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# Development of recommendations for the use of chloride sodium underground natural brines for regeneration of parallel-solid sodium-cationic filters with use of the cationite of Russian production as a filtering material

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**Abstract**. Currently, Na-cationic filters of parallel-flow type are widely used for the preparation of water coolant for the main and auxiliary circuits of thermal power plants. During their operation, various methods of regeneration are used, the most common of which are: regeneration with a solution of technical table salt and regeneration with natural underground brines. For the processes of regeneration of salt solutions developed application standards that characterize the basic parameters of the use of solutions for Na-cationic filters, such as the specific consumption of salt, the concentration of salt in the solution, the rate of passage of the regeneration solution. There are no similar norms for underground natural brines when used as regeneration solutions. There are General recommendations for the use of underground natural brines. In the present work, on the basis of experimental data, recommendations for the use of natural underground brines of sodium chloride composition for the regeneration of parallel-flow Na-cationic filters are developed.

## 1.  Introduction

The use of Na-cation exchanger filters for the preparation of a water coolant for main and auxiliary circuits of thermal power plants (TPPs) is currently in high demand. Filters of this type are used in the schemes of water treatment plants (VPU), the main tasks of which are: preparation of additional water for low-power boiler houses and district thermal stations; preparation of water for heating networks; production of water suitable for feeding thermal desalination plants [1–6]. In addition to the above methods, Na-cationite filters can be used as a preliminary stage of preparation of softened water before reverse osmosis plants; in schemes of parallel H-Na cationing; for softening of sea and a number of sewage, and also in the preparation of water for other purposes [3, 4, 7–11].

According to the data of [12, 13], for a total initial water hardness of up to 15 meq / dm$^3$, the limit of a possible reduction in the total stiffness with a properly selected filter material after applying one stage of Na-cationite filters is 0.05-0.2 meq / dm$^3$; The same index after application of the two-step Na-cationing scheme is 0.01 mg-eq / dm$^3$. According to the results of laboratory tests of strongly acidic cation exchanger of Russian production in Na-form, this indicator can be reduced to 5-10 μg-eq / dm$^3$

at a Na-form after a single stage of the filter with the initial water hardness equal to or less than 3 meq / dm$^3$.

One of the main roles in the operation of Na-cation-exchange filters is the regeneration process. This process can be organized both in a parallel circuit and in a countercurrent scheme. From the point of view of the depth of filtrate purification, the use of counter current regeneration is most effective [14], however, the organization of the process in this scheme is associated with a number of difficulties, so Na-cation-exchange filters with parallel regeneration are still widely used.

The process of regeneration of Na-cationite filters is also different in the way the regeneration solution is prepared. In this regard, there is a large number of methods for regenerating Na-cation exchanger filters, the most common of which is the regeneration with a solution of the technical NaCl salt. However, there are other ways of regeneration, which are presented below [3, 4, 8, 10, 15–20]: regeneration by natural underground brines of sodium chloride composition; regeneration with table salt; regeneration with concentrate obtained after reverse osmosis plants; regeneration of evaporators by purging water; regeneration by waste products of chemical industries, in the form of prepared purified brines; regeneration by sea water and technical salt in two stages; regeneration with reinforced recycled regeneration water; regeneration with a dewatering solution of washing water after Na-cation-exchange filters; regeneration by spent geothermal cooled waters.

The most widely used method of regenerating Na-cation exchanger filters, in addition to regenerating the solution with common technical salt, from the above methods, is the regeneration with natural underground chloride sodium brines. Only in Moscow is known about thirteen large power facilities, where the operation of wells with brines is carried out for the purpose of reducing the resins of ion-exchange filters [13, 14]

When comparing the efficiency of application for the processes of regeneration of Na-cation exchanger filters of the technical salt NaCl and underground natural sodium chloride brines, the quality of the obtained filtrate is obvious. However, from the economic point of view and from the point of view of operational convenience, the use of underground brines has its advantages, for example: when operating sodium chloride brines, there are no costs for transportation of chemical reagents – dry salt; No additional costs are required for salt preparation operations for use in the regeneration process.

For the processes of regeneration of Na-cationite filters using technical salt, there are normative documents and recommendations that provide the following parameters for regeneration [2, 4, 21]: the specific consumption of technical salt for regeneration is taken within the limits of 120-140 g / g-eq; the concentration of salt in the solution to achieve the greatest effect of regeneration should be measured in the range of 6 - 10%; the optimal rate of passage of the regeneration solution through the cationite layer should be 4-6 m / h. For processes of regeneration of Na-cation exchanger filters, natural subterranean brines of such recommendations, and even more so, there are no normative documents. There are only general provisions for use, underground brines. The main ones are presented below [4, 5, 22]: the natural underground brine must have a chloride sodium composition (that is, the concentration of chloride and sodium ions in the brine should be several times greater than the concentration of the remaining ions that make up the brine); the total hardness of the brine should not exceed 500 mg-eq / dm$^3$ with a total mineralization of 100–150 g / dm$^3$, and should not exceed 1500 mg-eq / dm$^3$ with a total mineralization of 250–300 g / dm$^3$.

General recommendations for the concentrations of the brines used (over sodium), for the brine flow rate and specific consumption during the regeneration process are absent. Moreover, the ways of ion exchanger regeneration by natural underground brines are also different at different energy objects. For example, in addition to the traditional method of regeneration, a contact method is used on a number of objects when the regeneration process passes in the volume of the filter by keeping the brine and cationite for a certain time (30–40 minutes) in contact.

The task of the presented studies was to determine the recommended parameters of the regeneration process of Na-cationite filters by underground natural chloride-sodium brines.

## 2. Results of experimental researches of "output curves" of sodium-cationic filter and processes of destruxtion of stronic acid cathionite of Russian production under exposure to natural underground brines

### 2.1. Results of experimental studies of the "output curves" of a Na-cation-exchange filter

To carry out the experimental studies, a laboratory stand was assembled (Figure 1) consisting of a filter column 4 filled with strongly acidic cation exchanger of Russian production in Na form 5, pump 3, for feeding treated water and regeneration solution, and also tanks 1 and 2, respectively for initial water and a natural solution with different sodium concentration. The internal diameter of the filter column was 22 mm, and the height of the cationite layer was 470 mm for all the experiments. As the initial treated water, water with a total hardness index of 3 meq / $dm^3$ was used. The same water was used for the processes of loosening and washing. The regeneration process was carried out by a parallel brine process with a natural brine with a total mineralization of 259 g / $dm^3$ with a total hardness of 0.9 g-eq / $dm^3$, and also, for comparison, a solution of common technical salt. Concentrations of the technical solution of common salt used were calculated with respect to the NaCl content of the solution, the concentration of the brine used was relative to the sodium ions in the brine. The considered scheme of the experimental setup is a one-step Na-cationing process, therefore the maximum obtained yield values of the filtrate according to the general rigidity correspond to the range from 50 to 200 μg-eq / $dm^3$, stated in [12, 13].
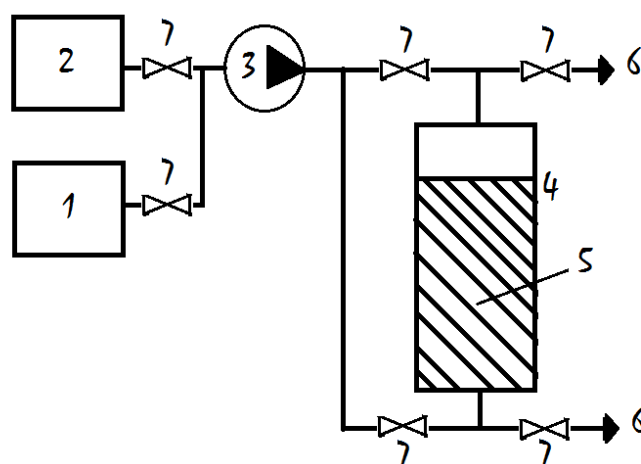


**Figure 1.** Diagram of an experimental laboratory installation.
1 – a container with initial treated water; 2 – a container with a regeneration solution; 3 – the pump; 4 – filter column; 5 – cation exchanger; 6 – drainage; 7 – gate valve.

The purpose of the first stage of the experimental work was to obtain the "output curves" of the Na-cationite filter following the results of its operation after the regeneration process carried out by 7, 10, 14 and 22% natural brine, as well as 10% solution of technical salt. The results of the work are shown in figure 2.

In figure 2 shows the "output curves" after the regeneration processes carried out at the rate of passage of the regeneration solution through the cation exchange bed equal to 5 m / h and the ratio of the volume of the regeneration solution to the volume of the cation exchanger loaded into the column is 5: 1. Similar "exit curves" were obtained for the regeneration conditions, with a constant transfer rate of the regeneration solution through the 5 m / h cationite layer, but with a ratio of the regeneration solution volume to the cation exchange of 3: 1 and 2: 1. According to the obtained experimental data (figure 3), a natural brine with a concentration of 7% was not considered further, in view of its low efficiency.

Let's pay attention to values of residual rigidity of a filtrate for a technical salt and natural brines of various concentration at filter operation before breakthrough (figure 3). When regenerating with natural

brines, the residual hardness is much higher (average value is 0.1 mg-eq / dm$^3$) than when regenerating with a technical salt (mean value is 0.02 meq / dm$^3$). Such a difference in the values of the residual stiffness is explained by the counterion effect, the mechanism of which is described in detail in [4, 22].
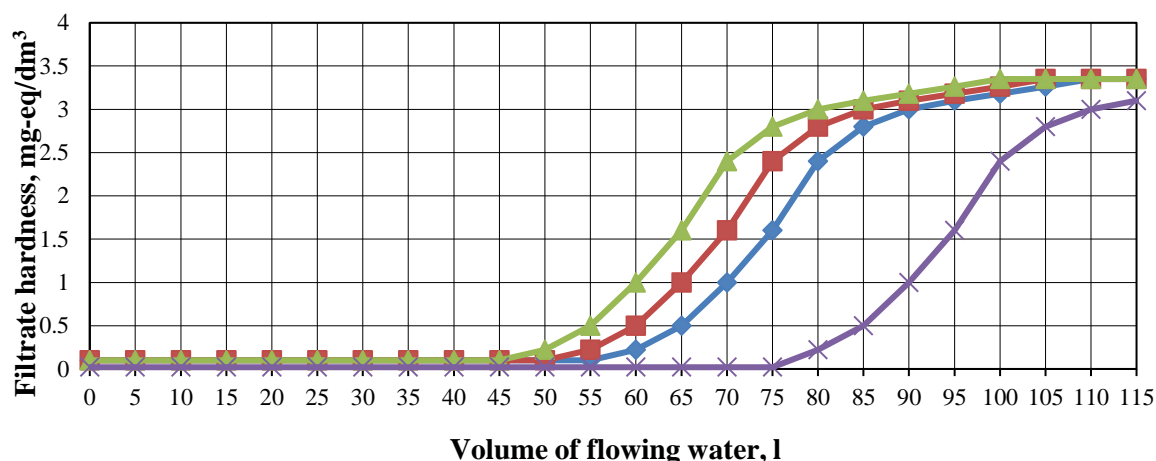


**Figure 2.** "Output curves" of Na-cation filter after regeneration processes of 7, 10, 14 and 22% by natural brine, as well as 10% solution of technical salt. Blue, orange and silver colour are brine and yellow are salt.

The next stage of the experimental work was aimed at determining the range of optimum values of the brine flow rate during the regeneration process of the Na cation filter. The process of regeneration of cation exchanger loaded into a laboratory filter column was carried out for brines with concentrations equal to 10, 14 and 22% in the content of the Na + ion at velocities of 3, 5, 7 m / h. The exchange capacitances of the cation exchanger were calculated from the obtained "output curves," the contact time of the brine and the cation exchanger used during the regeneration process was determined by the conditions of the regeneration process. The experimental results are shown in figure 3.
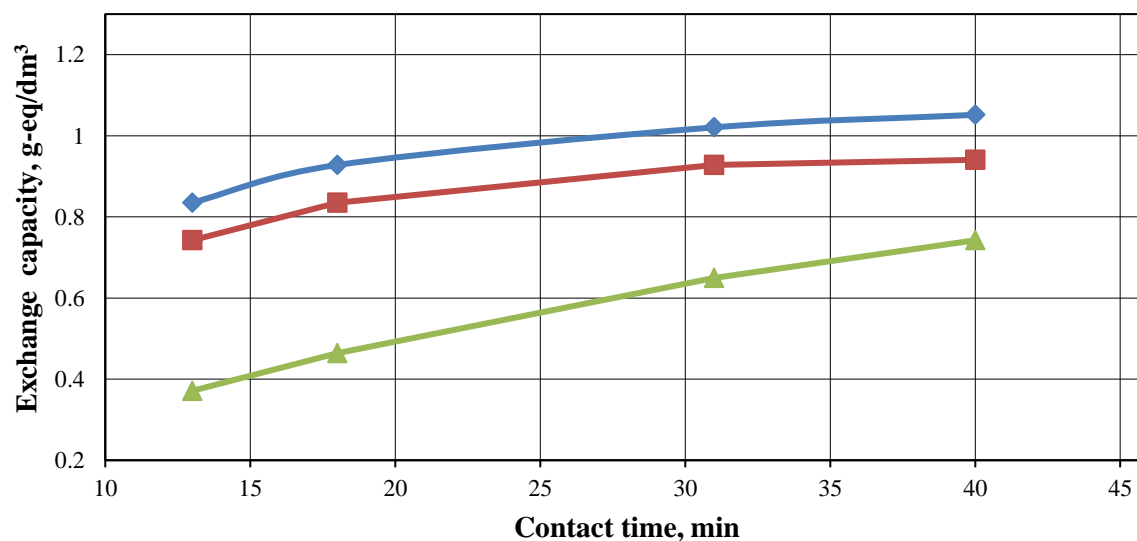


**Figure 3.** Average values of the exchange capacity of strongly acidic cationite of Russian production, depending on the time of contact of the cation exchanger with the regeneration solution of natural brine (the concentrations are calculated from the ion Na +): blue curve – 22%; maroon curve – 14%; salad curve – 10%.

From figure 3 that the values of the exchange capacity of cation exchanger after application of 10% brine during the regeneration process are significantly lower than the analogous values after application of 14% and 22% brine, and the value of the exchange capacity is 0.8 g-eq / dm3, which is the optimal operating value for This type of filter when regenerating 10% brine is unattainable. When regenerating 14% and 22% brines, the optimum contact time can be considered as the range from 18 to 25 min (the rate of flow of the regeneration solution is 4-6 m / h), as further increase in the contact time (decrease in the rate of passage of the regeneration solution is lower than 4 m / h) little increases the value of the exchange capacity and, in turn, can cause deterioration of the hydrodynamic conditions of the filter [2, 4].

*2.2. Results of research of processes of destruction of strongly acidic cationite of the Russian manufacture under the influence of natural underground brines.*

As can be seen from figure 3 values of the exchange capacity of strongly acidic cationite of Russian production after regeneration of 14% and 22% of brines practically do not differ. However, based on the results of a study of the wear processes (osmotic stability) of the cation exchanger used in the filtration and regeneration of the Na-cationite filter, the use of 14% brine proved to be preferable to the use of 22% brine for the same purposes. The surface of the cationite used was examined for damage prior to the start of the experiments, after 50 operating cycles (one cycle included filtering, loosening, regeneration and washing) and after 100 operating cycles. The study was carried out using a digital microscope DigiMicro Mobile, with magnification of 500 times.

On the surface of the cationite, which was regenerated with 14% brine, both after 50 cycles and after 100 cycles, minor damage was observed in some of the ion exchanger granules compared to the original commodity surface. The detected lesions were presented in the form of cracks, inclusions of characteristic white color, chips and deformations. Over 95% of the examined granules had no visible lesions. Investigation of the surfaces of the cationite granules, which was regenerated with 22% brine, after more than 50 cycles, more than 50% of the cationite granules examined had fractures in the form of chips, cracks and deformations, and after 100 cycles on the surface of the cationite granules significant grain structure fractures were recorded.

## 3. Recommendations for the application of natural chloride sodium underground brines for regeneration of sodium-cationic filters

Based on the results of the work, recommendations were developed for the application of natural chloride sodium subterranean brines for the regeneration of Na-cation-exchange filters of a parallel-type type. Their main provisions are given below:

to achieve the most efficient use of underground natural brines, their Na + concentration should be about 14%, further increase in concentration affects the exchange capacity of the cationite not significantly, but may lead to activation of processes of destruction of cationite granules;

when regenerating, the brine flow rate through the cation exchanger must correspond to a range of 4 to 6 m / h. An increase in the rate of passage of the regeneration solution leads to a significant decrease in the exchange capacity of the cation exchanger;

the contact time of the cation exchanger with the brine should be at least 25 minutes.

To these recommendations, when using natural underground brines, existing general recommendations should be added [4, 5, 22]:

to eliminate the enhancement of the counterion effect, the total hardness of the brine should not exceed 500 meq / dm$^3$ with a total mineralization of 100-150 g / dm$^3$, and should not exceed 1500 meq / dm$^3$ with a total mineralization of 250-300 g / dm$^3$;

The natural underground brine must have a sodium chloride composition.

As a result of the studies carried out to determine the osmotic stability of the cation exchanger, the percentage of destruction of the cation exchanger granules obtained during the regeneration of 14% by brine corresponds to the existing standards for the consumption of cation exchanger when operating in the first stage of the TPU using the technical salt for regeneration and amounts to 10% [21].

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