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RESEARCH INTO ION EXCHANGE SOFTENING OF HIGHLY MINERALIZED WATERS

M. Gomelya
Doctor of Technical Sciences,
Professor, Head of Department*
E-mail: m.gomelya@kpi.ua
V. Hrabitchenko
Postgraduate Student*
E-mail: shymasya@mail.ru
A. Trokhymenko
Ph.D, Associate Professor
Department of Environmental Health and Safety
Admiral Makarov National University of Shipbilding
Stalingrad Heroes ave., 9, Mykolaiv, Ukraine, 54025
E-mail: antr@ukr.net
T. Shabliy
Doctor of Technical Sciences, Associate Professor*
E-mail: dsts1@ukr.net
*Department of Ecology and Technology of Plant Polymers
National Technical University of Ukraine
"Kyiv Polytechnic Institute"
Peremohy ave., 37, Kyiv, Ukraine, 03056

Вивчено процеси натрій-катіонного пом'якшення високомінералізованих вод з використанням сильно- та слабокислотних катіонітів для стабілізації води. Показано, що слабокислотний катіоніт Dowex Mac-3 в натрій формі забезпечує ефективне вилучення іонів жорсткості із води при високих концентраціях іонів натрію (>1650 мг-екв/дм^3), що дозволяє ефективно переробляти високомінералізовані води

Ключові слова: знесолення води, катіоніт, пом'якшення води, регенерація катіоніту, кислотність, лужність

Изучены процессы натрий-катионного умягчения высокоминерализованных вод с использованием сильно- и слабокислотных катионитов для стабилизации воды. Показано, что слабокислотный катионит Dowex Mac-3 в натрий форме обеспечивает эффективное удаление ионов жесткости из воды при высоких концентрациях ионов натрия (>1650 мг-экв/дм^3), что позволяет эффективно перерабатывать высокоминерализованные воды

Ключевые слова: обессоливание воды, катионит, умягчение воды, регенерация катионита, кислотность, щелочность

1. Introduction

The processes of desalting, purification and conditioning of waters are often connected with ion exchange processes of their softening. These processes are used during stabilizing water treatment for water circulating cooling systems or before its reverse osmosis desalination. Ion exchange is also widely used during cleaning of saline solutions from ions of hardness before electrolysis (obtaining sodium hypochlorite and other oxidized compounds of chlorine).

Reagent methods of softening are always accompanied by formation and release of sediments, which significantly complicates the technology and are characterized by the lack of efficiency. On the other hand, efficiency of ion exchange desalination of water depends on the level of its mineralization. In this case, the application of ion exchange for the treatment of mineralized waters is considered to be problematic. Therefore, determining the conditions of ion exchange softening of mineralized waters is a relevant task.

2. Literature review and problem statement

Water desalting technologies increasingly use reverse osmosis and nanofiltering methods [1]. These methods are also widely used for the wastewater treatment [2]. The disadvantage of these methods is the use of expensive semipermeable membranes, which requires highly efficient pre-treatment of water to prevent the formation of deposits on the membranes. The paper [3] shows that improperly efficient mechanical cleaning of water before the baromembrane processes reduces the productivity of membranes and impairs their selectivity. In addition to efficient mechanical water purification, it is necessary to prevent deposition on the surface of a membrane of calcium sulfate and carbonate, which is quite possible if one considers that the content of sulphates in seawater reaches 35 mg-eqv/dm^3 while the hardness is 40–60 mg-eqv/dm^3.

The easiest way to stabilize the water with regard to the deposition of sediments is the use of antiscalants [4]. But because of their toxicity and large amounts of concentrates that are discharged during reverse osmosis water desalination, the problem of recycling the waste is considerably complicated. Less toxic are the antiscalants based on polyacrylic acids and their derivatives [5] but because of their high price, the cost of water purification significantly increases.

At the reagent softening of water [6], the technology of preliminary clarification of water is significantly complicated. In addition, water has a higher pH value. Stabilizing treatment of water by the removal of sulfates [7] implies the use of expensive aluminum coagulants and is accompanied by formation of large volumes of sediments, which complicates clarification of water. Application of ion exchange for stabilizing water treatment [8] is possible at a relatively low salt content. At high concentrations of sodium chloride, the processes of desorption of ions of hardness dominate the processes of sorption, which dramatically reduces the efficiency of water softening on strong acid cationites.

Low capacity on ions of heavy metals and ions of hardness also characterizes organic and inorganic ions in strongly mineralized water [9]. The use of weak acidic cationites in acidic form in the preliminary treatment of water provides efficient decarbonization of water with a low efficiency of its softening [10]. At low alkalinity of water and at a high level of mineralization, the application of weak acidic cationites in acidic form does not ensure its efficient softening [11]. In general, despite the widespread use of ion exchange in the conditioning of water [12], the use of this method for stabilizing treatment of salty natural and waste waters is not efficient. One of the disadvantages of application of weak acidic cationites for water softening is very low efficiency of their regeneration [13]. But that is exactly why it is expedient to use them in the softening of salt waters with high content of sodium ions.

3. The purpose and objectives of the study

The purpose of the work was to determine the effectiveness of ion exchange softening of highly mineralized waters depending on the type and form of ionite with subsequent regeneration of cationites for efficient desorption of ions of hardness.

To achieve the set goal, the following problems were solved:

– study of the processes of sodium-cationic softening of highly mineralized waters on strong- and weak acidic cationites;

– determining the efficiency of water decarbonization when using weak acidic cationite in acidic form;

– study of the processes of regeneration of strong- and weak acidic cationites with sequential use of the solutions of hydrochloric acid.

4. Materials and methods of the study

In the processes of ion-exchange water softening we used strong acidic cationite in the Na^+ form and weak acidic cationite Dowex Mac-3 in the acidic and Na^+ form. The processes of softening were performed during filtering of the model solutions through a layer of cationites in the volume of 20–50 cm^3 that were placed in the columns of diameter 19 mm. The consumption of solutions at sorption is 10–12 cm^3/min., at regeneration is 1–2 cm^3/min. In the selected samples with the volume of 200 cm^3 (at sorption) and 50 cm^3 (regeneration), we determined total hardness, calcium concentration, acidity and alkalinity.

For the sorption we used model solutions:

M1: H_{in}=50 mg-eqv/dm^3, A_{in}=5,8 mg-eqv/dm^3, C (Ca^{2+})=22 mg-eqv/dm^3, C (Mg^{2+})=28 mg-eqv/dm^3, C (Cl^-)=192 mg-eqv/dm^3, C (SO_4^{2-})=28 mg-eqv/dm^3, C (Na^+)=176 mg-eqv/dm^3, pH=8,0;

M2: H_{in}=50 mg-eqv/dm^3, A_{in}=4,0 mg-eqv/dm^3, C (Ca^{2+})=24 mg-eqv/dm^3, C (Mg^{2+})=32 mg-eqv/dm^3, C (Cl^-)=300 mg-eqv/dm^3, C (SO_4^{2-})=33 mg-eqv/dm^3, C (Na^+)=281 mg-eqv/dm^3, pH=8,2;

M3: H_{in}=90 mg-eqv/dm^3, C (Ca^{2+})=65 mg-eqv/dm^3, C (Mg^{2+})=25 mg-eqv/dm^3, C (Cl^-)=105 mg-eqv/dm^3, C (SO_4^{2-})=5 mg-eqv/dm^3, C (Na^+)=15 mg-eqv/dm^3, pH=7,5;

M4: H_{in}=150 mg-eqv/dm^3, C (Ca^{2+})=75 mg-eqv/dm^3, C (Mg^{2+})=75 mg-eqv/dm^3, C (Cl^-)=165 mg-eqv/dm^3, C (Na^+)=15 mg-eqv/dm^3, pH=7,3;

M5: H_{in}=59,5 mg-eqv/dm^3, A_{in}=3,1 mg-eqv/dm^3, C (Ca^{2+})=26,5 mg-eqv/dm^3, C (Mg^{2+})=33 mg-eqv/dm^3, C (Na^+)=478 mg-eqv/dm^3, pH=6,5;

M6: H_{in}=60 mg-eqv/dm^3, A_{in}=3,0 mg-eqv/dm^3, C (Ca^{2+})=24 mg-eqv/dm^3, C (Mg^{2+})=36 mg-eqv/dm^3, C (Cl^-)=1638 mg-eqv/dm^3, C (SO_4^{2-})=36 mg-eqv/dm^3, C (Na^+)=1617 mg-eqv/dm^3, pH=6,3;

M7: H_{in}=59 mg-eqv/dm^3, A_{in}=19 mg-eqv/dm^3, C (Ca^{2+})=26 mg-eqv/dm^3, C (Mg^{2+})=33 mg-eqv/dm^3, C (Cl^-)=500 mg-eqv/dm^3, C (SO_4^{2-})=33 mg-eqv/dm^3, C (Na^+)=493 mg-eqv/dm^3, pH=6,5.

For the regeneration we used a 10 % solution of hydrochloric acid.

The values of total exchange dynamic capacity of ionites and the degree of their regeneration was calculated by the known methods [10].

5. Results of ion-exchange softening of mineralized solutions

Results on softening the solutions M1 and M2 on strong acidic cationite KU-2-8 in the Na^+-form are given in Fig. 1. As can be seen in Fig. 1, TEDC of ionite on hardness ions decreases from 1744 to 1295 mg-eqv/dm^3 with increase in the concentration of sodium in the original solution from 176 to 281 mg-eqv/dm^3. In this case, the capacity up to the breakthrough decreased from 1050 to 495 mg-eqv/dm^3, respectively. Further increase in the content of sodium chloride in water was inexpedient because efficient desorption of hardness ions occurs in the 3 % solution of sodium chloride [11].

Unlike the strong acidic cationite KU-2-8, the weak acidic Dowex Mac-3 is characterized by high capacity on the ions of hardness not only during purification of the solutions with a low concentration of sodium chloride (Fig. 2), but at a significant level of mineralization (Fig. 3).

Thus, in the solution M5, the content of sodium chloride is close to 3 %, but TEDC of cationite under these conditions reached 3106 mg-eqv/dm^3.

More to the point, even at the concentration of sodium chloride close to 100 g/dm^3 (10 %), this cationite provided efficient removal of the ions of hardness from water. TEDC of ionite by the ions of calcium reached 1500 mg-eqv/dm^3, and by the ions of hardness as a whole – 2600 mg-eqv/dm^3 (Fig. 4). This indicates that this cationite in the Na^+-form is capable to absorb the ions of calcium and magnesium under conditions when, in the case of strong acidic cationites, desorption of the ions of hardness occurs. That is, this cationite is capable to absorb the hardness ions from solutions with high content of sodium ions.

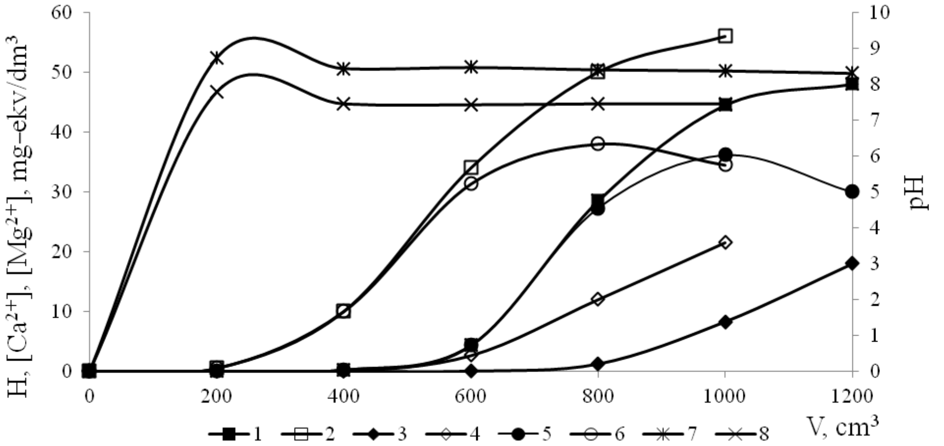

Fig. 1. Dependency of hardness (1; 2), concentration of calcium ions (3; 4), magnesium (5; 6) and pH (7; 8) on the passed volume of the model solution M1 (1; 3; 5; 7) and M2 (2; 4; 6; 8) through cationite KU-2-8 in the Na^+-form (V_i=20 cm^3); $TEDC_1$=1744 mg-eqv/dm^3, $TEDC_2$=1295 mg-eqv/dm^3, $TEDC_3$=1045 mg-eqv/dm^3, $TEDC_4$=870 mg-eqv/dm^3, $TEDC_5$=699 mg-eqv/dm^3, $TEDC_6$=457 mg-eqv/dm^3

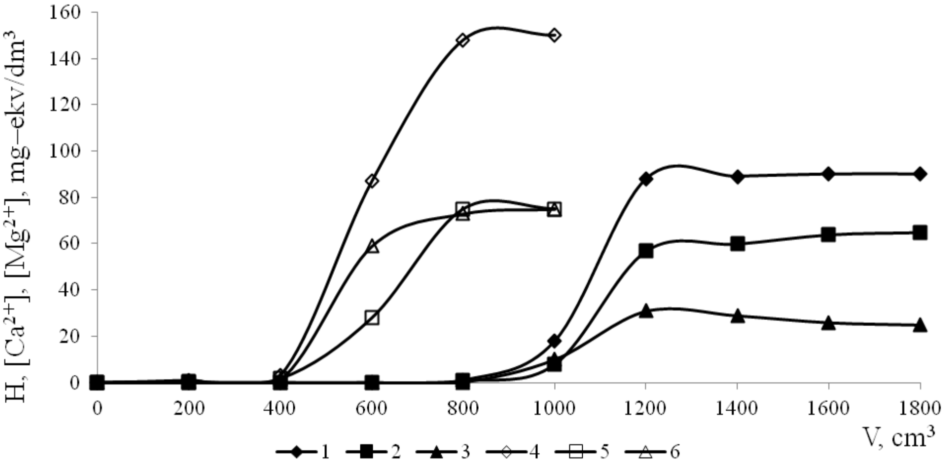

Fig. 2. Dependency of initial hardness (1; 4), concentration of calcium ions (2; 5) and magnesium (3; 6) on the passed volume of the M3 solution through ionite Dowex Mac-3 in the Na^+-form (V_i=20 cm^3); $TEDC_1$=4412 mg-eqv/dm^3, $TEDC_2$=3400 mg-eqv/dm^3, $TEDC_3$=1012 mg-eqv/dm^3, $TEDC_4$=4038 mg-eqv/dm^3, $TEDC_5$=2148 mg-eqv/dm^3, $TEDC_6$=1890 mg-eqv/dm^3

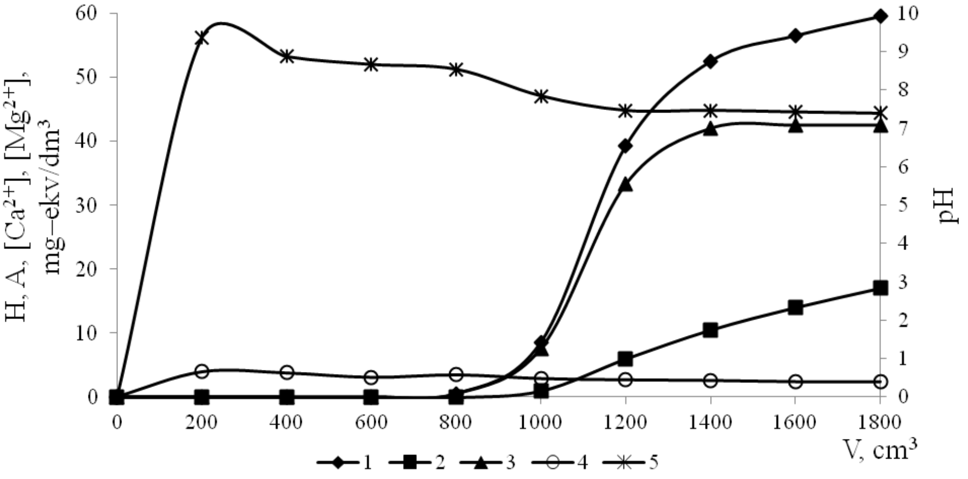

Fig. 3. Dependency of the output values of hardness (1), concentration of calcium ions (2), magnesium (3), alkalinity (4) and pH (5) on the passed volume of the solution M5 through cationite Dowex Mac-3 in the Na^+-form (V_i=20 cm^3); $TEDC_1$=3106 mg-eqv/dm^3, $TEDC_2$=1810 mg-eqv/dm^3, $TEDC_3$=1296 mg-eqv/dm^3

Interesting results were obtained in the processing of highly mineralized solutions on weak acidic cationite Dowex Mac-3 in acidic form. As is known [11], in the absence of carbonate and bicarbonate ions, this cationite in acidic form does not absorb cations of metals from the solutions of salts of strong acids. However, in the case of solutions with bicarbonate alkalinity, partial water softening happens with its complete decarbonization at the first stage (Fig. 5). When this occurs, water acidification and reducing its pH to 3–4 take place. Later on, when the cationite runs out of capacity, pH rises to 7 and alkalinity – to the initial values.

This effect can be used in the treatment of water with mineralization up to 2,0–2,5 g/dm^3. In this case, it is possible to consistently use cationite Dowex Mac-3 in acidic form and cationite KU-2-8 in Na$^+$-, which provides decarbonization and water softening at the stable value of pH at the level 7.

The processes of regeneration of cationites by acids and salts were well explored [14, 15]. The paper determined conditions of using exhausted regeneration solutions formed during regeneration of strong acidic cationites for the regeneration of weak acidic cationites. As can be seen in Fig. 6, during a sequential passage of the 10 % solution of HCl through cationites KU-2-8 and Dowex Mac-3, Ca, Mg-form achieved almost complete desorption of the hardness ions from both strong- and weak acidic cationite.

Efficient regeneration of strong acidic cationite is achieved by a significant excess of acid. In this case, the excess acid in the solution provided further desorption of the ions of hardness from weak acidic cationite, which even in a weak acidic medium transfers to associated form and easily absorbs the cations of metals [10]. This method of regeneration of cationites provides significant reduction in consumption of acid when using a two-step cationization of water during its softening and desalination.

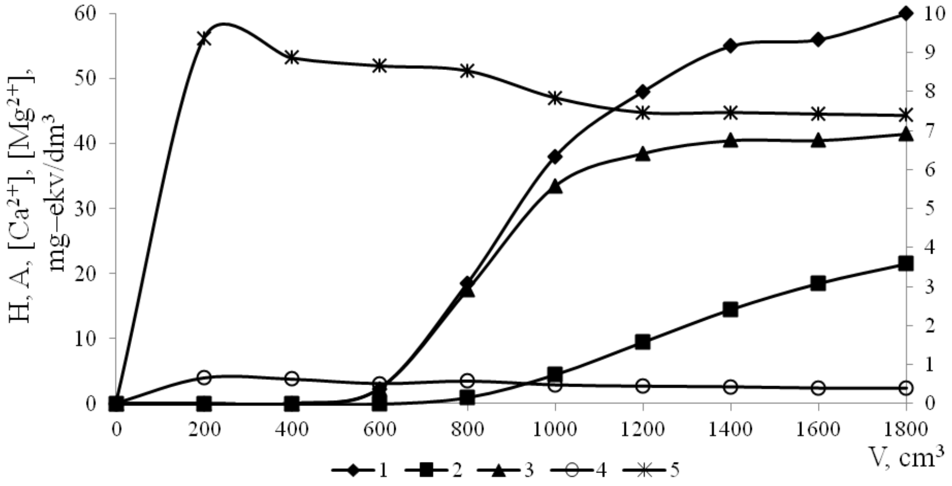

Fig. 4. Dependency of the output values of hardness (1), concentration of calcium ions (2), magnesium (3), alkalinity (4) and pH (5) on the passed volume of the solution M6 through a cationite Dowex Mac-3 in the Na$^+$-form (V_i=20 cm^3);
TEDC$_1$=2622 mg-eqv/dm^3, TEDC$_2$=1510 mg-eqv/dm^3, TEDC$_3$=1112 mg-eqv/dm^3

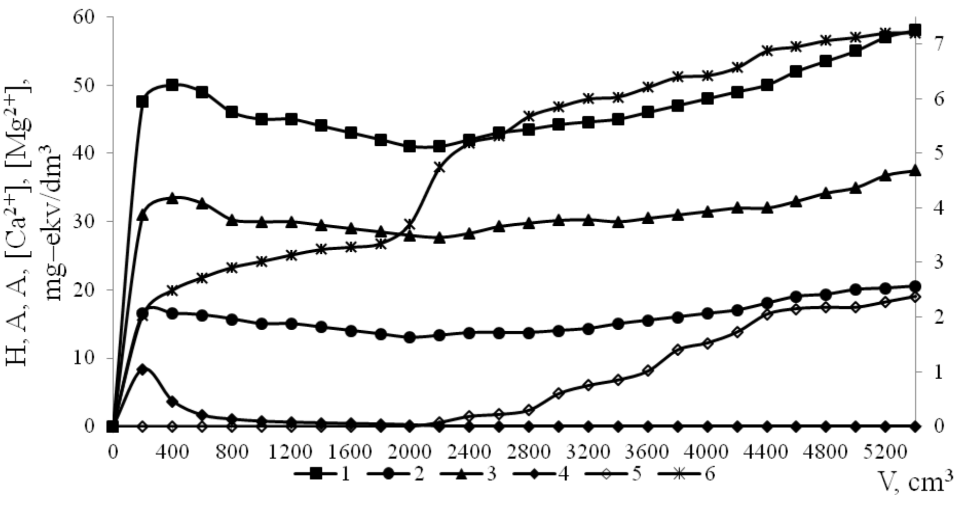

Fig. 5. Dependency of the output values of hardness (1), concentration of calcium ions (2), magnesium (3), acidity (4), alkalinity (5) and pH (6) on the passed volume of the solution M7 through cationite Dowex Mac-3 in the Na$^+$-form (V_i=20 cm^3)

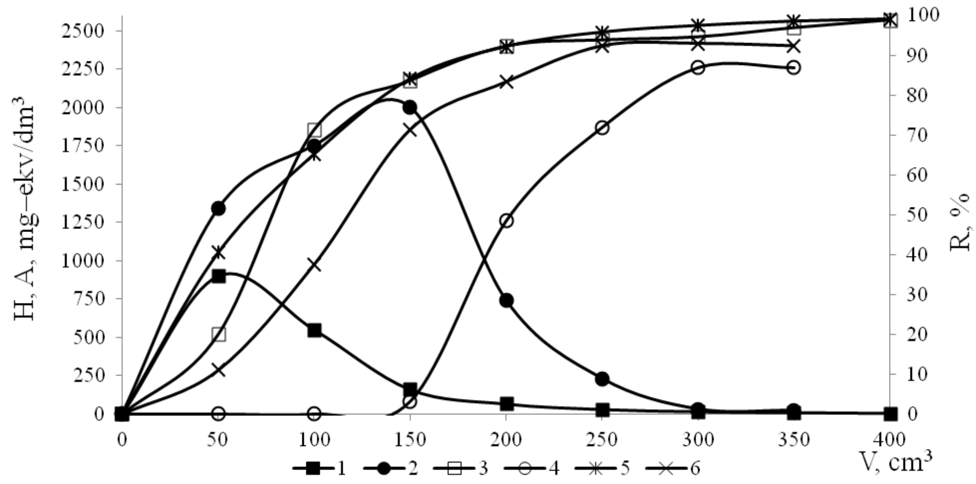

Fig. 6. Output curves of desorption of the ions of hardness (1; 2) and dependency of acidity (3; 4), degree of desorption of hardness ions (5; 6) on the passed volume of the 10 % solution of HCl sequentially through cationite KU-2-8 (1; 3; 5) and Dowex Mac-3 (2; 4; 6) in Ca, Mg form at the volume of ionite 50 cm^3

6. Discussion of the results of research into softening of mineralized solutions on strong- and weak acidic cationites

If we compare the data presented in Fig. 1–4, then one may note a significant reduction in the capacity of strong acidic cationite by the ions of hardness with increasing concentration of sodium ions in the solution. For weak acidic cationite this trend is less noticeable (Table 1). Even at the concentration of sodium chloride ≈100 g/dm^3, TEDC on the ions of hardness for cationite Dowex Mac-3 exceeds 2600 mg-eqv/dm^3. It should be noted that the selectivity of both cationites on calcium ions is higher compared to magnesium ions.

Table 1

Dependency of the exchange capacity of strong- and weak acidic cationites by calcium and magnesium ions depending on cationic composition of water

Cationite	Concentration of cations in solution, mg-eqv/dm^3			TEDC, mg-eqv/dm^3		
	Na$^+$	Ca^{2+}	Mg^{2+}	Ca^{2+}, Mg^{2+}	Ca^{2+}	Mg^{2+}
KU-2-8	176	22	28	1744	1045	699
	281	24	32	1295	838	457
Dowex Mac-3	15	65	25	4412	3400	1012
	15	75	75	4038	2148	1890
	468	26	33	3106	1810	1296
	1638	24	36	2622	1510	1112

In the case of weak acidic cationite, the selectivity by calcium ions increases along with the growth of concentration of sodium chloride in the solution. This is very important because in most cases the formation of deposits is caused by calcium compounds – carbonates and sulphates. Therefore, the duration of the filter cycle at the softening of water on cationite can be defined by the breakthrough of calcium ions. In general, this will significantly increase the efficiency of the use of cationites in the ion exchange softening of mineralized solutions.

The peculiarity of sodium-cationic water softening is the increased pH of the medium, up to 8–9, after the treatment of water at an ion exchange filter. It is typical for both strong- and weak acidic cationites (Fig. 1, 3, 4). It is predetermined by the transition of calcium and magnesium bicarbonates to sodium bicarbonate at the exchange of hardness ions to sodium ions. Of course, hydrolysis of sodium hydrogen carbonate is stronger because alkali is a significantly stronger base compared to calcium and magnesium hydroxides.

When using weak acidic cationite in acidic form, the sorption of the ions of hardness is only possible under certain concentrations of hydrogen carbonates or carbonates in water. Under other conditions, the acidification of water occurs, which leads to the transition of ionite to associated form and deterioration of its ion-exchange properties. According to reactions (1), the process is carried out by the scheme:

$$2PC(O)O^{-}H^{+}+MeCl_2\neq[PC(O)O^{-}]_2Me^{2+}+HCl, \qquad (1)$$

where P is the remainder of a polymer matrix

Me^{2+}–Ca^{2+}, Mg^{2+}.

Since hydrochloric acid is stronger than carbon acid of ionite, the reaction (1) does not occur. On the other hand, in the presence of hydrogen carbonates, the reaction proceeds with the release of carbonic acid (2), (3):

$$2PC(O)O^{-}H^{+}+$$
$$+Me(HCO_3)_2\leftrightarrow[PC(O)O^{-}]_2Me^{2+}+H_2CO_3, \qquad (2)$$

$$H_2CO_3\leftrightarrow H_2O+CO_2\uparrow. \qquad (3)$$

Therefore, the capacity of weak acidic cationite in acidic form on the ions of hardness is determined by bicarbonate alkalinity of water (Fig. 5). Reactions (2), (3) determine both decarbonization of water and its acidification.

Actually, it is the low acidity of carboxyl groups of cationite Dowex Mac-3 that provides high efficiency of its regeneration, including by exhausted regenerative solutions (Fig. 6).

7. Conclusions

1. The influence of concentration of sodium salts in aqueous solutions on the efficiency of their softening on cationites was determined. It was demonstrated that with increasing concentrations of cations of sodium in water, the capacitance of strong acidic cationite on the ions of hardness decreases. The capacitance of weak acidic cationite Dowex Mac-3 in the Na^+-form on the ions of hardness remains high with an increase in the concentration of sodium chloride in the solution of up to 100 g/dm^3.

2. It was found that when using weak acidic cationite Dowex Mac-3 in acidic form, decarbonization of water occurs with partial softening. Reducing water hardness on cationite in acidic form is limited by the level of hydrocarbonate alkalinity.

3. It was demonstrated that acidic regenerative solutions after regeneration of strong acidic cationite KU-2-8 in the Ca^{2+}, Mg^{2+} form may be used to regenerate weak acidic cationite Dowex Mac-3 in the Ca^{2+}, Mg^{2+} form. In this case, there is a complete regeneration of weak acidic cationite Dowex Mac-3, which is predetermined by low acidity of its carboxyl groups.

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