Wastewater from the regeneration of cation-exchange filters for water treatment

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Abstract. This scientific paper refers to the study of wastewater from the demineralized water production. The wastewater composition generated during the regeneration and washing of cation-exchange filters of the first and second stages in the water treatment shop of the Sterlitamak heat station was studied. Analysis of metal content in the wastewater of cation exchange filters was carried out by atomic absorption method on a «Saturn 3P1» apparatus. It is shown that these drains are of acidic type. More than 20 cations of various metals were found in the wastewater. The highest content is observed for sodium, calcium and magnesium ions in the drain. It is noted that the wastewater generated by the regeneration of cation-exchange filters without preliminary preparation is not suitable for electrochemical processing to produce acid and alkali.

1. Introduction
The enterprises of many branches of industry consume desalted water. The main technology for demineralized water producing is the ion-exchange one [1-3].

In the water treatment workshop of the Sterlitamak heat station, the process of demineralized water obtaining proceeds in two stages. The first stage (pre-treatment) includes liming of river water and filtering it through mechanical filters. At this stage, up to 65% of Ca$^{2+}$ and Mg$^{2+}$ ions and, up to 70% of Fe$^{2+}$ ions and up to 80% of suspended solids are recovered. The second stage is the treatment of water in ion-exchange filters. Ion-exchange treatment is carried out according to a two-stage scheme. The filters of the first stage are loaded with KU-2-8 cation-exchange resin and AN-31 low-basic anion-exchange resin. In the filters of the second stage, cation-exchange resin of the KU-2-8 type and highly basic anion-exchange resin of the AB-17 type are used. After processing in ion-exchange filters, water is obtained, purified from the original components 99.9%.

The regeneration of cation exchange and anion exchange filters is carried out with 4% solutions of sulfuric acid and sodium hydroxide, respectively. After regeneration, the filters are washed with desalted water. During the regeneration and washing of ion-exchange filters, the salt solutions are obtained, which concentration depends on the processing durability [4-12].

2. Materials and methods
This paper presents the results obtained in the study of wastewater produced during the regeneration and washing of cation-exchange filters of the first and second stages of the water treatment workshop of the Sterlitamak heat station.
Wastewater samples in each stage were taken each 10 minutes.

The analysis of the metal content in the wastewater of cation exchange filters was carried out by atomic absorption on a «Saturn 3P1» apparatus using various types of atomizers (flame and graphite furnace).

3. Results and discussion

Wastewater generated during the regeneration and washing of cation exchange filters is of acidic type. Figure 1 shows the dependence of the sulfuric acid concentration on the time of regeneration and washing of the filters. The increase in the sulfuric acid content in the period from 20 minutes to 110 minutes from the beginning of the regeneration process in the first stage and within 50 minutes from the beginning of the regeneration process in the second stage is determined by leaching of cations from the ion-exchange resin, and the succeeding sharp decrease in the acid concentration is subsequent to its shutdown and the beginning of the cation exchange filters washing with desalted water. The maximum acid content of 19 g/dm³ is observed in the time interval of 100÷110 min for the first stage and 34 g/dm³ in 50 minutes from the beginning of the regeneration process for the second stage. The average acid concentration in the effluent obtained by numerically integration of the dependence of its content on the time for the first stage in the interval 0÷140 min was 7.45 g/dm³, and for the second stage – 9.46 g/dm³.

![Figure 1](image_url)

**Figure 1.** Dependence of $\text{H}_2\text{SO}_4$ concentration in the effluent on the time:
1 – first stage, 2 – second stage.

More than 20 cations of various metals were found in the wastewater. It should be noted that the highest content in effluent was observed for sodium, calcium and magnesium ions.

The extraction of these metals from the first-stage ion-exchange resin begins simultaneously with the input of sulfuric acid (Figure 2).

The maximum ions concentration in wastewater corresponds to 2100 mg/dm³ for sodium, 803 mg/dm³ for calcium, 609 mg/dm³ for magnesium and may be reached in 60 minutes for sodium and in 80 minutes for calcium and magnesium after the regeneration process starts. After 110÷120 minutes from the beginning of the regeneration and washing of the resin, the content of sodium, calcium and magnesium ions in the effluent is almost zero.
The cations found in the wastewater of the second stage are the same as in the cation exchange resin regeneration the first stage. It should be noted that the highest ions content in the effluent is observed, similar to the first stage, for calcium, sodium and magnesium. Extraction of these metals from the ion exchange resin begins simultaneously with the input of sulfuric acid (Figure 3).

The maximum concentration of these ions in wastewater corresponds to 120 mg/dm³ for sodium, 232.2 mg/dm³ for calcium, 72.8 mg/dm³ for magnesium and is reached after 60 minutes for sodium and after 70 minutes for magnesium and 80 minutes for calcium.

After 140-150 minutes from the beginning of the regeneration and washing of the resin, the content of sodium, calcium and magnesium ions in the effluent is almost zero. Similar behavior during the regeneration and washing of ion-exchange filters is observed for other cations. The average concentrations of these metals in the effluents are presented in table 1.
Table 1. Average composition of wastewater generated during the regeneration and washing of cation exchange filters

| Substance      | Content in the effluent | Maximum permissible concentration, mg/dm³ |
|----------------|-------------------------|------------------------------------------|
|                | First stage, mg/dm³     | Second stage, mg/dm³                     |
| Sulfuric acid  | 7450                    | 9460                                     | 500                                    |
| Sodium         | 985.8                   | 43.51                                    | 200                                    |
| Calcium        | 463.0                   | 126.6                                    | 140                                    |
| Magnesium      | 294.7                   | 42.86                                    | 84                                     |
| Potassium      | 44.53                   | 25.56                                    | 10                                     |
| Strontium      | 4.79                    | 0.92                                     | 7.0                                    |
| Iron           | 2.90                    | 4.57                                     | 0.3                                    |
| Titanium       | 0.63                    | 0.22                                     | 0.1                                    |
| Copper         | 0.31                    | 0.057                                    | 1                                      |
| Zinc           | 0.26                    | 0.087                                    | 3                                      |
| Nickel         | 0.23                    | 0.22                                     | 0.02                                   |
| Barium         | 0.096                   | 0.052                                    | 0.1                                    |
| Manganese      | 0.058                   | 0.043                                    | 0.1                                    |
| Chromium       | 0.056                   | 0.033                                    | 0.05                                   |
| Plumbum        | 0.043                   | 0.012                                    | 0.003                                  |
| Vanadium       | 0.026                   | 0.029                                    | 0.1                                    |
| Rubidium       | 0.019                   | 0.0081                                   | 0.1                                    |
| Molybdenum     | 0.004                   | 0.0032                                   | 0.25                                   |
| Cadmium        | 0.0015                  | 0.0010                                   | 0.001                                  |
| Cobalt         | 0.0002                  | 0.0008                                   | 0.1                                    |

A number of metals have an average content in stock of more than 100 mg/dm³. These are sodium, calcium and magnesium ions, the average concentration of which is 986 mg/dm³, 463 mg/dm³, 295 mg/dm³, respectively, for the first stage and calcium ions, the average concentration of which is 126.6 mg/dm³ for the second stage. For a number of metals, the average concentration varies from 1 to 100 mg/dm³. These include potassium (44.5 mg/dm³), strontium (4.8 mg/dm³), iron (2.9 mg/dm³) – the first stage and sodium (43.5 mg/dm³), magnesium (42.9 mg/dm³), potassium (26.6 mg/dm³), iron (4.6 mg/dm³) – the second stage. Metals with an average concentration of 0.1 to 1 mg/dm³ include titanium, nickel, copper, zinc for the first step and titanium, nickel, strontium for the second step. The last groups are the metals, which average concentration is less than 0.1 mg/dm³. These are vanadium, chromium, manganese, cobalt, rubidium, molybdenum, cadmium, barium and plumbum for the first stage and copper, zinc, vanadium, chromium, manganese, cobalt, rubidium, molybdenum, cadmium, barium and plumbum for the second stage.
The concentration of a number of elements contained in the waste water resulting from the regeneration of cation-exchange filters exceeds the maximum permissible concentrations (MPC) for these elements, as shown in table 2.

| Substance   | First stage | Second stage |
|-------------|-------------|--------------|
| Sodium      | 4.9         | –            |
| Calcium     | 3.3         | –            |
| Magnesium   | 3.5         | –            |
| Potassium   | 4.45        | 2.56         |
| Iron        | 9.6         | 15.2         |
| Titanium    | 6.3         | 2.2          |
| Nickel      | 11.5        | 11           |
| Chromium    | 1.12        | –            |
| Plumbum     | 14.3        | 4            |
| Cadmium     | 1.5         | –            |

A significant excess of the MPC is observed for iron (15.2 times), nickel (11.5 times) and plumbum (14.3 times).

4. Conclusion
The greatest number of elements in river water is sorbed by cation-exchange filters of the first stage. Therefore, the wastewater of the first stage contains 87.99% of the total amount of impurity, and the wastewater of the second stage contains only 12.01%. In this case, the main content, both in the waste water of the first and of the second stages, falls on four elements. These are sodium, calcium, magnesium and potassium. In the effluent of the first stage, they make 99.46%, and in the effluent of the second stage make 97.25%.

Wastewater generated by the regeneration of cation-exchange filters is not suitable without preliminary preparation for electrochemical processing to produce acid and alkali. This is due to the fact that during the electrolysis the deposits of the calcium, magnesium and other metal hydroxides will precipitate in the cathode chamber subsequent to the formation of an alkaline medium in this chamber. These deposits will cover the surface of the cathode, as well as block the ion-exchange groups of the cation-exchange membrane.

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