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Analysis of Existing Methods for Softening Natural Waters

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ABSTRACT: One of the main reasons for the decrease in the efficiency of heat exchange equipment is the formation of scale on heat transfer surfaces. One of the defining qualities used in the freshwater industry is its hardness. This article analyzes the main methods of water treatment, which include the thermal method of water softening, reagent water softening methods, the ion exchange method, membrane methods of water softening.

I.INTRODUCTION

Nowadays, heat-and-power engineering is considered one of the most water capacious spheres of the industry. Technologies of water treatment in this sphere are a component of a normal operation mode of the heat power equipment. By and large, reliability of all thermal systems depends on quality of water treatment in heat-and-power engineering.

In the process of operation of heating equipment when using hard water, solid deposits are formed on the heating surfaces of heat exchangers, which are usually called scale. Scale has high mechanical properties and low heat transfer capacity and therefore is the cause of a number of technical difficulties and additional costs in the operation of the heat and power facilities of enterprises.

The main task of water treatment is to prevent undesirable processes - the formation of scale and corrosion - in all units of an industrial installation. Especially intensive scale formation on heat exchange equipment occurs in systems with a circulating water supply. One of such enterprises, using the recycling water supply system in production, is LLC "Mubarek" gas processing plant (GPP), which is one of the largest plants for the extraction of hydrocarbon gases in Uzbekistan.At MGPP, to cool the produced products, they mainly use recycling water supply systems. Cooling circulating water is exposed to a number of physicochemical effects: it is heated, cooled, aerated, evaporated, etc. As a result, it becomes corrosive, and also capable of depositing mineral salts on the walls of the pipes of heat exchangers and causing biological fouling of the surfaces washed by it (equipment, cooling towers, pipelines, etc.) We investigated the full chemical composition of the cooling and makeup water used at the MGPZ cooling towers (Table 1).

Table 1.

Results of complete chemical analysis of make-up and cooling water samples at cooling towers

№	Name of substance	Mmeasurement unit	Volume	
			From the make-up	From the cup to the cooling tower
1.	pH		8.7	8.7
2.	Rigidity	mg-ekv/dm^3	8.2	13.4
3.	Alkalinity	mg-ekv/dm^3	10.2	18.8
4.	Ca	mg-ekv/dm^3	5	8
5.	Mg	mg-ekv/dm^3	3.2	5.4
6.	Fe^{3+}	mg/ dm^3	3.2	3
7.	Fe^{2+}	mg/ dm^3	526.4	789
8.	Cu	mg/ dm^3	---	---
9.	SO_4^{2-}	mg/ dm^3	660	2200
10.	Cl^-	mg/ dm^3	350	760
11.	NO_3	mg/ dm^3	117	35
12.	NO_2	mg/ dm^3	0.1	17
13.	SiO_2	mg/ dm^3	100	375

Process of selection of water of salts Ca^{2+} and Mg^{2+}in water treatment received the name water softening.According to experimental data, the content shows that water has a very high hardness. Water with high hardness gives dense deposits on heat transfer surfaces [1] and this naturally leads to a sharp decrease in the heat transfer coefficient. The following softening methods are used to remove the formed deposits:

The thermal method is the oldest method for producing demineralized water (distillate) - distillation, evaporation. The main process is the transfer of water into the vapor phase with its subsequent condensation. The most important advantages of this method are the minimum amounts of reagents used and the volume of waste that can be obtained in the form of solid salts [2]. It is based on a shift in carbon dioxide equilibrium towards the formation of calcium carbonate:

$$Ca\,(HCO_3)_2 \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O \quad (1)$$

A shift in equilibrium occurs as a result of a decrease in the solubility of carbon dioxide with increasing temperature. Boiling can completely remove carbon dioxide and thereby significantly reduce the carbonate calcium hardness. However, it is not possible to completely eliminate the specified hardness, since calcium carbonate, although insignificantly (13 mg / l), is still soluble in water. In the presence of magnesium bicarbonate in water, the process of precipitation occurs as follows: first, a relatively well soluble (110 mg / l) magnesium carbonate is formed:

$$Mg\,(HCO_3)_2 \rightarrow MgCO_3 + CO_2\uparrow + H_2O \quad (2)$$

This salt is hydrolyzed during prolonged boiling, as a result of which a precipitate of poorly soluble (8 mg / l) magnesium hydroxide forms:

$$MgC0_3 + H_2O \rightarrow Mg(OH)_2 + CO_2\uparrow \ (3)$$

Thus, when water is boiled, the hardness due to calcium and magnesium bicarbonates is significantly reduced. This method can be used as an auxiliary method for reagent softening methods. Thermochemical softening occurs as a result of heating water above 100 °C and using lime and soda, less often caustic sodium and soda. The thermochemical method is often combined with phosphate to soften water.The disadvantages of this method are: the need for pretreatment on Na-cation exchange filters; the need for additional water consumption; in the case of a large non-return of condensate, a significant increase in the steam production of the boiler house is required to obtain secondary steam or excessive consumption of electricity to obtain primary steam [2].

Water softening by reagent methods is based on its treatment with reagents that form with calcium and magnesium, poorly soluble compounds: $Mg(OH)_2$, $CaCO_3$, $Ca_3(P0_4)_2$, $Mg_3(P0_4)_2$ and others, followed by their separation in clarifiers, thin-layer sedimentation tanks and lighting filters. Lime, soda ash, sodium and barium hydroxides and other substances are used as reagents [3]. Distinguish between water softening by liming and soda-liming:

Water softening by liming is used at its high carbonate and low non-carbonate hardness, as well as in the case when it is not required to remove non-carbonate hardness salts from water. When liming, slaked lime Ca(OH) is added to the solution to 10 pH. As a result, the following reactions take place:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O \qquad (4)$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O \qquad (5)$$

With soda-liming, slaked lime $Ca(OH)_2$ and soda Na_2CO_3 are added to the solution to a pH of about 10. As a result, the following reactions take place:

$$Ca(HCO_3)_2 + Ca(OH)_2 + Na_2CO_3 = 2CaCO_3\downarrow + 2NaOH + H_2CO_3 \qquad (6)$$

$$Mg(HCO_3)_2 + 2NaOH = Mg(OH)_2\downarrow + 2NaHCO_3 \qquad (7)$$

As follows from the reaction equations, in the process of formation and precipitation of a precipitate, hardness salts are extracted from the solution. Together with them, colloidal and suspended particles with associated contaminants are removed. Organic impurities are partially sorbed on the sludge flakes. Sedimentation processes are carried out in sedimentation tanks and clarifiers with a suspended sediment layer [2]. It is not possible to completely eliminate the rigidity by this method due to some solubility of $CaCO_3$ and $Mg(OH)_2$. Therefore, it is used for relatively shallow softening (up to 1.4 - 1.8 mg-eq / l). In addition, soda limescale is carried out when the treated water is heated at 90-95^{0}C. For alkaline waters, this treatment method is not applicable.

When using the unitary method, the water treatment process is as follows:

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \qquad (8)$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl \qquad (9)$$

It should be noted that it is formed during the reaction of sodium hydroxide with bicarbonate, which is necessary for addition to water; its dose is significantly reduced. With a high concentration of bicarbonates in water and a low non-carbonate hardness, excess soda can remain in softened water. Therefore, this method is used only taking into account the ratio between carbonate and non-carbonate hardness. In addition, one must take into account the high cost of caustic soda in comparison with lime.

When using the barium method, reagents that contain barium in water are first introduced to eliminate sulfate hardness. To soften it, it is treated with lime. The chemistry of this process is described as follows:

$$\frac{CaSO_4}{MgSO_4}+Ba(OH)_2 =\frac{Ca(OH)_2\downarrow}{Mg(OH)_2\downarrow}+BaSO_4\downarrow \tag{10}$$

$$Ca(OH)_2+Ca(HCO_3)_2=2CaCO_3\downarrow+2H_2O \tag{11}$$

$$\frac{CaSO_4}{CaCl_2}+ BaAl_2O_4= \frac{BaSO_4\downarrow}{BaCl_2\downarrow}+ CaAl_2O_4\downarrow \tag{12}$$

$$\frac{MgSO_4}{MgCl_2} + BaAl_2O_4 =\frac{BaSO_4\downarrow}{BaCl_2\downarrow}+ + MgAl_2O_4\downarrow \tag{13}$$

$$\frac{Ca(HCO_3)_2}{Mg(HCO_3)_2} +Ba\ Al_2O_4 = \frac{CaAl_2O_4\downarrow}{MgAl_2O_4\downarrow} +BaCO_3\downarrow+H_2O + C0_2 \tag{14}$$

The barium method is used very rarely due to its high cost of reagents. Flocculants with mechanical stirrers should be used to introduce $BaCO_3$, since $BaCO_3$ forms a heavy, rapidly settling suspension.

Cationization is the process of exchange of cations between substances (electrolytes) dissolved in water and a solid insoluble substance immersed in this water and called a cation exchanger. Depending on which of these cations the cation exchange resin is "charged", three processes are distinguished: sodium cationization (Na cationation), hydrogen cationization (H-cationization), and ammonium cationization (NH_4 cationization).

In sodium cationization, the exchangeable cation is sodium. When filtering hard water through a layer of sodium cation exchanger, sodium cations are exchanged for calcium and magnesium, which can be represented by the following reactions:

$$Ca^{2+} + 2Na^+R^-\rightarrow Ca^{2+}R_2^- + 2Na^+ \tag{15}$$

$$Mg^{2+} + 2Na^+R^-\rightarrow Mg^{2+}R_2^-+ 2Na^+ \tag{16}$$

Here, NaR is the symbol for sodium cation;

R-complex radical cation exchanger;

As a result of the above reactions, more or less complete replacement of Ca^{2+} and Mg^{2+} cations in water with sodium cations occurs, as a result of which the residual hardness of sodium-cationized water decreases to 10 µg-eq / l and below. The alkalinity and anionic composition do not change, and its salt content slightly increases. Moreover, the cation exchanger is regenerated with sodium chloride NaCl.

It should be noted that this method has a disadvantage: it is impossible to reduce the alkalinity of the source water. As a result, we can assert that by Na-cationization, the carbonate hardness of the source water is converted into an equivalent amount of sodium bicarbonate (with the formation of NaOH and CO_2).

Treatment of water with hydrogen-cationization (H-cationization) is based on filtering it through a layer of cation exchanger containing, as exchange ions, hydrogen cations. The process is described by the following reactions:

$$Na^+ + H^+R^-\rightarrow Na^+R^- +H^+ \tag{17}$$

$$Ca^{2+} + 2H^+R^-\rightarrow Ca^{2+}R_2^- +2H^+ \tag{18}$$

$$Mg^{2+} + 2H^+R^-\rightarrow Mg^{2+}R_2^- +2H^+ \tag{19}$$

$$HCO_3^-+ H^+\rightarrow CO_2\uparrow+H_2O \tag{20}$$

It follows from these reactions that during hydrogen-cationization, the carbonate hardness (alkalinity) of the treated water is completely removed, as a result of which a decrease in the dry residue of water occurs. Salts of calcium, magnesium, sodium and other cations are converted into free acids, since all cations are replaced by a hydrogen cation. Consequently, hydrogen cationization changes not only the cationic, but also the anionic composition of the treated water, since HCO_3 ions are removed [5]. The H-cationization process is always combined with Na-cationization or anionization, which makes it possible to neutralize the acidity and reduce the alkalinity of the treated water.

The method of Ammonium-cationization consists in the fact that all cations present in the treated water are replaced by filtering it through a layer of cation exchanger with an ammonium cation NH_4^+, which is an exchange cation. This can be represented by the following reactions:

$$Ca^{2+}+2NH_4R\rightarrow CaR_2 +2NH_4^+ \tag{21}$$

$$Mg+ + 2NH_4R\rightarrow MgR_2 + 2NH_4^+ \tag{22}$$

$$Na^++NH_4R\rightarrow NaR+NH_4 \tag{23}$$

Thus, in softened water mainly ammonium salts are present, as a result of which the hardness of the ammonium-cationized water becomes negligible.

The main disadvantage of the hydrogen cation process is the acidic reaction of softened water. This disadvantage is eliminated if hydrogen-cationization is replaced by ammonium-cationization. In this case, softened water containing ammonium salts will not have an acidic reaction. Ammonium cationization is used in water softening in combination with sodium cationization [5].

Water treatment by ion exchange methods differs from water treatment with chemical reagents in that the removed impurities do not form a sediment in the treated water and do not require constant dosing of reagents. However, it is periodically necessary to regenerate the depleted ion exchanger in order to restore it.

The main membrane methods for separating liquid systems include: reverse osmosis, ultrafiltration, dialysis, electrodialysis.

The reverse osmosis method consists in filtering solutions under pressure through semi-permeable membranes that allow the solvent to pass through and completely or partially retain molecules or ions of dissolved substances. The efficiency of removing various ions by reverse osmosis depends on their charge and size, which determine the degree of hydration, and increases with an increase in these characteristics. The maximum salt content of the concentrate is limited by its osmotic pressure and concentration polarization.Concentration polarization means that the concentration of a solute in a thin near-membrane layer increases due to the predominant transfer of water molecules through the membrane. Concentration polarization promotes salt saturation of the solution at the membrane surface and the deposition of poorly soluble salts on it. The effect of concentration polarization can be reduced by turbulizing the boundary layer of water.

Nanofiltration(NF) removes molecules and multiply charged ions ranging in size from 0.001 to 0.01 microns, organic molecules with a molecular weight above 300, and all viruses. Nanofiltration is able to remove ions with a charge greater than 1, and singly charged to pass - the extraction of NaCl is less than 50%. The selectivity for doubly charged cations and anions is high, for example, when filtering a $MgSO_4$ solution, the recovery exceeds 98-99%. Heavy metals are removed almost completely. As a result, the degree of desalination is lower than with reverse osmosis, the filtrate contains almost no hardness salts, i.e. it softens.The greatest advantage of water nanofiltration is a decrease not only in water hardness, but also in alkalinity, as well as removal of mechanical, organic and biological contaminants in water in the absence of the need to use reagents and solving problems with salt effluents according to a relatively simple scheme. The disadvantage of nanofiltration is the need for a more thorough pretreatment of water than with ion exchange, and significantly higher consumption of water and electricity, and volumes of waste, which are low in salt [6].

Water softening by dialysis is a method of separating solutes with significantly different molecular weights. It is based on different diffusion rates of these substances through a semipermeable membrane separating concentrated and dilute solutions. Under the action of a concentration gradient (according to the law of effective masses), solutes at different rates diffuse through the membrane towards the diluted solution. The solvent (water) diffuses in the opposite direction, reducing the rate of transport of solutes. Dialysis is carried out in membrane machines with nitro- and acetate cellulose film membranes.The effectiveness of a semi-permeable membrane for water softening is determined by the high values of selectivity and water permeability, which it must maintain for a long time. Electrodialysis is the process of removing solute ions from a solution by selectively transporting them through membranes that are selective for these ions, in a constant electric field.When a constant electric field is applied to a solution of ionized substances (electrolytes), a directed movement of ions of dissolved salts, as well as ions of H^+ and OH^-, occurs. Moreover, cations move to the cathode, and anions - to the anode. Upon reaching the cathode, cations, as well as water molecules, are reduced, for example:

$$2H_2O+2e\rightarrow H_2\uparrow+2OH^- \qquad (24)$$

$$2H2^{+}+2e\rightarrow H_2\uparrow \qquad (25)$$

Anions are oxidized at the anode:

$$4OH^- - 4e\rightarrow 2H_2O+O_2 \qquad (26)$$

$$2Cl^- - 2e \rightarrow Cl_2\uparrow \qquad (27)$$

If ion-exchange membranes are placed in the electrode cell: a cation-exchange membrane that allows only cations to pass near the cathode, and an anion-exchange membrane that allows only anions to pass near the anode, then the volume of the cell will be divided into three chambers. In this case, only cations migrating to the cathode can pass into the cathode chamber from the middle one, and anions migrating to the anode into the anode chamber. The concentration of ions in the middle chamber will decrease and, conversely, increase in the near-electrode chambers. Currently, multichamber electrolyzers with a large number of pairs of cation and anion exchange membranes are used. The selectivity of the membranes creates conditions under which neither cations nor anions can pass from the odd chambers into the adjacent chambers, due to the fact that the sign of their charge coincides with the sign of the cation-exchange and anion-exchange membranes, respectively. Therefore, in the even chambers there is a desalination process, and in the odd ones, on the contrary, the concentration of salts, as a result of which brine is formed in the chambers [7].

Thus, from the above listed main methods of water treatment in heat power engineering, he showed that when using the chemical method of softening, material costs are associated with constant dosing of chemical reagents. Membrane methods of water softening based on the use of pressure forces (ultrafiltration and reverse osmosis) of the membrane must pass the solvent (water), retaining as much as possible ionic and molecular impurities. When using electrical forces, the membranes must be permeable to ions and must not allow water to pass through. Material costs are associated with the need to maintain a pressure greater than osmotic (ultrafiltration and reverse osmosis), the need to apply a constant electric current to the solution (electrodialysis), as well as the need to periodically replace membranes due to their limited service life.

The water treatment technology should be selected individually for each object, taking into account the composition of the source water, the requirements for circulating water, the qualifications of the operating personnel, etc. Since the hardness of the cooling water should be moderate and the use of the ion-exchange method of water softening will reduce the cost of cleaning refrigeration compartments and will extend the life of the refrigerator. The lower the temperature of the cooled water in the refrigerator, the better it cools the methyldiethanolamine(MDEA) solution. This, in turn, leads to better gas purity, fewer electric motors in the AVZ-1 device and energy savings.

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