Composition of wastewater formed during regeneration of anion-exchange filters of water treatment plants

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Abstract. The main technology for obtaining desalted water is ion-exchange technology. In the process of regeneration and washing of ion-exchange filters, a large amount of waste water containing various compounds is formed. The article presents the composition of wastewater generated at the water treatment section of Sterlitamakskaya Combined Heat and Power Plant (CHPP) at the stages of regeneration and washing of anion-exchange resins. It is shown that the wastewater of anion-exchange filters contains in a large amount of sodium sulfate, sodium chloride and sodium hydroxide. Recommendations for equalizing these waste waters for their processing in a membrane cell are given.

1. Introduction
Enterprises of many industries consume desalted water. Such water, in particular, is used for feeding boilers of thermal power plants, in chemical technology, mining and other areas of industry. The main process for obtaining desalted water is ion-exchange technology [1-3].

The water preparation section of Sterlitamakskaya Combined Heat and Power Plant uses water of the Belaya River to produce desalted water. The process runs in two stages.

The first stage (pre-cleaning) involves liming the river water and filtering it through mechanical filters. At this stage, up to 65% of \(Ca^{2+}\) and \(Mg^{2+}\) ions, up to 70% of \(Fe^{2+}\) ions and up to 80% of suspended solids are removed.

The second stage is the treatment of water in ion-exchange filters. Ion exchange processing is carried out according to a two-stage scheme. The first-stage filters are loaded with a cation exchanger of KU-2-8 type and a low-basic anion exchanger of AN-31 type. In the second-stage filters, the cation exchanger of KU-2-8 type and the highly basic anion exchanger of AV-17 type are used. After treatment in ion-exchange filters, water purified from the initial components by 99.9% is obtained. Regeneration of cation exchange and anion exchange filters is carried out by 4% solutions of sulfuric acid and sodium hydroxide, respectively. After regeneration, the filters are washed with desalted water obtaining salt solutions the concentration of which depends on time of regeneration and washing. It is known that the treatment of salt solutions in membrane cells allows producing acids and alkalis [4-10]. However, in this case it is necessary to know composition of the wastewater and the dependence of the salt concentration in this water on time of regeneration and washing processes.
2. Results and discussion

We have studied the composition of wastewater formed during regeneration of anion-exchange filters at the water treatment section of Sterlitamakskaya Combined Heat and Power Plant. It was found that this waste water of both first and second stages contains $\text{SO}_{4}^{2-}$, $\text{Cl}^-$, $\text{OH}^-$ and $\text{SiO}_2^{3-}$ ions in the form of sodium salts. Dependences of concentration of $\text{SO}_{4}^{2-}$, $\text{Cl}^-$, $\text{OH}^-$ and $\text{SiO}_2^{3-}$ ions in waste water on regeneration time of anion-exchange resins and their washing are shown in Figures 1, 2 and 3. It should be noted that the zero-time reference in all experiments corresponds to the beginning of regeneration of ion-exchange resins.

The analysis of the experimental data (Figures 1 and 2) indicates that qualitatively the desorption process of $\text{Cl}^-$ and $\text{SO}_{4}^{2-}$ anions runs the same way at both the first (low basic anion exchanger) and the second (highly basic anion exchanger) levels. In both cases, the resin regeneration process begins with the supply of an alkali solution with the initial extraction of $\text{Cl}^-$ ions and then of $\text{SO}_{4}^{2-}$ ions. However, the retention time of these ions on the resin is not the same. Thus, in case of the first stage (low-basic anion exchanger), the maximum concentration of $\text{Cl}^-$ ions in the wastewater is reached after 20 minutes, and $\text{SO}_{4}^{2-}$ ions after 40 minutes. Then in case of the second stage (high-basic anion exchanger), the maximum concentration of $\text{Cl}^-$ ions in the waste water is reached after 25 minutes, and $\text{SO}_{4}^{2-}$ ions after 60 minutes from the start of regeneration process. In addition, $\text{Cl}^-$ ions are sorbed to a greater extent on first-stage anion exchanger, and $\text{SO}_{4}^{2-}$ ions on the second stage anion exchanger. This is indicated by the fact that the maximum content of $\text{Cl}^-$ ions in the first-stage wastewater reaches a value of 7.4 g/dm$^3$, while the maximum $\text{Cl}^-$ ion concentration in the second-stage wastewater is 2.75 g/dm$^3$. Similar indicators for $\text{SO}_{4}^{2-}$ ions are equal to 7.4 g/dm$^3$ and 22.1 g/dm$^3$, respectively. The increase in concentration of hydroxyl ions in wastewater at the beginning is determined by the progress of the ion exchange resin regeneration process. The subsequent decrease in hydroxyl ion content in wastewater after 60 minutes for the first stage and after 100 minutes for the second stage is associated with the beginning of the ion exchange resin washing process with desalted water. It can be seen that in wastewater of the first stage, there is still a sufficient number of $\text{Cl}^-$ and $\text{SO}_{4}^{2-}$ ions, and in wastewater of the second stage, these ions are practically absent. It should be noted that the wastewater of the second stage after 100 minutes from the beginning of the regeneration process contains only alkali and can be used to neutralize acidic effluents.

Unlike concentrations of $\text{SO}_{4}^{2-}$, $\text{Cl}^-$ and $\text{OH}^-$, the content of $\text{SiO}_2^{3-}$ in waste water is significantly lower. Experimental data (figure 3) indicate that the sorption of $\text{SiO}_2^{3-}$ ions is mainly carried out by a high-basic resin of the second stage. In the wastewater of the first stage, the maximum concentration of $\text{SiO}_2^{3-}$ ion reaches 450 $\mu$g/dm$^3$ 30 minutes after the start of the regeneration process. In contrast, the highest content of $\text{SiO}_2^{3-}$ ions in the second stage wastewater is at the very beginning of the regeneration process and is 2250 $\mu$g/dm$^3$. After 120 minutes from the beginning of the regeneration process, the concentration of $\text{SiO}_2^{3-}$ ions in the waste water of both the first and the second stages is practically zero. It should be noted that the concentration of $\text{SiO}_2^{3-}$ ions is given in terms of silicon oxide.
Figure 1. Concentration of $\text{Cl}^-$, $\text{SO}_4^{2-}$ and $\text{OH}^-$ ions in the first stage waste water over time.

Figure 2. Concentration of $\text{Cl}^-$, $\text{SO}_4^{2-}$ and $\text{OH}^-$ ions in the second stage waste water over time.
Figure 3. Concentration of SiO$_2$ ions in the wastewater over time.

The presented results show that the wastewater formed during regeneration and washing of anion exchange resins of water treatment plants contains mainly SO$_4^{2-}$, Cl$^-$ and OH$^-$ ions as sodium salts and can be used for production of alkalis and acids by their treatment in a membrane cell. At the same time, the concentration of ions in the wastewater will decrease when increasing regeneration time for more than 40 ÷ 60 min. Obviously, for the electrochemical treatment, not the entire volume of the waste water, but only the part with the highest salt content should be used. In case of the first stage (see Figure 1), the most suitable waste water is formed in the interval of 10 ÷ 60 min from the beginning of the regeneration process, and in case of the second stage (see Figure 2) this interval will be within 20 ÷ 80 min, respectively. To obtain the average concentrations of substances in the wastewater in time intervals indicated above, we used the method of numerical integration of the dependences presented in Figures 1-3. The calculation was made for the content of Na$_2$SO$_4$, NaCl, NaOH and SiO$_2$ compounds. In the first stage wastewater, suitable for electrochemical processing (see table 1), the sodium sulfate and sodium chloride content is practically the same (11.4 and 10.1 g/dm$^3$) and the alkali concentration is more than two times lower than the content of these salts.

The total salt content of the wastewater is 26.2 g/dm$^3$. The concentration of silicon oxide (2.78 $\times$ 10$^{-4}$ g/dm$^3$) is significantly lower than the content of the remaining salts. In the second stage waste water, the concentration of sodium sulfate (19.9 g/dm$^3$) and alkali (15.6 g/dm$^3$) is higher than in the waste water of the first stage, however the concentration of sodium chloride has a significantly lower value (1.8 g/dm$^3$). The total salt content of the second stage wastewater is 37.4 g/dm$^3$. The concentration of silicon oxide is also much lower (1.81 $\times$ 10$^{-5}$ g/dm$^3$) than other substances.
**Table 1.** Average content of wastewater formed during regeneration and washing of anion exchange resins.

| Substance | Concentration, g/dm$^3$ | First stage | Second stage |
|-----------|-------------------------|-------------|--------------|
| Na$_2$SO$_4$ | 11.4 | 19.9 |
| NaCl       | 10.1 | 1.8 |
| NaOH       | 4.7  | 15.6 |
| SiO$_2$    | 2.78·10$^{-4}$ | 1.81·10$^{-3}$ |
| Salt content | 26.2 | 37.4 |

3. Conclusion

Thus, the conducted studies allow us to proceed reasonably with an extraction from a wastewater formed during regeneration and washing of ion exchange resins of anion exchange filters of water treatment plants of its parts suitable for processing in a membrane cell to produce alkalis and acids.

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