The effect of mixtures of neutralizing amines on the dynamic exchange capacity of strong acid cationite KU-2-8

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Abstract. The dependence of the ion exchange capacity of strong acid cationite KU-2-8 on the concentration and structure of low-molecular organic compounds containing an amino group has been experimentally established. The mutual influence of neutralizing amines that are part of complex reagents that reduce the value of the exchange capacity of cations during operation of thermal power plant was revealed.

Key words: ion exchange capacity, amines, strong acid cationite KU-2-8

1. Introduction
Currently, there are many studies and, as a result, publications on the influence of nitrogen-containing organic compounds on the exchange capacity of cationite.

The objects of research were either low-molecular weight amines, such as cyclohexylamine, ethanolamine, or mixtures that include the above-listed compounds, as well as amines that have the properties of surfactants, such as N-oleyl-1,3-diaminopropylene, i.e. reagents such as Helamin, Cetamine, etc. Reagents that include surfactants are used for high-pressure boilers, and for low-and medium-pressure boilers water chemistry have become widely used using complex reagents that include only amines that can maintain the required pH value, and are used in other industries as corrosion inhibitors. These are cyclohexylamine (CGA), monoethanolamine (MEA), morpholine (Morph), and dimethylaminopropane (DMAE).

Since the properties and behavior of amines in a mixture may differ from those of individual compounds, the effect of compositions based on them on cationite in condensate treatment systems may also acquire a different character. Also, in the course of research, it is necessary to take into account that the compounds included in the complex reagent may consist of amines with different structures.

2. Experimental setup
To determine the effect of mixtures of neutralizing amines on changes in the dynamic exchange capacity of cationite compositions of the following composition were studied:

1. Composition 1: DMAE – 15%, Morph – 15%, H₂O – 70%.
2. Composition 2: CGA – 15%, Morph – 15%, H₂O – 70%.
3. Composition 3: IEA – 15%, CGA – 15%, H₂O – 70%.
4. Composition 4: DMAE – 10%, CGA – 10%, Morph – 10%, H₂O – 70%.

The experimental setup consisted of a column with technological parameters in accordance with [1], through which model solutions were passed and then, depending on the task of the experiment, either the concentration of calcium ions or the concentration of amines was determined.
The experiment consisted of several stages. Initially, model solutions based on calcium chloride and a mixture of amines were prepared on desalinated water, the compositions of which are given above. In accordance with [1], the concentration of calcium chloride was 3.5 mg-eq/l, and the concentration of complex neutralizing reagents was 5 mg/l and 35 mg/l. Solutions were passed through a column with a flow rate of 33 ml/min and at speed of 16 cm/min. After depletion of the cationite, it was regenerated with a 1% solution of sulfuric acid. The speed of the regeneration solution was 16 ml/min. After the regeneration procedure, the cationite was washed with desalinated water at a rate of 10 ml/min. The residual acid was monitored by the pH meter. The filtration and regeneration cycle performed several times until the difference in the exchange capacity values in the last two cycles did not exceed 5% of the average.

Control of ion saturation by calcium was carried out in accordance with [2], determination of the leakage of neutralizing amines was carried out using the method of photometric measurement of amines and amine alcohols in the air of the working zone [3].

Before conducting the experiment with mixtures of neutralizing amines, an experiment was conducted in which the model solution contains only calcium chloride. It was designated as a "blank" experiment.

The experiment with a solution of calcium chloride without neutralizing amines ("blank" experiment) was carried out in 5 filter cycles. Table 1 shows the values of the dynamic exchange capacity of strong acid cationite KU-2-8 only for 4 filter cycles, the average value for two post-filter cycles was 303.7 g-eq/m³. This value in the subsequent experiment was taken as a standard against which the results obtained during the main experiment were compared.

The experiment was completely repeated for model solutions prepared on desalinated water and containing, in addition to calcium chloride, neutralizing compositions with a total concentration of amines of 5 mg/l.

### 3. Results of the experiments

Table 1 summarizes the values of dynamic exchange capacities for all filter cycles of the first series. The percentage of reduction in the capacity of the first and last filter cycles is shown in table 2.

| Filter cycle | CaCl₂ | CaCl₂ + DMAE + Morph | CaCl₂ + DMAE + Morph + CGA | CaCl₂ + MEA + CGA | CaCl₂ + Morph + CGA |
|--------------|-------|----------------------|-----------------------------|------------------|---------------------|
| 1            | 384.6 | 354.0                | 350.1                       | 346.4            | 344.3               |
| 2            | 345.8 | 338.0                | 322.0                       | 323.8            | 321.8               |
| 3            | 308.0 | 311.5                | 304.0                       | 304.0            | 303.8               |
| 4            | 303.7 | 299.5                | 296.4                       | 298.3            | 295.0               |

| CaCl₂        | CaCl₂ + DMAE + Morph | CaCl₂ + DMAE + Morph + CGA | CaCl₂ + MEA + CGA | CaCl₂ + Morph + CGA |
|--------------|----------------------|-----------------------------|------------------|---------------------|
| 21.4         | 15.4                 | 15.3                        | 13.9             | 14.3                |

According to the data obtained during the first series, it can be concluded that the content of amines in this amount does not cause a strong effect on the capacity of the cationite (the decrease does not exceed 5%). But the reduction of the exchange capacity to values less than 300 g-eq/m³ when passing a model solution with amines occurs in 4 filter cycles, and when passing a solution of calcium chloride reaches a value of 302.3 g-eq/m³ only on the fifth filter cycle. At the same time, the percentage of decrease in the dynamic exchange capacity when passing a model solution of calcium chloride is much greater than when passing model solutions with amines. From the data in table 2, it also follows that in
the presence of neutralizing amines in the mixture of morpholine, the exchange capacity of the cationite decreases faster.

Fig. 1 shows the output curves for the calcium leakage during the skipping of the working solution containing a mixture of amines and the curves for the calcium leakage during the skipping of the working solution containing only calcium chloride ("blank") for the last filter cycles.

![Figure 1](image1.png)

**Figure 1.** The dependence of the calcium concentration of the "idle" experience and the experience with model solutions with a concentration of neutralizing amine mixtures of 5 mg/l.

From the obtained dependencies, it follows that the yield of calcium, when a mixture of neutralizing amines is contained in the solution, occurs earlier than during the "blank" experiment. This can be explained by the fact that the selectivity of the cation exchange resin by calcium ions and carbocations different.

For 1st series of experiments, output curves for mixtures of neutralizing amines at their concentration in a solution of 5 mg/l are also constructed (Fig. 2-5).

![Figure 2](image2.png)

**Figure 2.** Output curves for the mixture of DMAA + Morph at concentration 5 mg/l

![Figure 3](image3.png)

**Figure 3.** Output curves for the mixture of DMAA + Morph + CGA at concentration 5 mg/l

![Figure 4](image4.png)

**Figure 4.** Output curves for the mixture of MEA + CGA at concentration 5 mg/l

![Figure 5](image5.png)

**Figure 5.** Output curves for the mixture of Morph + CGA at concentration 5 mg/l
From the output curves, it follows that the leakage of neutralizing amine mixtures occurs earlier than the leakage on calcium.

The second series of experiments was performed on a model solution of amine mixtures with a concentration of 35 mg/l. The output curves for the calcium of each filter cycle for all solutions are shown in fig. 6.

**Table 3. Results of 2\textsuperscript{nd} series of experiments at the concentration of amine mixtures of 35 mg/l**

| Filter cycle | Dynamic exchange capacity of cationite, g-eq/m\textsuperscript{3} |
|--------------|---------------------------------------------------------------|
|              | CaCl\textsubscript{2} + DMAE + Morph | CaCl\textsubscript{2} + DMAE + Morph + CGA | CaCl\textsubscript{2} + MEA + CGA | CaCl\textsubscript{2} + Morph + CGA |
| 1            | 310.20                                                   | 308.97                           | 299.31                             | 297.10                             |
| 2            | 293.15                                                   | 291.49                           | 281.83                             | 280.30                             |
| 3            | 286.00                                                   | 283.00                           | 272.30                             | 269.50                             |

Comparison of the obtained results and analysis of the output curves shows that the yield of calcium when passing model solutions containing compositions with amines occurred earlier than during the idle experiment. Moreover, the fastest saturation occurs with ions of the solution containing a mixture of 3 neutralizing amines. In addition, the interaction between the cationite and a solution with a mixture of cyclic amines (Morph+CGA) (after skipping 10 litres of the working solution) occurs later than, for example, a solution with a mixture containing amines with a linear structure (after skipping 6 liters of the working solution).

The average values of exchange capacities during the second series, as well as the percentage decrease in comparison with the idle experience, are shown in table 4.
Table 4. The results of the experiments

| Composition       | Dynamic exchange capacity of cationite, g-eq/m³ |
|-------------------|-----------------------------------------------|
|                   | CaCl₂ | CaCl₂ + 5 mg/l of amines | % ↓ from “blank” experiment | CaCl₂ + 35 mg/l of amines | % ↓ from “blank” experiment |
| DMAE + Morph      | 303.7 | 299.50 | 1.41 | 286.00 | 5.90 |
| DMAE + Morph + CGA|       | 296.40 | 2.40 | 283.00 | 6.80 |
| MEA + CGA         |       | 298.30 | 1.15 | 272.30 | 10.40 |
| Morph + CGA       |       | 295.00 | 2.90 | 269.50 | 11.30 |

As can be seen from table 4, the DOE value after skipping solutions with an amine concentration of 35 mg/l is below the limit deviation. Moreover, a more significant decrease is observed in the presence of cyclohexylamine in the composition. In addition, it can be noted that a mixture of neutralizing amines with a cyclic structure (Morph+CGA) has the greatest effect on the exchange capacity of a strong acid cationite.

4. Conclusions
Mixtures of amines have a greater effect on reducing the dynamic exchange capacity of cationite, the greater their concentration in the mixture.

The structure of the molecules of low-molecular amines that are part of the compositions affects the value of the dynamic exchange capacity of cationites. The percentage of decrease in the dynamic exchange capacity when passing a solution with a mixture of Morph + CGA (amines with a cyclic structure) is higher (11.35%) than when passing a solution with a mixture of DMAE + Morph (DMAE-linear amine; 5.9%)

The leakage on neutralizing amines occurs earlier for all mixtures relative to the leakage on calcium. Moreover, the process of ionite saturation occurs differently for each of the mixtures, which may also be related to the structure of amino-containing compounds.

References

[1] GOST 20255.2-89 Ionites. Methods for determining the dynamic exchange capacity
[2] Methods for determining quality indicators. Water production of thermal power plants. Methods for the determination of alkalinity. Methods for determining stiffness. Methods for determining phosphates. Methods of determining the oxidizability of water /Approved. Glavtour. Ministry of energy of the USSR 15.12.88; Development. VTI; validity period, established from 01.10.89- M.: Roth. VTI, 1989. -58 p.
[3] Photometric determination of tertiary fatty amines and amino alcohols. Methodological guidelines for the determination of harmful substances in the air, issue XIX // M-vo health of the USSR. - M.: MZ USSR, 1984.