Comparison contemporary methods of regeneration sodium-cationic filters

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Abstract. Regeneration plays a crucial role in the field of efficient application sodium-cationic filters for softening the water. Traditionally used as regenerant saline NaCl. However, due to the modern development of the energy industry and its close relationship with other industrial and academic sectors the opportunity to use in the regeneration of other solutions. The report estimated data and application possibilities as regenerant solutions sodium-cationic filters brine wells a high mineral content, as both primary application and after balneotherapeutic use reverse osmosis and concentrates especially recycled regenerant water repeated. Comparison of the effectiveness of these solutions with the traditional use of NaCl. Developed and tested system for the processing of highly mineralized brines wells after balneological use. Recommendations for use as regeneration solutions for the sodium-cationic unit considered solutions and defined rules of brine for regeneration costs.

One of the current areas of application of ion-exchange technologies is softening of natural, sewage and sea water. [1]. The purpose of using ion exchange in this area is to produce water suitable for feeding steam and hot water boilers, thermal desalting plants, thermal networks. The most common scheme for purifying such water includes sodium-cation plants of a single-stage or two-stage type.

The sodium cationing process consists in filtering the source water through a layer of cation exchanger containing sodium cations as exchange ions. In this case, the cationite absorbs from the water the ions \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \), which determine its rigidity, and the equivalent quantity of Na\(^+\) ions passes into the water from the cation exchanger. The mechanism of the reactions taking place in this process can be written in the following form:

\[
2\text{Na}[\text{K}] + (\text{Ca}(\text{HCO}_3)_2/\text{Mg}(\text{HCO}_3)_2) = (\text{Ca}[\text{K}]_2/\text{Mg}[\text{K}]_2) + 2\text{NaHCO}_3;
\]

\[
2\text{Na}[\text{K}] + (\text{CaCl}_2/\text{MgCl}_2) = (\text{Ca}[\text{K}]_2/\text{Mg}[\text{K}]_2) + 2\text{NaCl},
\]

where \([\text{K}]\) is the insoluble cationite matrix [2].

The processes of ion exchange are reversible. Therefore, at a high concentration of Na\(^+\) ions in a solution in contact with the cation exchanger containing Ca\(^{2+}\) and Mg\(^{2+}\) ions, the reaction proceeds in the opposite direction. This process is used to regenerate the depleted cation exchanger by displacing previously absorbed calcium and magnesium ions from it with a concentrated NaCl solution.

The main technological parameters of the Na-cationing process of water - the working exchange capacity of this cationite and the residual rigidity of the filtrate - depend on the composition of the softened water and the ion-exchange regeneration regime (the amount of reagent, concentration and degree of contamination of the regeneration solution with calcium and magnesium).
The most important is the action of the so-called counterions, namely the concentration of Na\(^+\) ions in the softened water, and Ca\(^{2+}\) and Mg\(^{2+}\) ions in the regeneration solution. The increase in the concentration in the liquid phase of the ion contained in the cationite, according to the law of acting masses, inhibits the reactions of water softening or regeneration of the cation exchanger, directs these reactions in the opposite direction. Therefore, other things being equal, the higher the mineralization of the softened water, the greater the concentration of sodium ions in the softened water leaving the cation exchange filter and, consequently, the greater the counterion effect. The counterion concentration is determined not only by the initial content of the Na\(^+\) ion in the initial water, but also by the amount of Na\(^+\) that is obtained as a result of Na cationing. The concentration of Na\(^+\) in the softened water, which determines its residual hardness, is equal to the sum of the concentrations of all cations (including Na\(^+\)) in the initial water. A significant increase in the filtrate stiffness (over 20-30 μg-eq/dm\(^3\)) is usually observed with salt content of water ≥ 500 mg/dm\(^3\) [3].

For the regeneration of Na-cation exchanger filters at TPPs and in industry, depending on local conditions and the feasibility study, the following is used: technical common salt; Table salt; Underground natural brines; Specially purified underground natural brines (production wastes); Purge water evaporators; sea water; Reinforced repeated regeneration water; Washing water of Na-cation-exchange filters; Concentrate of reverse osmosis.

Technical salt is the most common regenerating agent for the regeneration of Na-cation exchanger filters. Specific salt consumption for regeneration is taken with the regeneration solution. The increase in the concentration of the regeneration solution is usually observed with salt content of water ≥ 500 mg/dm\(^3\) [3].

In this case, a three-fold change in the regeneration solution in the volume of the loaded cation exchanger is desirable.

In addition to technical salt, the most widely used in the regeneration of Na-cationite filters are natural brines. Natural brines belong to the sediments of the Vendian-Soryazh water-bearing complex, which lies at a depth of 1,150 - 1,200 meters from the surface of the earth. The characteristics of natural brines are presented in Table 1 [15].

| Index               | Notation | Unit of measurement | Value         |
|---------------------|----------|---------------------|---------------|
| Hydrogen index      | pH       | G/dm\(^3\)          | 5.0 – 6.6     |
| Sodium              | Na\(^+\) | G/dm\(^3\)          | 71.7 – 89.1   |
| Calcium             | Ca\(^{2+}\) | G/dm\(^3\)      | 7.1 – 12.7    |
| Magnesium           | Mg\(^{2+}\) | G/dm\(^3\)      | 2.2 – 5.9     |
| Strontium           | Sr\(^{2+}\) | G/dm\(^3\)      | 0.05 – 0.7    |
| Lithium             | Li\(^+\) | G/dm\(^3\)         | 0.002 – 0.007 |
| Chlorides           | Cl\(^-\) | G/dm\(^3\)         | 102.8 – 161.7 |
| Sulphates           | SO\(_4^{2-}\) | G/dm\(^3\)      | 0.05 – 0.7    |
| Hydrocarbons        | HCO\(_3^{-}\) | G/dm\(^3\)      | 0.004 – 0.07  |
| Bromides            | Br\(^-\) | G/dm\(^3\)         | 0.07 – 1.5    |
| Total mineralization| -        | G/dm\(^3\)         | 240 – 280     |
| Brine temperature   | t        | °C                   | 20 – 30       |

The main requirements to the quality of extracted brines from the point of view of their application for the purposes of regeneration of Na-cation exchanger filters of TPP of thermal power plants are as follows: the brine must have a sodium chloride composition; The brine rigidity should not exceed 500 mg-eq/dm\(^3\), with a mineralization of 100-150 g/dm\(^3\), and not more than 1500 mg-eq/dm\(^3\), with salinity of 250-300 g/dm\(^3\). The presence of counter ions in the regeneration solution due to the contamination of the regenerating agent with calcium and magnesium compounds leads to a decrease in the cationite regeneration effect, respectively, its working exchange capacity decreases [3].

The main indicators determining the efficiency of the regeneration regime and the amount of working capacity of Na-cation exchanger absorption are the reagent consumption and the concentration of the regeneration solution. The higher the consumption of the reagent, the fuller the regeneration of the
cation exchanger, thereby increasing the working capacity of the cation exchanger. However, there is no direct proportionality between the salt consumption and the degree of regeneration of the cation exchanger [4].

The effect of increase in exchange capacity with an increase in salt consumption of more than 300 g/g-eq is markedly reduced. In practice, the consumption of salt for regeneration is assumed to be within the range of 120-140 g/g-eq for economic and environmental reasons, therefore the working exchange capacity does not reach the values of the total.

The effect of cationite regeneration increases with increasing concentration of NaCl solution. However, with a constant consumption of the reagent, such an increase in its concentration leads to a corresponding decrease in the volume of the regeneration solution. The latter circumstance reduces the effect of regeneration of the cation exchanger, since Ca\(^{2+}\) and Mg\(^{2+}\) ions displaced from the cation exchanger are distributed in a smaller volume. On the other hand, a decrease in the volume of the salt solution reduces the exchange of the latter in the space between the cationite grains (usually a threefold change of liquid in this space is desirable), which also reduces the completeness of regeneration.

The greatest effect of regeneration is achieved in the range of salt concentrations from 6 to 10% [6]. For better use of salt, two-step regeneration is recommended: first diluted (2 - 3%), and then more concentrated (10 - 12%) saline solution. At the beginning, when the cation exchanger is saturated with Ca\(^{2+}\) and Mg\(^{2+}\), the latter are sufficiently well replaced by a weak salt solution; The "remains" of these cation exchangers are displaced by a small amount of a stronger and less depleted reagent solution.

The effect of regeneration of the cation exchanger at a given consumption of the reagent to a certain limit increases with the duration of contact between the salt solution and the cation exchanger. The optimal contact time is 25-35 minutes [6]. Increasing the duration of the contact gives a slight improvement in the regeneration effect. During this time, the diffusion of Na\(^{+}\) ions deep into the cationite grains and Ca\(^{2+}\) and Mg\(^{2+}\) ions from the cationite into the solution is successfully completed. This determines the optimum filtration rate of the regeneration solution through the cationite layer, which at a bed height of 1.5-2.0 m is 4-6 m/h [3]. Speed below 4.0 m/h is not recommended for the hydrodynamic conditions of the filter.

The increase in the temperature of the regeneration solution intensifies the diffusion of ions in the cation exchanger and thereby improves the effect of regeneration of the cation exchanger; Therefore, in some plants, the salt solution is preheated to 35-40 °C. In this case, it is also advisable to preheat to this temperature also the cationite itself by passing through a filter of warm water, since the volume of the regeneration solution is small and when its contact with the "cold" cationite, its temperature is greatly reduced. Lowering the temperature, weakening the diffusion processes, reduces the cationite regeneration effect, and also worsens the process of water softening. Therefore, it is not recommended to work on Na-cationite filters with a temperature below 15 - 20 °C [3].

On the basis of NRU "MPEI" it was decided to carry out experimental work to obtain data comparing the efficiency of regeneration of the Na-cationite filter using a technical salt and brines of various concentrations. The relevance and significance of this work is confirmed by the increased interest and successful application of various types of regeneration of Na-cationite filters in a number of works [7 – 11]. For the experiments, the cation exchanger KU-2-8 was used in the sodium form. The cation exchanger was loaded into an ion exchange column with an internal diameter of 22 mm. The height of the cation exchange was 350 mm. Preliminary washing of the cation exchanger was carried out 10 cycles of 6 hours each. The washing was carried out with water with a total hardness of 3.35 mg-eq/dm\(^3\). The water transmission rate was not more than 20 m/h. Between the preliminary washings the cation exchanger was regenerated with an 8% solution of technical salt. The specific consumption of salt was 120 g/g-eq. Regeneration was carried out using a parallel-current method. The rate of passage of the regeneration solution was not more than 5 m/h.

During the experiments, the cycles of regeneration by the common technical salt consisted of skipping 1 liter of a 10% solution of common industrial salt through a layer of cation exchanger KU-2-8 in Na-form. The skip speed was not more than 5 m/h. Cycles of regeneration by underground natural brines consisted of skipping 1 liter of 7, 10 and 14% solutions of the underground natural brine
through a layer of cation exchanger KU-2-8 in Na-form. The skip speed was not more than 5 m/h. Characteristics of the underground natural brine used in the experimental work: total mineralization 253.15 g/dm$^3$, total hardness 0.88 g-eq/dm$^3$. The number of cycles for each type of regeneration solution was 10 repetitions (10 experiments for 10% solution of table salt, 10 experiments for 7% solution of underground natural brine, 10 experiments for 10% solution of underground natural brine, 10 experiments for 14% Natural brine). The skip speed was not more than 5 m / h. Characteristics of the underground natural brine used in the experimental work: total mineralization 253.15 g / dm$^3$, total hardness 0.88 g-equiv/dm$^3$. The number of cycles for each type of regeneration solution was 10 repetitions (i.e., 10 experiments for 10% solution of table salt, 10 experiments for 7% solution of underground natural brine, 10 experiments for 10% solution of underground natural brine, 10 experiments for 14% natural brine). Based on the results of the work, the averaged values of the residual stiffness of the filtrate of the Na-cationite filter versus the volume of the transmitted water were obtained. These dependencies are shown in Fig. 1 and Fig. 2.

**Figure 1.** Output curves of Na-cationite filter after regeneration with 10% solution of common technical salt and after regeneration with 10% solution of natural underground brine.

From Fig. 1 it can be seen that the volume of water that passes through to breakthrough during regeneration by common salt is 1.5 times greater than when regenerated by natural underground brine. In Fig. 2 shows a comparison of the output curves of the filter during regeneration with a 7, 10 and 14% solution of natural underground brine. With an increase in the concentration of sodium in the brine, the volume of water that passes through is increased to break through the hardness ions, and the working exchange capacity of the cation exchanger grows.
Figure 2. Output curves of the filter when regenerating 7, 10 and 14% solution of natural underground brine.

The experimental work carried out showed that the volume of water that passes through before the hardness ion breakthrough during regeneration with a 10% solution by common salt is much higher than the volume of the water passed before the hardness ions break through when regenerating with a 10% solution of natural underground brine. The optimum concentration, which allows to get as close as possible to the indices of the regeneration solution of sodium chloride, is the concentration of 14% of the regeneration solution of the underground natural brine. The average value of the working exchange capacity of the cation exchanger after regeneration with 10% solution by common salt was 1636 g-eq/dm³, and after regeneration with a 10% solution of natural underground brine - 1083 g-eq/dm³. The averaged values of the working exchange capacity of the cation exchanger for regeneration of 7 and 14% of the solution of natural underground brine were 730 and 1536 g-eq/dm³, respectively.

The use of underground natural brines for the regeneration of Na-cationite filters is complicated by the presence in them of a large number of hardness ions, which does not allow achieving the completeness of regeneration.

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