The Survey of Sorption Ion-Exchange Properties of Paleozoic Zeolites Before and After Regeneration

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Abstract. The presented results of experimental studies on the removal of iron ions, manganese, ammonium nitrogen, strontium and cadmium from aqueous solutions by the paleozoic zeolites of the Urals in dynamic conditions. Experiments have been carried out on the regeneration of mineral zeolite filters in order to restore the sorption properties of the explored minerals. The results of the researches show that ion-exchange minerals can be used as highly effective sorbents, with a large ion-exchange capacity and a multifaceted ability to restore the original properties.

1. Introduction
Investigation of ion-exchange properties of Paleozoic zeolites is necessary for the possible use of natural minerals in the field of environmental protection, with the aim of increasing the time of protective action.

Surface and underground waters of the West Siberian artesian basin are characterized by increased contamination with substances of natural and technogenic origin: ammonium nitrogen, manganese, iron, strontium, cadmium, etc. Removal of pollutants from natural and waste water is provided by a complex of technological purification processes, one of which is filtration. When filtering, granular materials of natural or artificial origin are used. In the world practice, research is being conducted on the use of sorbents possessing ion-exchange properties of zeolites, zeolite-montmorillonite rocks, etc. [1,2]. Paleozoic zeolites of the Urals for the purification of polluted waters are highly promising. Zeolite ores contain 90-95% ion-exchange minerals, do not contain toxic and heavy impurities [3].

2. Equipment and devices used in studies
2.1 Sorption and ion-exchange properties of natural minerals
The purpose of this work was to study the sorption-ion exchange properties of Paleozoic zeolites in removing impurities of various nature from solutions and methods for regenerating the filter material. Studies have noted that ion-exchange properties depend on the nature of the sorbent and the composition of the impurities [8-10]. Sorption properties have been studied under various physicochemical conditions (size of fraction, temperature, impurity concentration in solution). In the study of Paleozoic zeolites, a technique developed by the Institute of Mineralogy, Geochemistry and Crystallochemistry of Rare Elements was applied [3,5].

Work performed under the subject study of the chemical and physical properties of zeolite rocks of the Paleozoic of the Urals. The experiments were carried out in the laboratories of the Tyumen Industrial University, on the basis of the Tyumen Central Laboratory [1,2].

3. Results and discussion
3.1. Discussion of research processes
In the study of ion-exchange and sorption properties of zeolites, the ability of regeneration processes, the time the protective actions were carried out experiments on sorption in dynamic conditions before regeneration of the ions of iron, manganese, strontium, cadmium, ammonia-nitrogen purified by passing
solutions through the sorbent layer with a height of 50 cm. Solutions were prepared on the basis of tap water of the city of Tyumen with the following content of the main components (mg/ dm$^3$): K$^+$ =3.7; Mg$^{2+}$ = 11.8; Ca$^{2+}$=31.0; NH$_4^+$= 0.4 (averaged composition). The water was injected salt of the investigated pollutants found in the West Siberian artesian basin according to other authors. [1-5] The experiments were carried out by filtration of solutions through a layer of mineral sorbent fraction 0.3-0.6 mm, placed in a burette with a diameter of 1.2 cm. The flow rate of the solution was regulated so that the filtration rate was 2.5 m/hour. Samples for chemical analyses were taken every 0.1 dm$^3$ filtered liquid.

Research of sorption ability of filters to remove from the solution the ions NH$_4^+$ were carried out at the introduction into water of 10 mg/ dm$^3$ ammonium nitrogen. The first traces of ammonium nitrogen in filtered water was noted in 23 dm$^3$. 26.8 dm$^3$ filtered liquid experience was discontinued. And the regeneration of 5% NaCl solution. There were four of regeneration, which showed that the mineral filter is increased exchange capacity. The results are shown on the chart. (Figure 1) After fourth regeneration of exchange capacity increased 1.8 times compared to the first experience.

Figure 1 Dependency of sorption ability zeolite-montmorillonite breed on regenerations’ quantity over ammonium nitrate. The maintenance of NH$_4^+$ in filtered water 10.0 mg/ dm$^3$; the filtration rate 4.0 ml/min, the granular filter fraction 0.3-0.6 mm, the sorbent’s weight 50.0 g, the height of the filterable layer 50 cm.

Notion: 0-4 – curves of sorption: 0 – regeneration; 1 – after the first regeneration; 2 – second; 3 – third, 4 – fourth regeneration.

The sorption capacity of mineral filters in dynamic conditions for extracting ions of iron and manganese from solution was investigated similarly to the experiments on the sorption of ammonium nitrogen. Filtration of a solution containing 20.0 mg/ dm$^3$ of iron, using zeolite sorbent showed it to a very high ion exchange capacity. (Figure 2)
Figure 2 Dependency of sorption ability zeolite-montmorillonite breeds on regenerations’ quantity over the iron. The maintenance of iron in filtered water 10.0 mg/dm$^3$; the filtration rate 4.0 ml/min, the granular filter fraction 0.3-0.6 mm, the sorbent’s weight 50.0 g, the height of the filterable layer 50 cm.

Notion: 0, 1 - curves of sorption: 0 - before regeneration, 1 - after the first regeneration.

13.6 dm$^3$ filtered water the iron content was not recorded. 16.2 dm$^3$ in filtered water detected a sharp increase in the content of Fe$^{2+}$ and 10 mg/dm$^3$. Carried out desorption with 5% solution of NaCl in a volume of 1.5 dm$^3$ fully regenerated granular filter. After regeneration experiments were conducted repeatedly. The presence of iron in the filtrate were recorded in 20.8 dm$^3$; the adsorption capacity after regeneration compared to the non regenerated filter is increased 1.5 times. Repeated second regeneration led to a sharp decrease in the exchange capacity, already on 5.0 dm$^3$ in the filtrate there were traces of Fe$^{2+}$. Study on the purification of water from manganese were carried out on solutions containing 0.5 mg/dm$^3$ of manganese. The first traces of manganese found in 29.9 dm$^3$ of the filtrate, 36 dm$^3$ Mn$^{2+}$ content was 0.45 mg/dm$^3$. A grainy filter has been activated 5% NaCl solution. In 0-6.5 filtrate ion content of manganese ranged from 0.01-0.1 mg/dm$^3$. In the following amounts 7.5-15.0 dm$^3$ filtered water fluctuations in the content of manganese was in the range of 0.03-0.3 mg/dm$^3$. Further filtering of the recorded concentration of manganese 0.28-0.8 mg/dm$^3$. (Figure 3)

Figure 3 Dependency of sorption ability zeolite-montmorillonite breeds on regenerations’ quantity over manganese. The manganese’s maintenance in filtered water 0.5 mg/dm$^3$; the filtration rate 4.0 ml/min; the sorbent’s weight 50 g; the height of the filterable layer 50 cm.

Notion: 0,1 – manganese’s curved maintenances in filtered water after: 0-before regeneration; 1-first regeneration

Repeated regeneration has not led to the recovery of the sorption capacity of granular filter.

Studies on the removal of strontium from solutions of spent granular filters by filtration through them
of water enriched with strontium in the amount of 20.0 mg/dm$^3$. T V Germanova and I R Valieva were investigated sorption processes for extraction from solutions of strontium and lead in the presence of competing cations in solution are Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, but at lower concentrations of strontium. [1-3] the First traces of strontium recorded in 17.3 dm$^3$ filtered water. (Figure 4)

![Figure 4](image)

**Figure 4** The sorption in dynamic conditions by the zeolite-montmorillonite granular filter of strontium ions from water; the fraction 0.3-0.6 mm; the filtration rate 4.0 ml/min. The original distilled water enriched with ions Sr$^{2+}$ (mg/dm$^3$) – 20.

Notion: 0, 1, 2 - content of strontium cations in filtered water after: 0 – before regeneration; 1 – first regeneration; 2 – second regeneration.

In samples 202-210 contents of strontium in the filtrate was 1.8 mg/dm$^3$. In the process of experimental work was conducted 2 regeneration. Studies indicate that after each regeneration of zeolite sorption capacity of the filter increased by 15-20%. These figures make zeolite filters are highly promising for their application purification of highly polluted waters strontium, ammonia, cadmium etc.

The ion-exchange properties of zeolites with cations of cadmium. The experiments had two aims: determination of exchange capacity of the filters cadmium ions and the number of possible regenerations. Filtered solution containing 5.0 mg/dm$^3$ of cadmium. The first traces of cadmium were recorded in 3.3 dm$^3$ of filtrate. With further filtering, a gradual increase in the content of cadmium in filtered solution: in 3.65 dm$^3$-1.12 mg/dm$^3$, in 4.7-5.0 mg/dm$^3$. During the experiments, there were two regeneration. After the first regeneration the cations of cadmium in filtered solution was found in 56 (2.9 dm$^3$) sample. Further, there was a rapid increase in the solution and 68 (3.4 dm$^3$) amounted to 6.75 mg/dm$^3$. The second regeneration. The third filtration have shown that after the second regeneration of sorption properties of granular filter was not recovered. Already in the fourth sample (0.2 dm$^3$) content of cadmium in leachates exceeded 5 mg/dm$^3$. (Figure 5).

3.2. Discussion of research results

The analysis of own research and the data of other authors [1-4] on the sorption capacity and the ability to regenerate zeolites show that the ion exchange processes depend on the concentration, temperature of the solutions and the composition of the counterions. There are two types of regeneration under which the sorption capacity of the filters changes. When cleaning the liquid from ammonium nitrogen, strontium, iron at each subsequent regeneration, the ion exchange capacity increases by 15-40%, and when filtering solutions with cadmium and manganese decreases, which increases or decreases the protective action time of the filters, which should be taken into account when selecting and calculating resources technological equipment. The ion-exchange capacity calculated under specific physico-chemical conditions indicates the high sorption capacity of the zeolites. (Figure 1-5).
Figure 5 Dependency of sorption ability zeolite-montmorillonite breeds on regenerations’ quantity over cadmium. The cadmium’s maintenance in filtered water 5.0 mg/dm$^3$; the filtration rate 4.0 ml/min, the granular filter fraction 0.3-0.6 mm, the sorbent’s weight 50.0 g, the height of the filterable layer 50 cm.

Notion: 0,1,2 – cadmium’s curved maintenances in filtered water after: 0-before regeneration; 1-first regeneration; 2- second regeneration.

The results of studies of sorption capacity and the ability to regenerate mineral filters shown in figures 1-5.

4. Conclusion
The presented results of studies on the sorption ability and the ability to regenerate Paleozoic zeolites during the filtration of solutions containing ammonium nitrogen, iron, manganese, strontium, cadmium indicate their high efficiency. Even with contamination of solutions tens of times higher than normal, the protective action and sorption capacity does not decrease. Low cost, acid resistance, ecological safety of zeolite sorbents allows using them in exchange processes both with regeneration and without regeneration, followed by the use of spent zeolites as cement raw materials or flux.

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