeneity and dispersion of bulk and powder materials is sieve analysis. This type of analysis is regulated by GOST 6613-86, GOST 3584-5. The essence of the method lies in the fact that the powder is sifted through sieves with different mesh sizes, installed sequentially one above the other. The sieves with the largest mesh are located at the top, then the mesh size of the sieve is successively reduced. Sieve analysis makes it possible to determine the particle size, separate particles of different sizes from each other, and calculate the quantitative ratio of particles of different dispersity [12–17]. The results of the research are shown in Table 1.

Table 1 Disperse composition of solid particles of mechanical impurities

Kuimazar waters

Particle size, mkm	<0,25	0,5-0,25	0,5-1,0	1,0-2,0	2,0-3,0	3,0-5,0	5,0-10	10-20	20-50	Σ
B %	24,3	16,9	14,4	11,6	9,4	7,3	6,8	5,4	3,9	100

Table 1 shows that the concentration of solid particles of mechanical impurities with a size of 20-50 microns in the composition of circulating waters is 3.9%, 10-20 microns particles 5.4%, 5-10 microns particles 6.8%, further size reduction solid particles of mechanical impurities up to 0.25 mkm, its concentration increases to 24.3% i.e. with a decrease in the size of solid particles, their concentration gradually increases. The results of the obtained data are also illustrated in Fig.1.

Fig.1. Concentration of solid particles of mechanical impurities in the composition of circulating waters

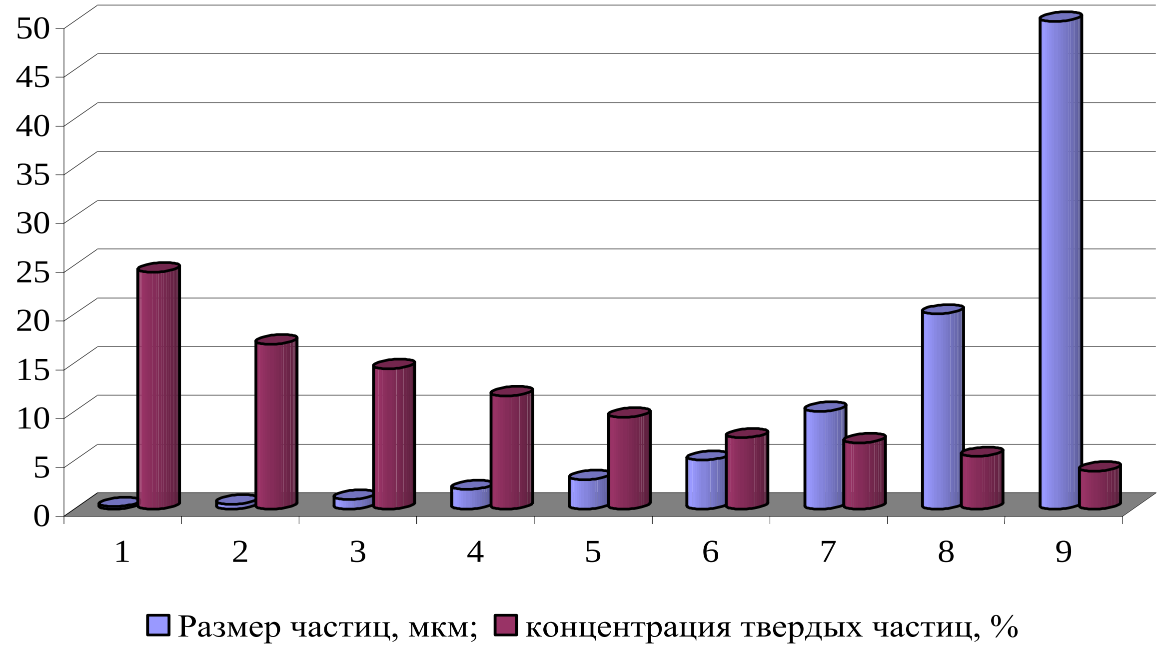


Figure 1 also shows that in the composition of the circulating waters of an oil refinery, fine particles <0.25 μm make up 24.3%. Finely dispersed solid particles practically do not precipitate, due to their imperceptible resistance to the medium, therefore, in order to intensify the purification process of solid fine particles, it is advisable to coagulate or enlarge them.

During the purification of circulating waters in the gravitational field, mechanical coagulation of solid particles is also observed. When studying the coagulation of solid particles in a gravitational field, it was observed that coarse solid particles settle faster than fine particles; when settling, coarse particles adhere to fine particles, and large flakes appear. The results are shown in table.2.

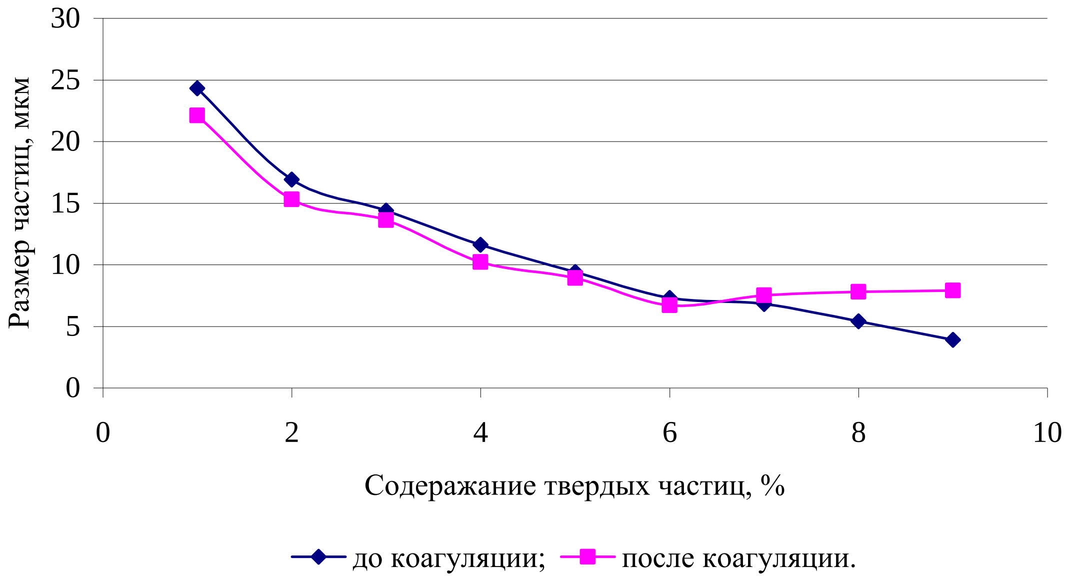
Table 2 Sticking together of solid particles in a gravitational field

Particle size, µm	<0,25	0,5-0,25	0,5-1,0	1,0-2,0	2,0-3,0	3,0-5,0	5,0-10	10-20	20-50	Σ
	Down the drain									
%	24,3	16,9	14,4	11,6	9,4	7,3	6,8	5,4	3,9	100
	After settling									
%	22,1	15,3	13,6	10,2	8,92	6,7	7,5	7,78	7,9	100

Results and Discussion

Table 2 shows that the amount of fine solid particles (from <0.25 µm to 3.0-5.0 µm) of mechanical impurities decreases from 22.1% to 6.7%, the amount of coarse particles (5.0- 10÷20-50 µm) increases from 7.9% to 7.9%. The results of the conducted studies are also illustrated in Figure 2.3.

Fig.2. Enlargement of solid particles of mechanical impurities before and after sedimentation



It can be seen from Fig. 2 that the content of fine particles up to 25 µm is 24.3%, after settling, their concentration decreases to 22.1%, and the content of 0.5-0.25 µm particles is 16.9%, after settling its content is reduced to 15.3%. This is explained by the fact that finely dispersed solid particles in the gravitational field do not really stick together with each other, due to the insufficient turbulent mode of motion inside the apparatus. Finely dispersed solid particles practically do not precipitate, due to their imperceptible resistance to the medium. A sufficient turbulent regime of motion within the apparatus results in sufficient collision of the solid particles so that the solid particles adhere to each other, while their mass increases and also their settling rate is accelerated. In order to solve this problem, we have installed a filter (Fig. 2.1), designed for deep purification of process water from fine solid particles of mechanical impurities.

Natural water contains various organic and inorganic substances. They can be divided: Basic ions: cations: Ca^{2}+, Na+, K+, Mg^{2}+, sometimes Fe^{2}+, Mn^{2}+, Fe^{3}+); anions: SO_3^{2-}, $HSiO_3^{-}$, $S_2O_3^{2-}$, (sometimes , $HSiO^{3}$-,).

Dissolved gases: nitrogen, hydrogen sulfide, carbon dioxide, oxygen, methane. Nutrients: phosphorus, silicon, iron, various forms of nitrogen (ammonia, nitrite, nitrate). Trace elements: elements that are contained in water in amounts less than 10-3%. Organic substances: These can be various kinds of plant and animal organisms, microorganisms and products of their interaction with the environment [18-21].

The volume fraction of liquid in suspension was determined [10]:

$$\varepsilon = \frac{V_{ж}}{V_{ж} + V_{тв}}, \qquad (1)$$

where $V_{ж}$- volume of liquid in suspension; $V_{тв}$- volume of solids in suspension.

During sedimentation, the suspension is divided into two layers - sludge and clarified liquid (*h*-height of the clarified liquid). At the settling surface *F* m^2, the volume of the clarified liquid is *h*F m^3 [10]:

$$V = \frac{hF}{\tau} м^3 / c, \qquad (2)$$

where *h* is the height of the liquid layer, m; τ - settling time, sec.

Required settling surface [10]:

$$F = \frac{V}{\omega_0} м^2 \qquad (3)$$

The volume *V* of the clarified liquid at its density $\rho_ж$ l kg/m3 is [10]:

$$V = \frac{G_{ж}}{\rho_{ж}},$$

then we get:

$$F = \frac{G_{ж}}{\rho_{ж}\omega_0} \qquad (4)$$

where $G_ж$ is the liquid volume, м^3; $\rho_ж$ – liquid density, kg/m^3; ω_0 – speed of free settling of the smallest solid particles, m/s.

Accordingly, the sedimentation surface or the cross-sectional area of the sump was determined by the equation [10]:

$$F = \frac{1{,}3G_c}{\rho_{ж}\omega_0}(1-\beta) м^2, \qquad (5)$$

where G_c is the volume of dry matter, m^2; β is the ratio of the weight content of dry matter in suspension and sediment $\beta = \frac{x_1}{x_2}$ (concentration of the solid phase in water x1 = 6.006%, concentration of the thickened suspension x2 = 15.1%).

The settling rate of solid particles was calculated:

$$\omega_o \tau = h. \qquad (6)$$

The capacity of the settling tank for the thickened suspension was determined [10]:

$$G_{\text{сг.}} \frac{G_{\text{тв}}}{x_2}. \qquad (7)$$

Accordingly, the capacity of the sump for clarified liquid will be [10]:

$$G_{\text{ж}} = G_{\text{с}} - G_{\text{сг.}}. \qquad (8)$$

The sedimentation diameter of solid particles was determined from the data of sedimentometric analysis:

$$d_s = \sqrt{18 \cdot 10^7}\ \mu H / (\rho_1 - \rho_2)\, g\tau, \qquad (9)$$

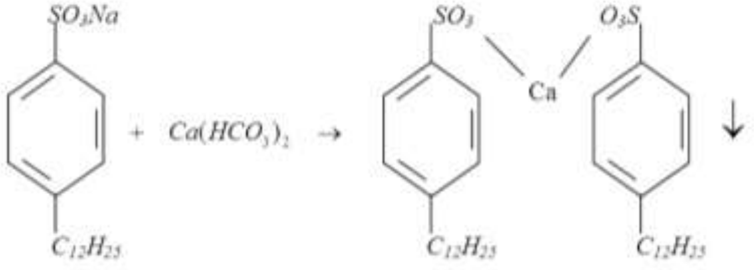
where μ is the dynamic viscosity of the medium, Pa*s; ρ_1 is the density of solid particles, g/cm3; ρ_2 – medium density, g/sm^3; H is the height of particle settling, cm; g is the acceleration of gravity, m/s^2; τ - settling time, s.

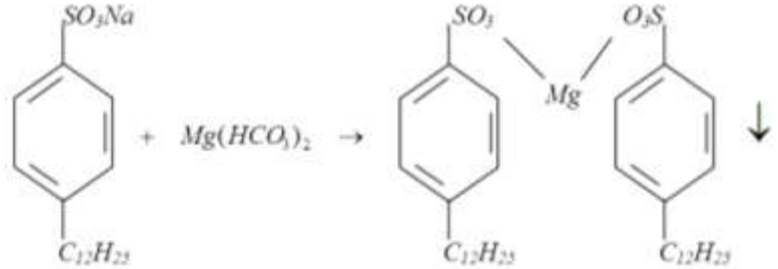
To determine the average concentration of solid fine and coarse particles of mechanical impurities in the composition of the circulating technical waters of an oil refinery, we conducted a series of experiments. All experiments were carried out at ambient temperatures. During the experiments, 100 ml of polluted water (brought from the Kuymazar lake water) was taken for filtering, after which the paper filter was dried in an oven of the brand - SNOL 1,6.2,5.1 / 11-I2 for an hour at a temperature of 110 the filter was cooled in a desiccator for 30 min, then weighed with an error of 0.0002 g using an electronic balance brand - FA1004G. Calculations for the determination of solid particles of mechanical impurities were calculated as the arithmetic mean of the results of ten parallel experiments. The conducted experiments show that the total concentration of mechanical impurities in the composition of the Kuymazar waters averaged 6.006%.

The following reagents were used to reduce the hardness of circulating waters: a mixture of Na_3PO_4 + sulfonal; Na_2PO_4; Na_2PO_4+sulfonal; $Ca(OH)_2$; 0.2% Na_3PO_4. When using such reagents, the following chemical reactions occur:

$$Ca(HCO_3)_2 + Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 3Na^+. \qquad (10)$$

$$Mg(HCO_3)_2 + Na_3PO_4 \rightarrow Mg(PO_4)_2 \downarrow + 3Na^+. \qquad (11)$$





$$Na_2HPO_4 + Ca(HCO_3)_2 \rightarrow Ca_3(PO_4)_2 \downarrow + 2Na^+. \tag{12}$$

$$Na_2HPO_4 + Mg(HCO_3)_2 \rightarrow Mg_3(PO_4)_2 \downarrow + 2Na^+. \tag{13}$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O. \tag{14}$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2Mg(OH)_2 \downarrow + 2CaCO_3 \downarrow + 2H_2O. \tag{15}$$

$$Na_3PO_4 + Ca(HCO_3)_2 \rightarrow Ca(PO_4)_2 \downarrow + 3Na^+. \tag{16}$$

$$Na_3PO_4 + Mg(HCO_3)_2 \rightarrow Mg(PO_4)_2 \downarrow + 3Na^+. \tag{17}$$

The mass fraction of mechanical impurities was calculated using the known formula, %:

$$M = [(m_1 - m_2) / m_3] \cdot 100,$$

where, where, m1 is the mass of the cup with the filter after filtration, *g*; m_2 is the mass of a cup with a clean filter, *g*; m_3 is the weight of the sample of water, *g*.

Kuymazar waters were used for softening and purification of circulating from mechanical impurities. Each experiment was carried out at an initial hardness of the studied water of 47 mg-eq/l. The results of the conducted studies on the softening of the investigated water are shown in Tables 3-7. is the mass of the cup with the filter after filtration, g; m2 is the mass of a cup with a clean filter, g; m3 is the weight of the sample of water, g.

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Table 3 The results of reducing the hardness of the Kuymazar waters using Na_3PO_4 + sulfonal reagents (water hardness 47 mg-eq / l)

№	Mass of the investigated water, ml	Reagent concentration (Na_3PO_4 + sulfonic acid), mg	Hardness of water, mg-eq./l
1	10	0,01	30
2	10	0,03	20
3	10	0,04	15
4	10	0,05	6

5	10	0,07	5
6	10	0,09	3
7	10	0,1	3

From Table 3 it can be seen that when adding the reagent Na_3PO_4 + sulfonal 0.01 mg per 10 ml of water, its hardness was 30 meq/l, and when 0.03 mg was added, the water hardness decreased to 20 meq/l, further addition of the reagent 0.04÷0.07 mg, the hardness of the test water gradually decreases within 15÷5 meq/l, and when the reagent 0.09 mg is added to 0.1 mg, this indicator remains unchanged, i.e. . was 3 mg-eq./L. In the course of the experiments, to reduce the hardness of this water, experiments were also carried out with the Na_2PO_4 reagent (Table 4).

Table 4 The results of reducing the hardness of Kuymazar waters using Na_2PO_4 reagents (water hardness 47 mg-eq / l)

№	Mass of the investigated water, ml	Reagent concentration (Na_2PO_4), mg	Hardness of water, mg-eq./l
1	10	0,01	31
2	10	0,03	24
3	10	0,05	22
4	10	0,07	21
5	10	0,08	20
6	10	0,1	18
7	10	0,2	18

When conducting wholesales to reduce water hardness, the Na_2PO_4 reagent was added in the range of 0.01÷0.2 mg per 10 ml of the water under study. The results show that the water hardness decreased from 31 meq/l to 18 meq/l. The experiments were also carried out with the reagent Na_2PO_4+sulfonal (Table 5).

Table 5 The results of reducing the hardness of the Kuymazar waters using Na_2PO_4 + sulfonal reagents (water hardness 47 mg-eq / l)

№	Mass of the investigated water, ml	Reagent concentration (Na_2PO_4 + sulfonic acid), mg	Hardness of water, mg-eq./l
1	10	0,01	22
2	10	0,03	16
3	10	0,05	15
4	10	0,07	14

5	10	0,08	14
6	10	0,1	14
7	10	0,2	14

In order to reduce the hardness of the Kuymazar waters, the Na_2PO_4 + sulfonal reagent was added in the range of 0.01÷0.2 mg per 10 ml of the studied water, as a result, the water hardness decreased from 22 mg-eq./l to 14 mg-eq./l, when adding a reagent from 0.07 to 0.2 mg, the water hardness reading remains unchanged, i.e. this figure was 14 mg-eq./l. We also carried out a series of experiments to reduce the hardness of water with the reagent $Ca(OH)_2$.

Table 6 The results of reducing the hardness of the Kuymazar waters with the help of reagents $Ca(OH)_2$ (water hardness 47 mg-eq / l)

№	Mass of the investigated water, ml	$Ca(OH)_2$ reagent concentration, mg	Hardness of water, mg-eq./l
1	10	0,01	35
2	10	0,03	40
3	10	0,05	42
4	10	0,07	45
5	10	0,08	50
6	10	0,1	50
7	10	0,2	50

From Table 6 it can be seen that with the addition of $Ca(OH)_2$ reagent 0.01 mg per 10 ml of water, the hardness was 35 mg-equiv./L, with the addition of 0.03 mg, the water hardness was 40 mg-equiv./L, and with the addition of 0.05 mg, the water hardness rose to 42 mg-eq./l, further addition of the reagent in the range of 0.08÷0.2 mg, the water hardness rose to 50 mg-eq./l and remains unchanged. This is due to the fact that due to the content of significant amounts of calcium salts ($Ca^{\cdot\cdot}$ ions) lead to an increase in water hardness.

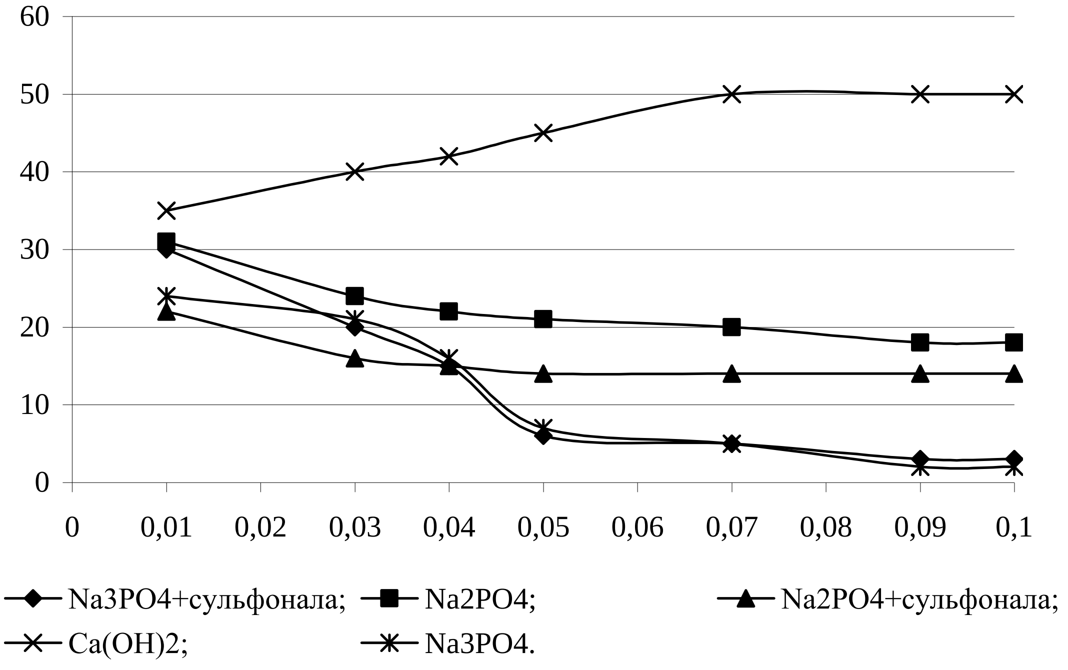
Таблица 7 The results of reducing the hardness of the Kuymazar waters using Na_3PO_4 reagents (water hardness 47 mg-eq / l)

№	Mass of the investigated water, ml	Reagent concentration (Na_3PO_4), mg	Hardness of water, mg-eq./l
1	10	0,01	24
2	10	0,03	21
3	10	0,05	16
4	10	0,07	7

5	10	0,08	5
6	10	0,1	2
7	10	0,2	2

Table 7 shows that when the Na_3PO_4 reagent 0.01 mg is added, the hardness of water decreases to 24 meq/l, and when the reagent 0.03 mg is added, its hardness decreases to 21 meq/l. Further addition of the reagent from 0.05 to 0.08 mg water hardness is reduced from 16 meq/l to 5 meq/l. When adding a reagent of 0.1 and 0.2 mg, the water hardness decreases to 2 meq/l and this indicator did not change.

Fig.3. The results of reducing the hardness of circulating waters with various reagents



CONCLUSION

Thus, the studies conducted to reduce the hardness of the circulating waters of an oil refinery show that the reagents are: a mixture of Na_3PO_4 + sulfonal; Na_2PO_4; Na_2PO_4+sulfonal; $Ca(OH)_2$ are unsuitable for reducing the hardness of circulating waters (Fig. 3.3), because the reduction in water hardness is not achieved to the limit using these reagents. To reduce the hardness of circulating technical waters, it is advisable to use a 0.2% Na_3PO_4 reagent.

For the correct use of circulating water, in addition to softening, the operating and design parameters of the installation also affect. For the purpose of preliminary purification of circulating water from coarse particles of mechanical impurities, a laboratory cylindrical settling tank was used, which, coarse solid particles settle in a gravitational field in a laminar mode. The geometric dimensions of the laboratory sump are: height - 0.2 m; length 0.4 m; width - 0.3 m, i.e. the installation volume is 0.024 m3/h.

Thus, the studied water is a mixture with finely dispersed solid particles <0.25÷50 μm and a high hardness of 47 mg-eq/l. Finely dispersed solid particles with an insufficient turbulent mode of motion inside the apparatus do not adhere very well to each other, and practically do not settle due to imperceptible resistance on the medium. Industrial water is considered to be a colloidal dispersed system, in its composition the size of solid particles ranges from 0.25□10-6-50□10-6 m, fine particles do not settle for any duration of settling. To solve this problem, it is advisable to add a filter apparatus to the technological scheme.

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