Removal of radionuclides by analcime-bearing rocks

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Abstract. The study of the removal of radionuclides (uranium, radium and thorium) in static conditions from aqueous solutions by analcime-bearing rocks and pure analcime was carried out. The high removal efficiency of all studied radionuclides by analcime-bearing rocks was determined. Analcime was efficient in removing of thorium only.

1. Introduction
Natural zeolites and zeolite-bearing rocks are widely used in environmental protection, for example, for wastewater purification (removal of heavy metals, petroleum products, phenol, ammonium and radioactive elements).

Zeolite-bearing rocks are widespread in Komi Republic (Russian Federation); zeolite mineralization is represented by analcime. Although analcime-bearing rocks refer to poor zeolite raw due to low analcime content (from 1–3 to 20–30 %), these rocks are considered as sorption raw of mixed composition because zeolites associate with clay minerals which are in amount of 50–70 % and also possess sorption properties.

Our study focused on testing analcime-bearing rocks and pure analcime as potential adsorbents for radionuclides removal and their ability to retain adsorbed radionuclides.

2. Materials
Analcime-bearing rocks are represented by siltstones and argillites and rare marls. These rocks are characterized by the high content of clay component (50–70 %), which is saturated by iron oxides and hydroxides. Also quartz (10–30 %), analcime (1–30 %), feldspars (2–10 %), carbonates (2–5 %), pyroclastic material are represented. In the rocks analcime is found as isometric crystals, microoolitic concretions, microgeode aggregates or cryptocrystalline cement. Analcime aggregates encrust roundish and oval cavities, and also fill microfractures in the rocks. The clay minerals are represented by disordered mainly swelling, mixed-layer phase (illite-smectite, illite-chlorite), while kaolinite and chlorite are insignificant [1].

3. Methods
The experiments were carried out for both analcime-bearing rocks and pure analcime to determine the role of analcime in the process of radionuclides removal. For the experiments the sorbents were crushed to -1.0 mm size class. The removal tests were carried out at the room temperature from aqueous solutions of uranyl nitrate, radium chloride and thorium chloride. The ratio of solid and liquid was 1:10 (3 g of sorbent and 30 ml of solution), the duration of phase contact was 24 hours, pH solution was 6. Acidity of liquid was adjusted to desired level by concentrated solution (13 mol/l) of ammonium hydroxide. After the removal test sorbents were separated from liquid by filtering, content of radionuclides in the filtered material was
determined, and the removal efficiency of uranium, thorium and radium was calculated. Content of radionuclides in the filtered material was determined by standard methods. Uranium, thorium and radium content were determined by luminescent method, photocolorimetric method using reagent arsenazo III and emanation method [2, 3, 4], respectively.

In order to check the ability of analcime-bearing rocks and pure analcime to retain radionuclides the 3 step extraction procedure using processing with distilled water, 1M ammonium acetate (\(\text{CH}_3\text{COONH}_4\)) and 1M hydrochloric acid (HCl) was carried out.

4. Results and Discussion

4.1. Removal of radionuclides
The obtained results showed that analcime-bearing rocks efficiently removed all studied radionuclides: the removal efficiency of thorium was 100%, radium – from 99.2 to 99.8%, uranium – from 98.5 to 99.7%. As for analcime, it effectively removed only thorium (the removal efficiency was 98%), while radium and uranium removal efficiency were much less – 64.2 and 55.4%, respectively.

4.2. Extraction of radionuclides
The results of radionuclide extraction are represented in the figures 1-3. It was found that thorium was retained most strongly by analcime-bearing rocks (figure 1). Insignificant extraction of thorium to solution by distilled water (1.0–2.7%) and ammonium acetate processing (0–0.7%) was observed. Only in acid medium significant thorium extraction (38.0–68.0%) was determined, which was probably caused by destruction of analcime and clay minerals structures. Analcime retained thorium less strongly during distilled water and ammonium acetate processing: 6.1 and 20.4% of radionuclide was extracted, respectively. Acid processing led to extraction of 48.3% of thorium.

![Figure 1](image.png)

**Figure 1.** Results of thorium extraction by processing with distilled water, 1M ammonium acetate and 1M hydrochloric acid.
Significant radium extraction to solution from analcime-bearing rocks (41.4–49.2 %) and analcime (more than 60 %) by ammonium acetate processing was probably caused by inclination of radium to ion exchange (figure 3). However, radium was retained strongly by analcime-bearing rocks and analcime during distilled water processing: it was extracted less than 1.0 and 3.6 %, respectively. Acid processing also promoted the high radium extraction.

![Figure 2](image_url)

**Figure 2.** Results of radium extraction by processing with distilled water, 1M ammonium acetate and 1M hydrochloric acid.

Analcime retained uranium quite strong: 2.3 % was extracted during distilled water processing and 12.1% was extracted during ammonium acetate and acid processing. Analcime-bearing rocks also retained uranium strongly during distilled water processing, however 17.6–25.4 and 22.4–34.7 % of radionuclide extracted to solution by ammonium acetate and acid processing, respectively.
5. Conclusions
The results of radionuclides removal showed that analcime-bearing rocks demonstrated high removal efficiency of thorium, uranium and radium, while analcime was efficient in removing of thorium only; radium and uranium removal efficiency was 64.2 and 55.4 %, respectively.

According to the results of radionuclides extraction, thorium was retained most strongly, its insignificant extraction to solution by distilled water and ammonium acetate processing was observed. Analcime retained uranium quite strongly, while analcime-bearing rocks retained it strongly only during distilled water processing. The high radium extraction (about 50 % from analcime-bearing rocks and more than 60 % from analcime) was probably caused by its inclination to ion exchange.

6. Acknowledgements
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