Reagent purification and pre-treatment of water in water supply systems with desalination complex

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Abstract. The work is devoted to the investigation of the process of reagent purification of seawater, using the example of the Black Sea water, purification of recycled water, as well as the development of a technological scheme for the purification and preparation of sea and recycled water system, taking into account the composition of pollutants, salt content and the productivity of the water treatment unit for the water supply system with desalination complex.

1. Introduction
The marine area is continuously connected with its external environment. It is influenced by various external and internal conditions such as: a variety of natural phenomena, industry, industrial and communal construction, household activities and much more. The consequence of these influences is the introduction into the aquatic environment of new, uncharacteristic substances - pollutants, which impair the quality of water. In addition, natural marine and oceanic waters in themselves are characterized by a fairly high hardness and a high content of such toxic ions, having in some countries maximum permissible concentrations (MPCs), like bromine, fluorine, iodine, boron.

For long-term operation of water supply systems with desalination complexes [1], the quality of the original desalinated and recycled water must meet certain stringent requirements. This entails the need to develop a water purification system, including its preliminary preparation before desalination. At the same time, the cost of this system can be two or three times higher than the cost of the desalination plant itself.

When water is desalinated by distillation in evaporators, serious difficulties are caused by rapid overgrowth by the scum of heat exchange surfaces. This is due to the high rigidity inherent in the seawaters. The formation of scale on the heat transfer surfaces of the evaporators leads to a sharp decrease in their efficiency; there is a need for frequent stopping and cleaning of evaporators, the use of antiscale reagent, which is associated with high operating costs. When membrane methods of desalination are used, the high sensitivity of membranes to various kinds of impurities of organic and inorganic character requires the use of advanced pre-treatment schemes in reverse osmosis plants. Both for reverse osmosis and for electrodialysis, hardness salts, especially calcium stiffness, are the most dangerous. In this connection, the problem of pre-treatment and softening of seawater before its desalination is highly topical.

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After the use of water by consumers obtained in the water supply system with desalination complex, the water from the household and industrial water supply system of the settlement gets into the sewage system, from which the waste water enters the additional pre-treatment unit [1], whose task should be to bring the quality of this recycled water to the level of MPC.

2. Subject and method of research

2.1. Subject of research
Researches of the process of reagent purification of seawater were carried out using the example of the Black Sea water. A water sample was taken in the vicinity of Nizhneimeretskaya Bay in Sochi (Nizhneimeretinskaya Bay, Sochi, Krasnodar Territory, Russia 43.397218, 39.966488).

Reseaches of the process of reagent purification of recycled water are carried out on the example of model and real sewage (recycled) waters of a non-ferrous metallurgy plant containing such types of pollutants as: suspended substances, petroleum products, heavy metals, hardness salts.

2.2. Methodology of research
The main technological problems of preparation and purification of marine and industrial wastewater include the need to select the most efficient coagulant-flocculant and to create an optimal technological regime for its use. The hybrid aluminum-silicon reagent FCS-9 [2] was chosen as the base reagent in the work, because of its high relative coagulating and flocculating ability. Reagent treatment of water was carried out with FCS-9 reagent with activating additives, which used a soda solution and sodium orthophosphate. The reagent concentration (in terms of Al₂O₃) was varied from 20 to 70 mg/l.

Methods of atomic spectrometry, ion chromatography and titrimetric analysis were used to determine the concentration of various cations and anions in seawater. Determination of the content of the main cations in seawater was carried out by the method of atomic emission spectrometry with inductively coupled plasma. The measurements were carried out using an emission spectrometer with inductively coupled plasma Profile Plus. The method of ion chromatography was used to determine the concentration of the main anions in seawater. The measurements were carried out on a chromatograph "Stayer". Determination of the total mineralization (dry residue) of seawater was carried out by evaporation. The determination of the total rigidity was carried out by the titrimetric method.

Modeling of recycled water composition was carried out according to the rules of model solutions preparation. Model waters with a given concentration of iron and copper were prepared by adding to the distilled water a known amount of their salts FeCl₃·6H₂O and CuSO₄·5H₂O respectively. The prepared water was settled until a fixed concentration of pollutants was established, after which it was filtered through a filter with a pore size of 100-200 μm. Model waters containing petroleum products were prepared by dispersing transformer oil in water. The initial concentration of all pollutants (iron, copper and petroleum products) in model solutions was 10 mg/l, and the pH of solutions was in the range of 6.8 – 7.5.

Model waters with a given concentration of suspended solids were prepared by adding kaolin (clay) suspension to distilled water. To study the kinetics of sedimentation of suspended solids during spontaneous settling (without reagents), and also during sedimentation using FCS-9 reagent, model waters with an initial clay content of 150 mg/l were used.

Methods of electrochemical, colorimetric and photocolorimetric analysis were used to determine the main characteristics and physico-chemical composition of model and real recycled waters. The concentrations of iron, copper and aluminum were determined by photometric method using a Spekol 1300 spectrophotometer. The essence of the method for determining petroleum products is associated with the determination of the content of an oil-soluble dye (sudan, azobenzene), previously dissolved in a model hydrocarbon (diesel fuel, gasoline, toluene and others).
3. Research results

3.1. Results of reagent treatment of the Black Sea water

3.1.1. Results of preliminary softening of seawater. As a result of preliminary studies, it has been established that in connection with the fact that seawater is characterized by a rather high rigidity (≈ 1350 ppm for the Black Sea), the capacity of the hybrid reagent is not sufficient to reduce it and effectively coagulate pollutants, including toxic ions. To eliminate this problem, it is proposed in the work to first reduce the rigidity of seawater using reagent methods.

Reagent methods of water softening are based on water treatment by substances that bind calcium and magnesium ions to practically insoluble compounds [3]. For the most effective softening of seawater, the method of successive water treatment with Na$_2$CO$_3$ solution for pre-softening and then sodium orthophosphate solution Na$_3$PO$_4$·12H$_2$O together with FCS-9 reagent for softening and removal of "residual" phosphates is proposed.

The process of reducing carbonate and non-carbonate hardness using a soda solution and sodium orthophosphate is described by the following reactions (for magnesium, similarly):

- \[ \text{Ca}(\text{HCO}_3)_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Ca}(\text{CO}_3)\downarrow + 2\text{NaHCO}_3; \]
- \[ \text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Ca}(\text{CO}_3)\downarrow + 2\text{NaCl}; \]
- \[ \text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{Ca}(\text{CO}_3)\downarrow + \text{Na}_2\text{SO}_4; \]
- \[ 3\text{Ca}(\text{HCO}_3)_2 + 2\text{Na}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2\downarrow + 6\text{NaHCO}_3; \]
- \[ 3\text{CaCl}_2 + 2\text{Na}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2\downarrow + 6\text{NaCl}; \]
- \[ 3\text{CaSO}_4 + 2\text{Na}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2\downarrow + 3\text{Na}_2\text{SO}_4 \]

The use of FCS-9 reagent allows to significantly increase the rate of these reactions, intensify the purification process, and also reduce the phosphate ions and sodium introduced into the water by adding a soda solution and sodium orthophosphate.

In the course of experimental researches it was established that the degree of purification from the hardness salts strongly depends on the kind of activating additives introduced into the water during the purification process. To soften very hard water (600 ppm and more), it is necessary to use a solution of soda together with a solution of sodium orthophosphate and reagent FCS-9. In this method, the degree of purification reaches values of about 95%. When softening water of medium hardness (up to 600 ppm) it is sufficient to use only a soda solution together with FCS-9 to intensify the process. It is possible to obtain drinking water, the total hardness of which corresponds to the norm [4].

Table 1 presents the results of studies on the softening of the highly rigid seawater of the Black Sea with an initial rigidity of 1350 ppm.

| Parameter          | Initial | Method 1 | Method 2 | Method 3 |
|--------------------|---------|----------|----------|----------|
| Hardness, ppm      | 1350    | 600      | 225      | 50       |
| Phosphates, mg/l   | 0,0     | 0,00     | 15,00    | 3,50     |
| Sodium, g/l        | 0,12    | 0,40     | 4,00     | 0,20     |
| pH                 | 7,61    | 7,75     | 8,00     | 7,50     |
Softening was carried out in three different ways:
1. Adding to the water 10 ml/l 10% soda solution.
2. Adding to the water 10 ml/l 10% soda solution and 5 ml/l 10% sodium orthophosphate solution.
3. Adding to the water 10 ml/l 10% soda solution, 5 ml/l 10% sodium orthophosphate solution and 30 mg/l FCS-9 (in terms of Al₂O₃).

When 10 ml/l of 10% soda solution is added to the seawater, followed by sedimentation and filtration, the water hardness decreases from 1350 to 600 ppm (Method 1). When added together with a soda solution 5 ml/l 10% sodium orthophosphate solution, the intensity of clarification rises sharply, while the water hardness decreases to 225 ppm (Method 2). However, in this case there is an increased concentration of phosphate ions in the treated water, which is 15 mg/l. With the simultaneous introduction of a solution of soda, sodium orthophosphate and 30 mg/l FCS-9 (in terms of Al₂O₃) it is possible to reduce the concentration of hardness salts to 50 ppm (Method 3). In this case, the content of "residual" phosphate ions decreases to a value corresponding to the norm [4]. This fact confirms the effectiveness of the use of a hybrid aluminum-silicon reagent to intensify the process of purification and removal of residual phosphorus ions. It should be noted that, as mentioned above, the use of the reagent FCS-9 without activating additives does not lead to a noticeable decrease in water hardness.

### 3.1.2 Results of re-treatment of seawater

After reducing the overall hardness of seawater, a hybrid aluminum silicon reagent FCS-9 can be reused to reduce the concentration of various impurities, including toxic ones. Based on the results of preliminary studies conducted with samples of seawater, an optimal dosage was chosen to be 60 mg/l (in terms of aluminum oxide) FCS-9. At this dosage, the pH value was 6.0. The content of residual aluminum and iron in the treated seawater did not exceed the level of maximum permissible concentration. With the addition of large doses of the reagent (> 60 mg/l), the residual aluminum and iron content in the treated water significantly increased and exceeded the MPC level. Table 2 presents the results of reagent treatment of the softened seawater of the Black Sea using FCS-9 reagent.

#### Table 2. Results of reagent treatment of the Black Sea water.

| Parameter                  | Initial water | Water after reagent treatment | MPC          |
|----------------------------|---------------|-------------------------------|--------------|
| Total mineralization, g/l  | 17.0          | 15.0                          | -            |
| pH                         | 6.42          | 6.00                          | 6.5-9.5      |
| Boron, mg/l                | 0.2           | 0.15                          | 1.0          |
| Bromine, mg/l              | 0.25          | 0.2                           | -            |
| Fluoride, mg/l             | 1.0           | 0.5                           | 1.5          |
| Iodine, mg/l               | 0.07          | 0.05                          | -            |

It is established that during reagent treatment the total mineralization of water decreases by 2 g/l, which may be associated with the removal of a part of the insoluble salts. The content of toxic ions in the test sample of the Black Sea water does not exceed the MPC level. However, reagent treatment using FCS-9 reagent tends to reduce the concentration of toxic ions in seawater.
3.2. Results of reagent treatment of model waters simulating the composition of recycled waters

When using the reagent method of recycled water treatment, it is necessary to calculate the amount of reagent required for water treatment of different composition. For accurate prediction of the use of these or other reagents, the calculated doses are established on the basis of data obtained as a result of trial water treatment in laboratory conditions (trial coagulation), taking into account the permissible residual doses of reagents in water, established by the standards [4].

The results of experiments on primary treatment with hybrid aluminum-silicon reagent FCS-9 model waters with total iron, copper and petroleum products are shown in figure 1.

![Dependence of residual concentration of pollutants on reagent dose](image)

**Figure 1.** Dependence of the residual concentration of model pollutants on the reagent dose

It was found that the optimal dose of FCS-9 for effective water purification from total iron is a dose of 20-30 mg/l (figure 1). Wherein the degree of purification reaches values over 99%. The optimal dose for water purification from copper and petroleum products is also 20-30 mg/l. Wherein the concentration of copper is reduced by 90%, and the concentration of oil products by 95%.

The minimum value of residual aluminum in treated water is observed at doses of FCS-9 20-40 mg/l. In this case, the amount of residual aluminum in the treated water is 5-10 times lower than the MPC norm, equal to 0.2 mg/l. Corresponding to these doses, pH values are in the range of 6.0-8.0.

Figure 2 shows a graph of the time dependence of the suspended solids concentration. It can be seen that the highest degree of clarification is achieved in the case of the reagent FCS-9. Already 10 minutes after the introduction of the reagent, the suspended solids concentration was less than 40 mg/l, while without the use of the reagent, the concentration was about 60 mg/l. This fact testifies to the high efficiency of the use of the FCS-9 reagent as an intensifier of the clarification process of clay-containing waters.
1234567890

Figure 2. Dependence of suspended solids concentration on time

It should be noted that after preliminary reduction of rigidity, re-treatment of seawater with reagent FCS-9 and its purification from such pollutants as iron, copper, petroleum products, suspended solids, does not differ from the treatment of recycled water containing these pollutants. In this regard, the FCS-9 reagent can also be used to purify seawater from these pollutants, after preliminary softening.

4. Development of the technological scheme of the purification and pre-treatment system

The basic technological scheme of the purification system and the pre-treatment of sea and recycled water (Figure 3) includes the following main nodes:
- softening module;
- reagent processing module [5];
- a flotation phase separation module, equipped with a blowing and collecting device for foam, zones of formation, sedimentation and removal of sediment, a unit for the collection of purified water, with a total residence time of water in the flotator of at least 10 minutes;
- fine cleaning module on SHS filters;
- drainage and sedimentation module.

The main parts of the purification and pre-treatment system are the reagent processing module and the flotation phase separation module (flotator). Wherein there may be several flotators. Flotators are located directly in the water and are divided into different groups. In each group of flotators it is possible to obtain waters of different quality (depending on requirements). This method of location of the flotators was introduced during the development of technology for surface water treatment facilities at the Moscow International Business Centre (MIBC), also known as "Moscow City", with a capacity of 5000 m³/h.
Figure 3. Technological scheme of the purification and the pre-treatment system

The initial seawater is fed through the pre-coarse filter 1 by means of the pump 2 to the softening module, where it is softened using three reagents 7, 8, 9 (soda solution, sodium orthophosphate and FCS-9 solution). Reagents are fed by means of regulating valves 4, 5, 6 and ejector 3. After softening, water through the additional filter 10 enters the module of reagent treatment and flotation phase separation module in order to release fine and dissolved impurities, including toxic ones. In the reagent treatment module, water is treated with FCS-9 reagent and, if necessary, by activating additives (containers 15, 16, 17). The supply of reagents and additives is carried out by means of regulating valves 12, 13, 14 and an ejector 11. In the flotation phase separation module, the flow of reagents with water is sent to the reaction chamber of the flotation unit 21, where it freely flows and collides with the oppositely directed counterflow of water enriched, by means of the water-air ejector 18, with air. The air flow is controlled by the regulating valve 19 and the rotameter 20. Thus, effective mixing of streams takes place in the reaction chamber of the flotator 21, favoring the rapid distribution of reagents throughout the entire volume of treated water and the formation of coagulated flakes and sediments, some of which are removed at the top and bottom of the flotation cell, and clarified water enters further filtration. In the fine cleaning module, water is supplied by pump 22 and is filtered on SHS filters 23 and 24, operating on the principle of filtration from the tangential flow. Here, the water is divided into two streams: water that does not pass through the filter elements and contains the bulk of the impurities (concentrate) retained by the filter element and the filtered water. Water flows that do not pass through the filter elements are sent to the sludge processing unit 25, and the filtered water flows enters the inlet of the desalination section.

The flotation sludge (foam) of the flotation removal zone of the flotation reactor's chamber and the flocculent sediment from the sludge removal zone also enter to the sludge processing unit 25. In the sludge processing unit 25, the sludge is dewatered and compacted into the dry sediment 26, and the liberated water is sent to the head of the system before the coarse filter (filtrate).

Recycled waters formed as a result of water users activities enter the purification stage, where they are treated in a similar way and can be further used for various agricultural and other purposes.
4.1. Results of reagent treatment of recycled (waste) waters
A study of the efficiency of treatment of recycled water containing all types of mentioned model pollutants according to the technological scheme of the purification and pre-treatment system (without a softening module) was carried out on an experimental stand using the example of real waste (recycled) waters of a non-ferrous metallurgy plant. The injection inlet of the mixing ejector was fed a dose of 30 mg/l of the reagent FCS-9 in terms of aluminum oxide. Sampling of processed water was provided for water analysis at different stages of treatment. Sampling zones are indicated in figure 3:

- **I** – initial contaminated water sample;
- **II** – water sample after reagent treatment;
- **III** – filtrate sample after filtration module

Table 3 shows the test results.

| Parameter                  | Unit of measurement | Maximum permissible concentration [4] | Water sampling zone |
|----------------------------|---------------------|---------------------------------------|--------------------|
|                            |                     |                                       | I  | II  | III |
| pH                         | pH units            | 6.5-9.5                               | 6.91 | 6.63 | 7.30 |
| Total mineralization       | mg/l                |                                       | 2536 | 975  | 349  |
| Total hardness             | ppm                 |                                       | 600  | 390  | 225  |
| Petroleum products         | mg/l                |                                       | >20  | 0.8  | 0.05 |
| Total iron                 | mg/l                | 0.2                                   | 6.0  | 0.1  | 0.01 |
| Manganese                  | mg/l                | 0.05                                  | 5.0  | 0.1  | 0.01 |
| Copper                     | mg/l                | 2.0                                   | 28.0 | 5.4  | 0.2  |
| Aluminum                   | mg/l                | 0.2                                   | 0.2  | 0.05 | 0.01 |

Based on the data provided in table 3, it can be concluded that the water parameters obtained after treatment at the experimental stand meet the standards [4]. On the basis of this, it can be concluded that the water obtained after purification can be used for various agricultural, domestic and technological needs.

5. Conclusion
The process of reagent treatment of seawater in the Black Sea has been studied, the concentrations of the main cations and anions contained in the Black Sea water have been determined. It has been established that after a preliminary softening and re-treatment using the FCS-9 hybrid aluminum-silicon reagent, the total mineralization of water decreases by 2 g/l, which may be due to the removal of sparingly soluble salts. The content of toxic ions in the waters of the Black Sea practically does not
exceed the MPC level. However, in the reagent treatment using the FCS-9 hybrid reagent, the concentration of toxic ions in seawater tends to decrease.

It was found that the optimal dose of FCS-9 for effective purification of model water with total iron is 20-30 mg/l. At the same time, the purification degree reaches values over 99%. The optimal dose for water purification from copper and petroleum products is also 20-30 mg/l. The concentration of copper is reduced by 90%, and the concentration of petroleum products is reduced by 95%. In addition, an example of the high efficiency of the FCS-9 reagent as an intensifier of the clarification of clay-containing waters is shown.

The technological scheme and the experimental stand of the purification system and the pre-treatment of sea and recycled water have been developed. It has been established that with the reagent treatment of real recycled waters, the concentration of heavy metals and petroleum products is reduced by 99%, and the residual aluminum content in purified water is an order of magnitude lower than in the original one.

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