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RESULTS OF HARDNESS REDUCTION IN TECHNICAL WATER

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Abstract: The paper presents the results of Mubarek water hardness reduction using Na_3PO_4+sulfanol (water hardness 40 mg-eq/l), Na_2HPO_4 reagent, as well as the results of Mubarek water hardness reduction using Na_2HPO_4 + sulfanol, $Ca(OH)_2$ reagent. The research on reducing the hardness of recycled water of the oil refinery showed that the reagents Na_3PO_4 + sulfanol; Na_2HPO_4; Na_2HPO_4+sulfanol; $Ca(OH)_2$ are considered unsuitable for reducing the hardness of recycled water, as these reagents did not reduce water hardness indicators to the norm. To reduce the hardness of recycled water of industrial enterprises it is recommended to use Na_3PO_4 reagent at a concentration of 0.15 %.

Keywords: industrial water, water supply, hardness, reagent, physical and chemical treatment.

Аннотация: В статье представлены результаты снижения жесткости воды в Мубареке с использованием Na3PO4+сульфанола (жесткость воды 40 мг-экв/л), реагента Na2HPO4, а также результаты снижения жесткости воды в Мубареке с использованием Na2HPO4 + сульфанола, реагента Ca(OH)2. Проведенные исследования по снижению жесткости оборотной воды нефтеперерабатывающего завода показали, что реагенты Na3PO4 + сульфанол; Na2HPO4; Na2HPO4+сульфанол; Ca(OH)2 считаются непригодными для снижения жесткости оборотной воды, так как эти реагенты не снижали показатели жесткости воды до нормы. Для снижения жесткости оборотной воды промышленных предприятий рекомендуется использовать реагент Na3PO4 в концентрации 0,15 %.

Ключевые слова: промышленная вода, водоснабжение, жесткость, реагент, физико-химическая обработка.

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Annotatsiya: hujjatda Na3PO4+sulfanol (suvning qattiqligi 40 mg-eq/l), Na2HPO4 reaktivi yordamida muborak suvining qattiqligini kamaytirish natijalari, shuningdek, Na2HPO4 + sulfanol, Ca(OH)2 reaktivi yordamida muborak suvining qattiqligini kamaytirish natijalari keltirilgan. Neftni qayta ishlash zavodining qayta ishlangan suvining qattiqligini kamaytirish bo'yicha olib borilgan tadqiqotlar shuni ko'rsatdiki, Na3PO4 + sulfanol; Na2HPO4; Na2HPO4+sulfanol; Ca(OH)2 reagentlari qayta ishlangan suvning qattiqligini kamaytirish uchun yaroqsiz hisoblanadi, chunki bu reagentlar suvning qattiqlik ko'rsatkichlarini me'yorga kamaytirmagan. Sanoat korxonalarining qayta ishlangan suvining qattiqligini kamaytirish uchun Na3PO4 reaktividan 0,15% konsentratsiyada foydalanish tavsiya etiladi.

Kalit so'zlar: sanoat suvi, suv ta'minoti, qattiqlik, reaktiv, fizik va kimyoviy tozalash.

Introduction

Water hardness is the property of water to contain calcium Ca^{2+} and magnesium Mg^{2+} ions. There are two types of water hardness: non-carbonate hardness (permanent hardness) - caused by dissolution of calcium and magnesium sulphates in water; carbonate hardness (temporary hardness) - caused by dissolution of calcium and magnesium bicarbonates in water. The total hardness of water is equal to the sum of these hardnesses. Total hardness is measured by the sum of milligrams of calcium and magnesium ion equivalents in 1 litre of water. Water with a hardness of 1-1.5 mg eq/l is very soft, less than 1.5-3 mg eq/l is soft, with a hardness of 3-6 mg eq/l is medium, 6-10 mg eq/l is medium hardness, and with a hardness greater than 10 mg eq/l is very hard. The hardness of natural water varies, the hardness of river and lake water is 0.1-0.2 mg eq/l (Taiga and tundra) and the hardness of groundwater, sea and ocean water is 80-100 mg eq/l. Water hardness causes deposits to settle on the walls of steam boilers. In central water supply, the hardness of the water mainly consumed is allowed up to 7 mg eq/l. In case of high water hardness, water softening methods are used [1].

Water is used in the processes of nature, as well as in industry, in the production of raw materials, as a source of energy, for cooling and heating, and in many other sectors. Water is also important in human life, and not only for living organisms. Water has a qualitative and transparent form, is formed as a result of natural processes without the influence of the external environment. Nowadays, the increase in the number of settlements in our country leads to the rapid development of technology. Opening of large and small industrial enterprises increases their demand for water. Discharge of wastes into water by man, wasting more water than his own needs leads to decrease in water consumption. Factors leading to water

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loss: human waste dumping into water, harmful substances emitted by industrial enterprises affect the environment. Even a tiny bit of oil extracted from a river pollutes the water. Their release of various bacteria leads to the destruction of water bodies. Nowadays, we use modern equipment to purify water from contaminants. When water is contaminated with various substances, we have to purify it using technological methods. An example of natural water purification is the presence of below ground green weeds and fungi in water. In order to protect water bodies, it is necessary to treat them thoroughly before discharging water into the water body. In addition, industrial wastewater is highly toxic and rich in chemicals. Therefore, it is advisable to apply a closed-loop system when using wastewater in production. Wastewater contains a large number of pollutants. One of them is bacteria. There are many ways to purify water. The first one is the reduction method, the second is destructive. In the reductive method, valuable substances are extracted from wastewater and sent for recycling. In the destructive method, water is decomposed using oxidation or recovery methods from pollutants. When constructing new facilities, the amount of wastewater in sewage treatment plants must be properly accounted for in the first place. In wastewater treatment plants, wastewater is re-treated, neytralised and the sludge produced from it is disposed of. The treated wastewater is discharged into water bodies and used for irrigation. Large chemical plants use several million cubic metres of clean water per year [2].

At gas production enterprises, wastewater is not amenable to modern treatment methods due to high salt content, partial formation, natural origin and diversity of mineral and organic substances. Especially toxic are waste waters of gas fields with hydrogen sulphide, containing large amounts of dissolved hydrogen sulphide, hydrosulphide and sulphide ions. Decontamination of such waters should be carried out by underground disposal. Gas processing enterprises are characterised by a variety of chemical composition and physical properties of industrial wastewater. The most toxic are considered to be the waters of plants processing hydrogen sulphide-containing gases. Together with gas and hydrocarbon condensate, the plants receive a certain part of mineralised formation water, which is not discharged from production at gas fields. As a result, plant water has a high salt content and is additionally contaminated with a wide range of mineral and organic reagents used in gas processing technology. Such water cannot be effectively treated and must be buried underground [3].

The following physical parameters are often used in wastewater characterisation: colour, odour, nature and amount of solids, cooling rate, temperature, density, flow characteristics, mixing (horizontal and vertical), diffusion rate. In addition, hydrogen ion concentration (PH), salt content, dissolved

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oxygen content, BOD, nitrate content, phosphate content, metal content (copper, lead, iron, zinc, nickel, cadmium, mercury), petroleum products, organic compounds (pesticides, fertilisers, detergents) and carbon content need to be determined [4].

In this regard, the problem of industrial wastewater management will be of great importance to researchers. Researchers believe that wastewater in the oil and gas industry is the term used to refer to wastewater released as a by-product of crude oil and gas exploration. The produced water from oil and gas drilling is one of the largest waste streams. It can be salt water that has accumulated in the underground layers where wastewater enters during the oil and gas extraction process. To meet disposal standards, the wastewater must be treated. Wastewater varies depending on the process used and can contain large amounts of hazardous organic and inorganic compounds, dissolved gases, heavy metals and naturally occurring radioactive materials [5].

In the process of water purification from colloidal particles sometimes it is necessary to apply complex methods. The choice of method depends on the state of the particle - colloidal, molecular or dissociated ionic. The following physico-chemical methods are used to remove colloidal particles - flotation, coagulation and flocculation to remove the kinetic stability of colloidal particles. Physico-chemical methods are also used to remove dissolved particles. Different types of sorbents, aeration-desorption, extraction, distillation and membrane methods are used to purify particles in molecular state. Ion exchange, reverse (reverse) osmosis and magnetic water treatment are effective for removing ions from dissociated substances [6].

Mechanical mixtures consist mainly of undissolved sand, clay, other solid particles and salt crystals with a high degree of dispersibility. Solid particles not only destabilise the water emulsion, reduce the efficiency of equipment and pipelines due to the formation of salts and sludge, increase fuel consumption due to reduced heat exchange coefficient in heat exchange equipment, formation of foci of corrosion processes, and sometimes centrifugal pumps, spigots, valves and seals lead to erosive destruction of valves. Mechanical mixtures form a "liquid-solid" system dispersed by process water, and the separation process is carried out in separators and sumps available at mines [7].

Heat treatment - boiling, when water is heated, microorganisms are killed by high temperatures. Activated clay is rich in nitrogen, phosphorus and trace elements (copper, molybdenum, zinc). After heat treatment it can be used as a fertiliser. However, due to the presence of heavy metal salts, possible negative consequences of its use must be taken into account. Obtaining heavy metal ions

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and other harmful substances from wastewater ensures a harmless biomass that can be utilised. As a feed additive or fertiliser. If large amounts of sewage sludge containing heavy metal salts are generated, it is recommended to incinerate the sludge. In Germany, a method of producing substitutes for oil and coal based on activated clay has been proposed. According to calculations, the amount of heat produced by burning 350.000 tonnes of activated clay is equal to the amount produced by burning 350.000 barrels of oil and 175.000 tonnes of coal. The search for other ways to utilise sedimentary and active clays from wastewater treatment is ongoing [8].

Membrane treatment - water is fed into a special sieve, which passes only water molecules under pressure. From the point of view of environmental safety, membrane technologies of wastewater treatment are preferable to classical methods. Treated water reserves can be returned to rivers and reservoirs and used for artificial fish breeding, and treated "grey" water can be used for the needs of urban infrastructure (grass watering, road cleaning, fire extinguishing, etc.). The membrane module separates the clay mixture and is an alternative to the active clay sedimentation method widely used in secondary sedimentation tanks used in conventional biological treatment systems. The effluent solution contains acceptable COD (chemical oxygen demand) and BOD (biochemical oxygen demand) values, and bacteria and viruses are destroyed to a maximum of 99.9 %. Membrane-based wastewater treatment methods solve a number of water treatment problems, including: desalination of mine water; treatment of heavy metal electroplating effluents; treatment of hydrometallurgical wastewater; treatment of wash effluents; wastewater treatment; and treatment of liquid radioactive waste [9].

Flotation is a process of separation of suspended and emulsified pollutants from water into a frothy layer as a result of adhesion to gas bubbles supplied from below into the liquid to be treated. The process of treating industrial wastewater including surfactants, oil, petroleum products, oils, fibrous materials by flotation involves the formation of particle-bubble complexes. It is the treated liquid, which assumes floating of complexes and removal of the formed foam layer from the surface. The particle in it can be pressed against the surface of the gas bubble only if the particle is not wetted by the liquid or is only weakly wetted [10].

Ion exchange is the process of interaction between a solution and a solid phase that has the ability to exchange its own ions for other ions in solution. The substances that make up the solid phase are called ion exchangers, those that can absorb positive ions from electrolyte solutions are called cation exchangers and negative ions are called anion exchangers [11].

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Mechanical methods of water treatment are widely used in industrial ecology at the initial stage of treatment of polluted wastewater from suspended particles and mechanical impurities. Various designs of gravity, inertial and centrifugal apparatuses allow their selection depending on the volume of particles to be treated, productivity and wastewater The development and selection of effective methods and technical means is one of the main tasks of environmental engineers. Correct justification of the necessary type of apparatus increases the efficiency of water treatment, which allows reducing the number of apparatuses in a multi-stage water treatment system to standard values. The present instruction on stopping water in hydrocyclone is a technique of experimental study of particle cleaning process, processing of results of which allows to estimate the efficiency of water treatment in hydrocyclone, as well as to determine its technological level [12].

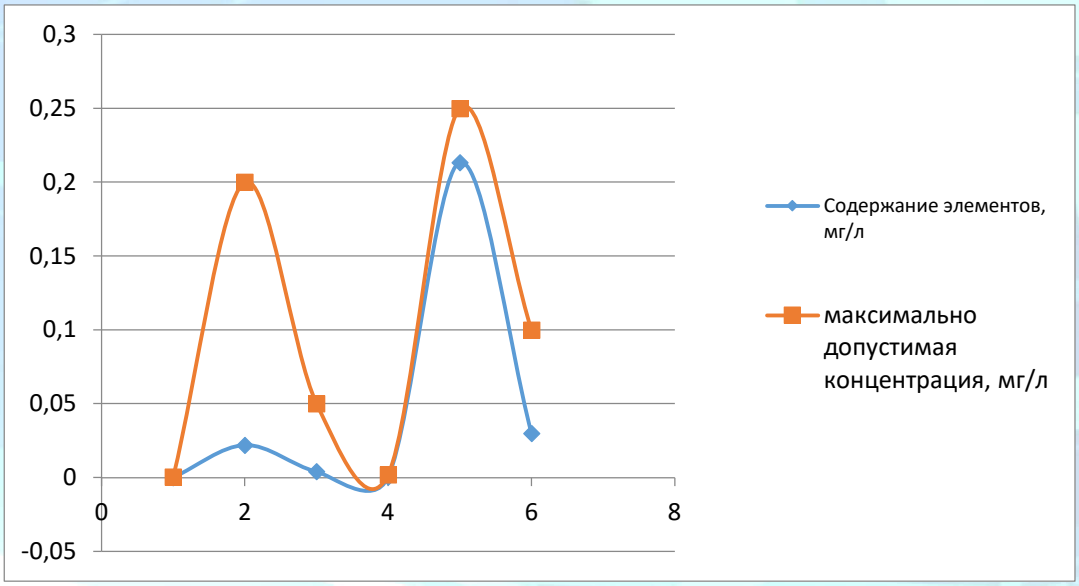
Centrifugation and hydrocyclisation. It is based on the use of centrifugal forces to separate pollutants and water. The centrifugal field method of wastewater treatment has significant advantages over sedimentation, which include the high permeability of hydrocyclones and centrifuges. Centrifuges and hydrocyclones are used to separate mineral, organic and mechanical impurities from wastewater [13].

Physical and chemical methods of purification: Coagulation is the process of enlargement of colloidal particles in the liquid due to electrostatic forces of intermolecular interaction. Coagulation results in the formation of aggregates - larger (secondary) particles consisting of a small (primary) cluster. Primary particles in such aggregates are bound directly by intermolecular interaction forces or through a layer of surrounding (dispersive) medium. Coagulation is accompanied by a gradual increase in particle size and a decrease in their total number in the volume of the dispersion medium (in our case liquid). One of the types of coagulation is flocculation, in which small suspended particles under the influence of substances with special additives (flocculants) form flocculation clusters with loose intensive sediment. Various mineral coagulants are used for industrial wastewater treatment [14].

Methods and Materials

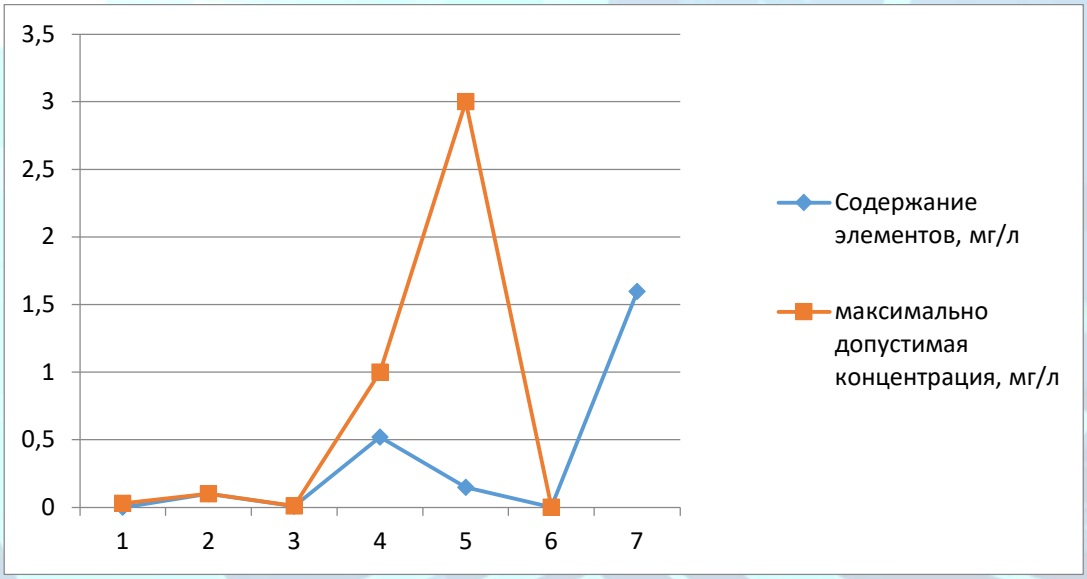
Before treatment of recycled water of oil refinery from mechanical impurities and its softening, elemental composition of water from Mubarek GCC was studied by conducting researches together with specialists of the Institute of Geology and Hydro-mineral Resources ‘Gydrochym’. The obtained results are presented in Tables 2.1 and 2.2.

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Pic.1. Analysis of elements in the composition of Muborak water

The amount of Hg in Muborak water is 0.000078 mg/l, and according to the MDC its concentration should not exceed 0.0005 mg/l (Table 2.1). The amount of Al is equal to 0.022 mg/l, and according to the MDC this indicator is equal to 0.2 mg/l. In addition, the content of other elements (Pb, Ni, Se, Cu, Zn, Cd, Sr) was determined in the investigated water. The obtained results are presented in Table 2.



Pic. 2. Elemental analysis of Mubarek water

Diagram 2 shows that the amount of Pb in Mubarek water is 0.0004 mg/l, according to regulatory requirements this indicator should not exceed 0.03 mg/l. The conducted studies have shown that the amount of elements in the investigated water does not exceed the regulatory requirements (Tables 2.1 and 2.2).

The amount of cations and anions in the water was also studied during the research (Table 2.3).

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Table 1

Composition of cations and anions in Mubarek GCC water

Cations	content in 1 litre		
	mg/l	mg-ekv/l	%-ekv/l
Na^+	215	8,5	37,5
K^+	4	0,92	4,5
NH_4^+	<0,11	-	-
Ca^{2+}	172	8,60	38
Mg^{2+}	50	4,60	20
Fe^{3+}	<0,4	-	-
Fe^{2+}	<0,2	-	-
Total		**22,62**	**100**
Anions	**content in 1 litre**		
	mg/l	**mg/l**	**mg/l**
Cl^-	201	8,50	37,5
SO_4^{2-}	704	12,04	53
NO_2^-	<0,01	-	-
NO_3^-	6	0,08	0,3
CO_3^-	-		
HCO_3^-	120	2,0	9,2
Total		**22,62**	**100**

The studies revealed the presence of various cations in the water (Table 2.3).

For example, it was found that the water under study contained 37.5% Na+ cations, 4.5% K^+, 38% Ca^{2+} and 20% Mg^{2+}, while other cations, particularly Fe^{2+} and Fe^{3+}, were absent. Of the anions, Cl-37.5%, 53%, - 9.2 %, no ions , and CO_3^{2-} - were detected.

In addition, other indicators of Mubarek GCC water were analysed. (Table 2.4).

Table 2

Physico-chemical parameters of Mubarek water

Hardness, mg-eq/l, total	40
Carbonate	28
Non-carbonate	12
pH	6,5
CO_2 free. mg/l	22
CO_2 agreg. mg/l	4

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Oxidability, mg O_2/litre	1,26
SiO_2 mg/l	10
H_2S mg/l	-
PO_4 mg/l	
Dry residue:	
experiment, mg/l	1488
estimated, mg/l	1419
Physical properties:	transparent
Transparent	lightly salted
Taste	Light yellow
Colour	It has a peculiar odour of gas
Smell	-
Precipitate	unchanged

Table 2 shows that the total hardness of Mubarek water is 40 mg-eq/l, hydrogen indicator - pH 6.5 or almost neutral, free CO_2 - 22 mg/l, CO_2 agg. - 4 mg/l, acidification is 11.26 mg O_2/l, SiO_2 is 10 mg/l, H_2S wa PO_4 are absent. Besides, physical properties of this water were determined: transparency - transparent, taste - slightly salty, colour - colourless, odour - odourless, sediment - absent, changes during storage - no changes.

The Bukhara Oil Refinery (BOR) uses Kuimazor water for cooling crude oil and gas condensate feedstock, which is contaminated with mechanical impurities containing large and small dispersed particles and has high hardness. The use of such waters for cooling hydrocarbon raw materials leads to the fact that the internal surface of heat-exchange equipment becomes rough, heat and mass transfer processes deteriorate as a result of increased hydraulic resistance of the equipment.

A research unit for deep treatment of recycled water from mechanical impurities and reduction of its hardness has been developed (Fig. 3.1).

The device consists of the following parts: 1 - water settling device, 2 - filter for separation of small solid particles of mechanical mixtures, 3 - mixing tank for mixing process water with reagents, 4 - tank for purified water, 5 - heat-exchange device for cooling of oil and gas condensate raw materials, pump - 6. In addition, 11 - installation with pumps for liquid supply and 12-17 - gate valves for regulation of liquid flow.

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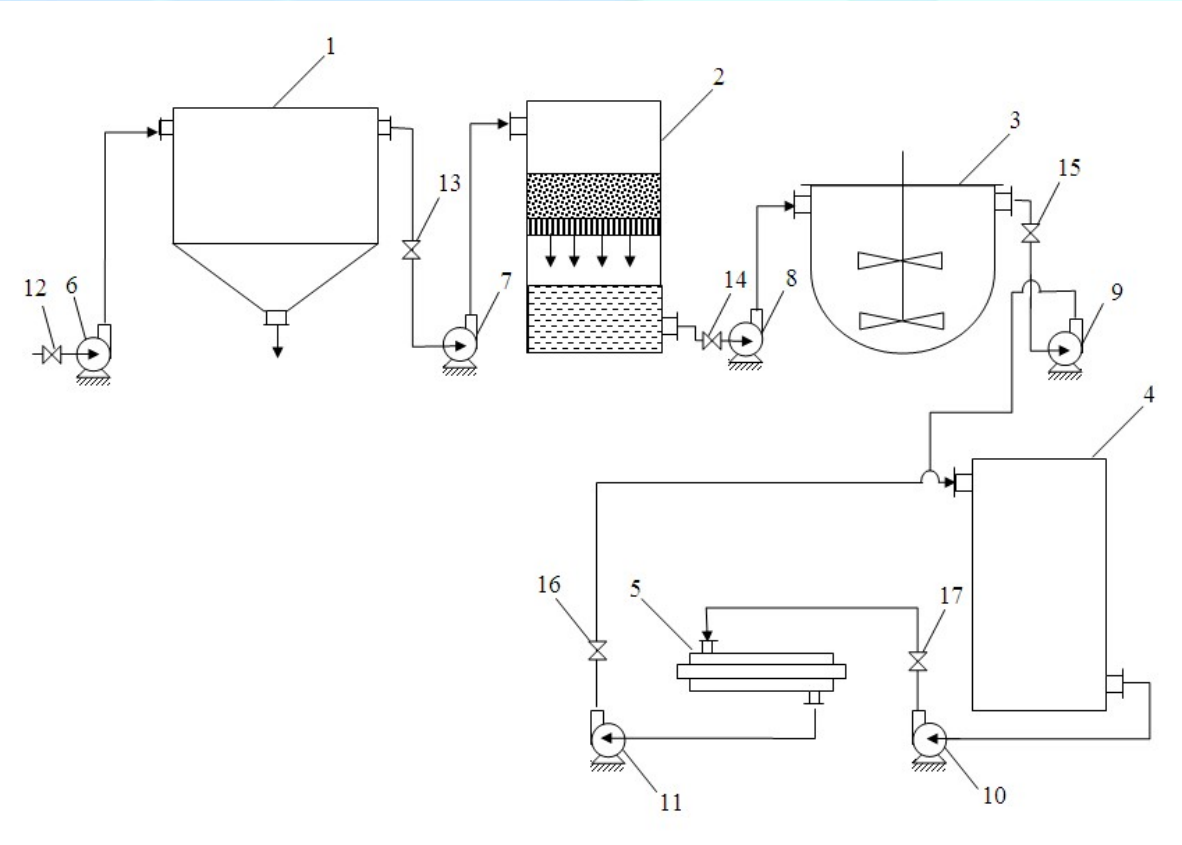


Fig. 3.1. Technological line of purification and softening of recycled water from mechanical impurities: 1 - settling tank; 2 - nutch filter; 3 - agitator; 4 - tank for purified water; 5 - heat exchange device; 6-11 - pumps; 12-17 - gate valves.

The device works in the following order: with the help of pump 6 contaminated water is supplied to settling tank 1 for settling of large solid particles of mechanical impurities, the flow of raw materials entering the system is regulated through gate valve 12, after which the water is purified from large dispersed particles. is supplied through the pump to recirculation filter 2, where the water is purified from small dispersed solids, then with the help of pump 8 is supplied to tank 3 with a mixer for water softening with various reagents.

In the mixer, 0.15 percent of tricalcium phosphate is added to the process water to separate calcium ions, with sodium replacing calcium ions and tricalcium phosphate visibly precipitating. Carbonate and sulphate ions form soluble compounds with potassium and remain in the water, they do not affect the required parameters of process water, and their level is significantly lower than the permissible norm. The sludge is separated in the reducer filter. Water purified from small impurities and softened for cooling of hydrocarbon raw materials is collected in tank 4, from where it is supplied to heat exchanger 5 with the help of pump 13, and water from heat exchanger 5 with the help of pump 11 is supplied to heat

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exchanger unit 6 - with the help of pump 11 tank capacity - at 4 water is constantly circulated in the system.

A series of experiments was carried out to determine the average concentration of small and large solid particles of mechanical impurities in the technical recycled water of an oil and gas processing plant. All experiments were carried out at room temperature.

In the experiments, 100 ml of sample water (Mubarek water sample) was filtered for purification, after which the paper filter was dried in the SNOL 1.6.2.5.1/11-I2 oven at 110°C for one hour, the paper filter was cooled in the dryer for 30 minutes, and then weighed to the nearest 0.0001 g using an electronic scale FA1004G. Calculations for determining the particulate content of mechanical impurities were carried out using the arithmetic mean of the results of five parallel experiments. The experiments showed that the total concentration of mechanical impurities in the composition of Mubarek waters averaged 7.07 %.

The following reagents and their combinations were used to reduce hardness of recycled water: Na_3PO_4 + sulfanol; Na_2HPO_4; Na_2HPO_4 + sulfanol; $Ca(OH)_2$; Na_3PO_4 mixtures.

3. Results and discussions

Mubarek waters were used for treatment and softening of recycled water from mechanical impurities. The initial hardness of each experimental water was 40 mg-eq/l. The results of research on softening of experimental water are presented in Fig. 1.

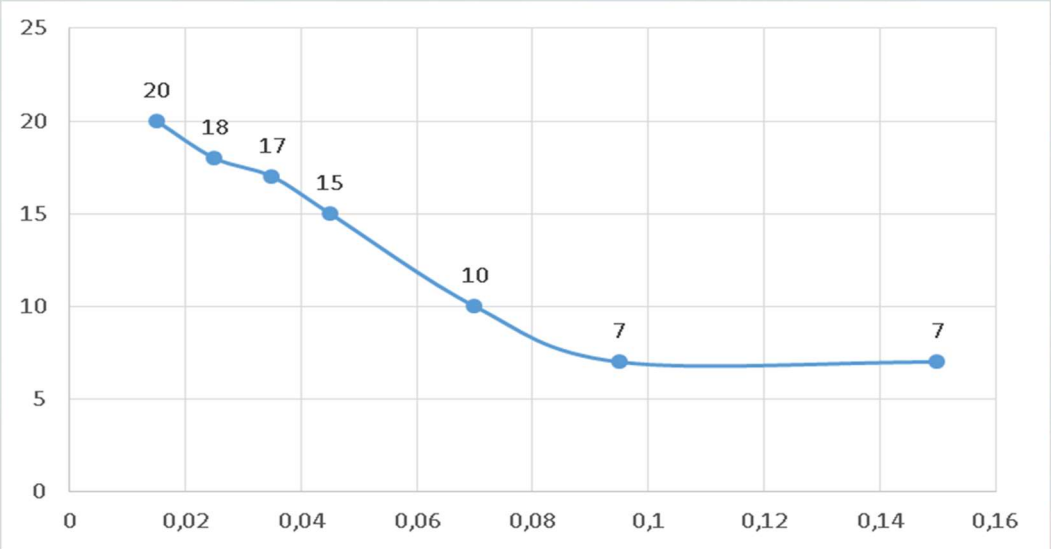


Figure 1. Results of Mubarek GChC water hardness reduction using Na_3PO_4+sulfonal reagent (water hardness 40 mg-eq/l)

Figure 1 shows that when 0.015 mg of Na_3PO_4+ sulphonic reagents were added to 10 ml of water, its hardness was 20 mg-eq/l and when 0.025 mg was added, the water hardness decreased to 18 mg-eq/l. At subsequent addition of 0.035

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÷ 0.07 mg of reagent the hardness of experimental water gradually decreased to 17 ÷ 10 mg-eq/l, and at addition from 0.095 mg to 0.15 mg of reagent this index did not change, i.e. it was 7 mg-eq/l.

Experiments using Na_2HPO_4 reagent were also conducted to reduce the hardness of this water and the results are shown in Figure 2

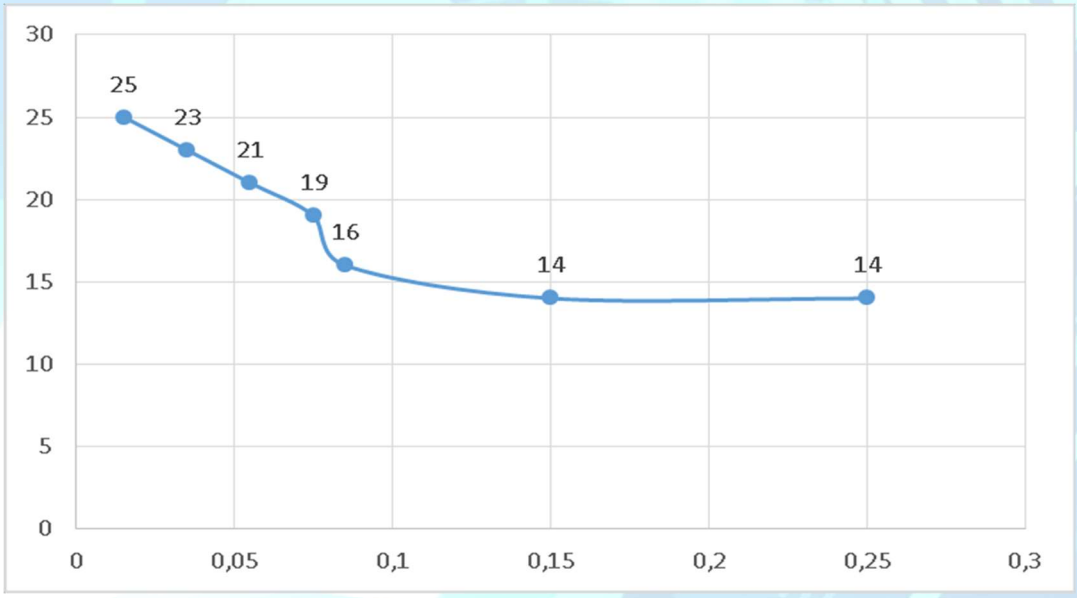


Figure 2. Results of water hardness reduction using Na_2HPO_4 reagent (water hardness 40 mg-eq/l)

To reduce the hardness of water during the experiment, Na_2HPO_4 reagent was added to 10 ml of the test water in an amount ranging from 0.015 to 0.35 mg. The results showed that water hardness decreased from 25 mg-eq/l to 15 mg-eq/l. Further experiments were also carried out with Na_2HPO_4 sulfone reagents, which are shown in Fig. 3.

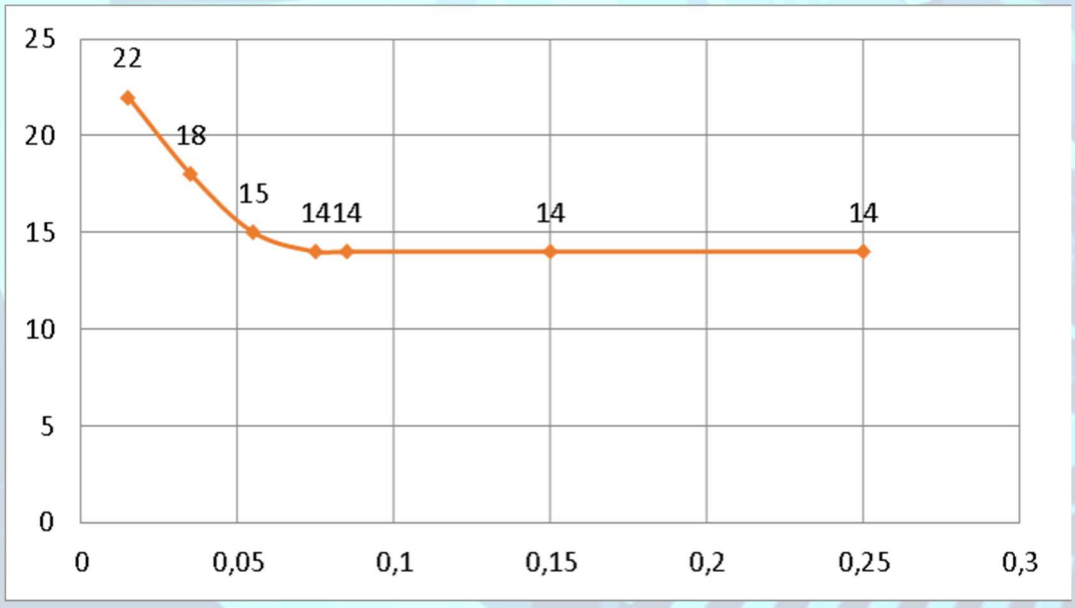


Figure 3. Results of technical water hardness reduction using Na_2HPO_4 + sulphanol reagent (water hardness 40 mg-eq/l)

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To reduce the hardness of Mubarek water, Na_2HPO_4+sulfonate reagent was added to 10 ml of water sample in the amount of 0.015÷0.25 mg, which resulted in reduction of water hardness from 22 mg-eq/l to 14 mg-eq/l, whereas when 0.075 mg to 0.25 mg of reagent was added, water hardness remained unchanged and was 14 mg-eq/l.

A series of experiments were also conducted to reduce water hardness using $Ca(OH)_2$ reagent and the results are shown in Fig. 4.

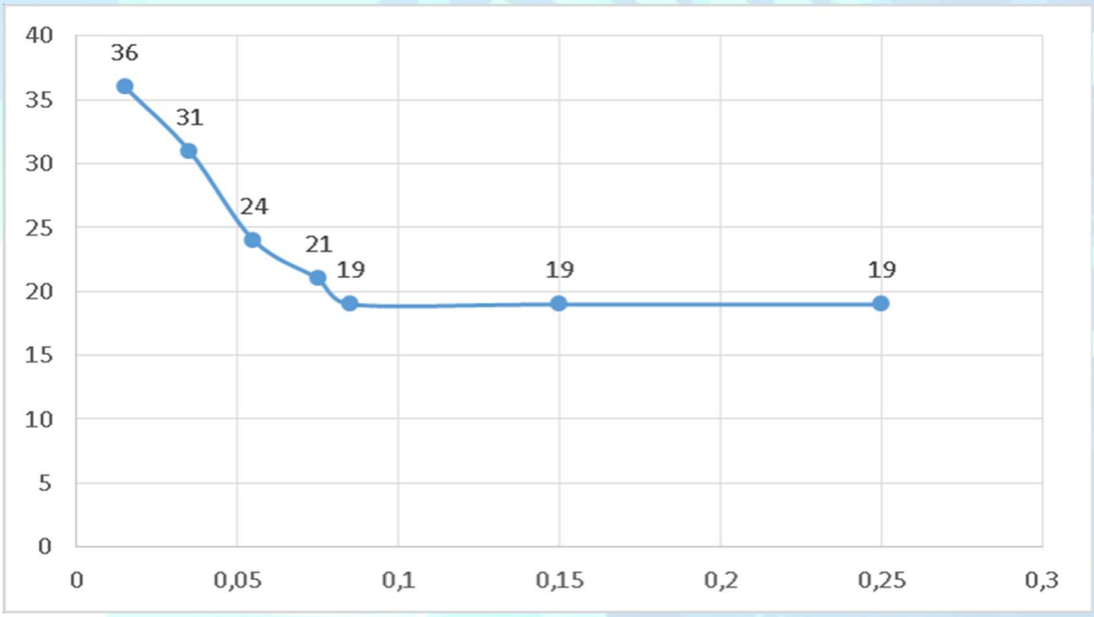


Figure 4. Results of technical water hardness reduction using $Ca(OH)_2$ reagent (water hardness 40 mg-eq/l)

The use of relatively inexpensive $Ca(OH)_2$ reagent showed that when 0.015 mg $Ca(OH)_2$ was added to 10 ml of water sample, the hardness of water decreased from 47 mg-eq/l to 36 mg-eq/l, when 0.035 mg was added, the hardness of water was 31 mg-eq/l, and when 0.055 mg was added, the hardness of water was 24 mg-eq/l, when reagent in the range of 0.085÷0.25 mg was added, the hardness decreased. When adding $Ca(OH)_2$ to the water sample, the hardness decreased from 47 mg-eq/l to 19 mg-eq/l, but continuing the experiment, increasing the content of the reagent did not give results, which can be explained by the fact that $Ca(OH)_2$ precipitates only hydrocarbonates, for the precipitation of sulfates it is advisable to use other compounds.

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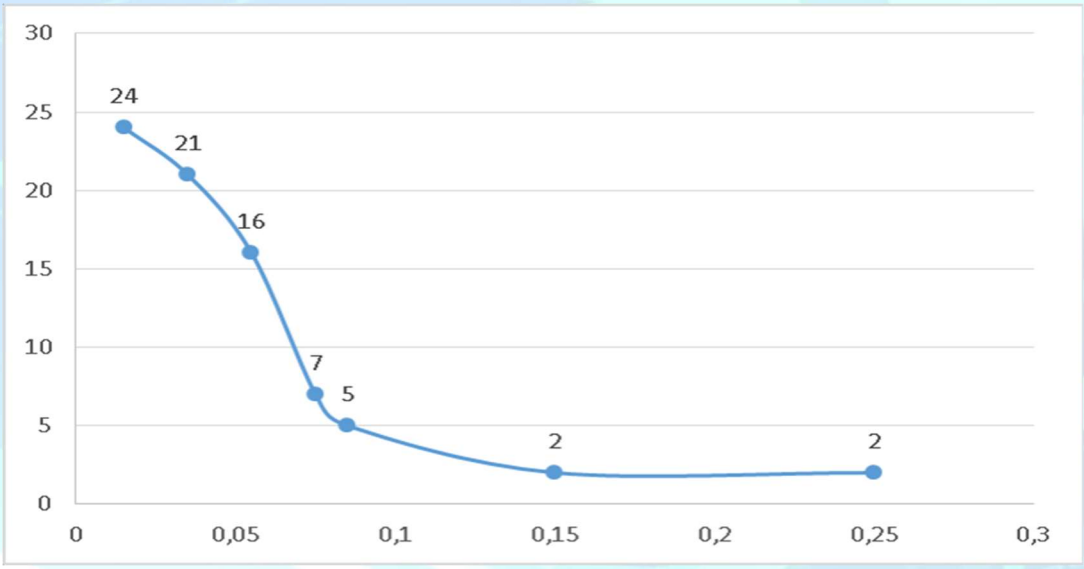


Figure 5. Results of technical water hardness reduction using Na_3PO_4 reagent (water hardness 40 mg-eq/l)

Fig. 5 shows that when 0.015 mg of Na_3PO_4 reagent was added, the water hardness decreased to 24 mg-eq/l, and when 0.035 mg of reagent was added, the hardness decreased to 21 mg-eq/l. On subsequent addition of 0.055 to 0.085 mg reagent, the water hardness decreased from 16 mg-eq/l to 5 mg-eq/l. Water hardness decreased to 2 mg-eq/l when 0.15 and 0.25 mg reagent was added, and this value remained unchanged.

4. Conclusion

Thus, the conducted studies on reducing the hardness of recycled water of the oil refinery showed that the reagents Na_3PO_4 + sulfonic mixture; Na_2HPO_4; Na_2HPO_4+sulfonic; $Ca(OH)_2$ are considered unsuitable for reducing the hardness of recycled water (Fig. 4), as these reagents did not reduce the water hardness indicators to the norm. It is recommended to use Na_3PO_4 reagent at a concentration of 0.15 % to reduce the hardness of recycled water of industrial enterprises.

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