Localization of iodine-129 in geological disposal facilities for radioactive waste with the use of bentonites, modified with silver compounds

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Relevance of the topic. Radioactive iodine is one of the main ^{235}U fission products and is a part of the 1 and 2 class radioactive waste (RW) (high-level and long-lived medium-level radioactive wastes). It poses a significant threat to human and the rest of the biosphere due to its organotropy and high mobility in the environment. Immobilization and further migration in the environment of radioidine occurs as iodide-anions I^- and iodate-anions IO_3^-. Geological disposal facility (GDF) for 1 and 2 class RW is currently designing in the Russian Federation and will be constructed in the 'Eniseisky' site (Krasnoyarsk Region) using bentonite clay-based engineered safety barrier (ESB) as its key isolating element. These barriers will securely retain the most of the radionuclides within disposal facility due to high cation exchange capacity and low water permeability of bentonites. However, bentonite barriers will not prevent the migration of anionic species of radioiodine. Thus, the inclusion of a certain amount of material with sorption properties towards anionic species of iodine will solve the problem of localization of radioiodine within the GDF on the "Eniseisky" site and ensure its safety for human and the environment. Analysis of the scientific literature shows that Ag, Cu(I), Pb, Hg и Tl-containing sorbents, that are able to uptake the iodine as a result of forming insoluble iodides and iodates, are the mostly investigated for preventing radioiodine migration from GDF. In this case, materials with high specific surface area modified with insoluble silver compounds, such as Ag, Ag_2O and AgCl, are characterized as having the highest selectivity and irreversibility of anion iodide sorption due to the lowest solubility of AgI and $AgIO_3$, and the greatest stability of silver towards aggressive media impact, therefore these sorbents are of the greatest interest.

The aim of the work is the development of bentonite-based silver-containing sorbents selective for anionic species of iodine, which are designed for use as a component of engineered safety barriers in geological disposal facilities for radioactive waste.

The main objectives of the work are:

1. Development of methods for the modification of bentonite clays with silver as Ag, Ag_2O and AgCl capable of uptake the anionic species of radioactive iodine.
2. Determination of the stability of silver and its compounds on modified bentonite in various media, including those corresponding to the expected operating conditions of the sorbent at geological disposal facilities for radioactive waste.
3. Determination of the sorption properties of the modified bentonite obtained towards I^- and IO_3^- in various conditions, including simulated possible environments at geological disposal facilities for radioactive waste.
4. Determination of I^- diffusion coefficients for samples of compacted modified bentonite.
5. Prediction of the long-term isolating capacity of modified bentonite-containing engineered safety barriers towards radioactive iodine.

Scientific novelty.

1. New methods of bentonites modification with Ag, Ag_2O and AgCl, without application of hazardous reactants and idiosyncratic reactions, are developed.
2. Sorption properties of Ag-, Ag_2O- and AgCl-modified bentonites towards anionic species of radioiodine in aqueous media of various chemical composition are defined for the first time.
3. Stability of Ag and AgCl in modified bentonite towards leaching in solutions with ionic strength values 0 – 3 $mol \cdot L^{-1}$ and pH values 7 – 12,4 is shown.
4. Regularities of the Ag и AgCl distribution in bentonite structure are determined for the first time.
5. Apparent and effective diffusion coefficients of I^- in samples of compacted Ag- and AgCl-modified bentonite is determined for the first time using through-diffusion method.
6. The calculated prediction by means of PhreeqC software showed that engineered safety barriers containing 10 % wt. of the bentonite modified with AgCl at 0.5% Ag from the clay weight will ensure that specific activity of ^{129}I in the geosphere will be below the intervention level for 2000 years after the beginning of the ^{129}I migration.

Theoretical and practical significance.

1. The optimal conditions of the reactions of the deposition of Ag, Ag_2O and AgCl on the surface of bentonite clays are determined.

2. Ag- and AgCl-containing bentonite-based materials with the high sorption capacity and selectivity towards I^-, and Ag_2O-containing bentonite-based materials with the high sorption capacity and selectivity towards I^- and IO_3^- are obtained.

3. The influence of bentonite structure, amount, chemical form of silver and its deposition method on I^- sorption is determined, I^- sorption isotherms on Ag and AgCl-containing bentonite are calculated, I^- sorption mechanisms on Ag- and AgCl-containing bentonite are determined.

4. High tendency of Ag_2O of reducing to Ag during bentonite modification is determined, therefore low stability of Ag_2O deposited on bentonite is shown.

5. High stability of Ag and AgCl on modified bentonite in media with various chemical composition, ionic strength and pH is shown.

6. Influence of bentonite modification method on the distribution of Ag and AgCl in bentonite structure is determined.

7. The effect of silver chemical form and its deposition method on the I^-migration rate in the compacted bentonite is determined in the I^-diffusion investigation.

8. Based on the results of studies of I^- sorption and diffusion, as well as sorbent stability, it was found that the most promising for use in the composition of engineered safety barriers of the geological disposal facility for radioactive waste is the AgCl-modified bentonite of 10^{th} Khutor deposit in the amount of 0.5% wt. Ag from clay weight in two stages: Ag deposition by $[Ag(NH_3)_2]OH$ reduction with formaldehyde evolving during hexamethylenetetramine thermal hydrolysis with subsequent Ag conversion to AgCl by treatment with $FeCl_3$ + HCl solution.

9. Based on the experimental data a calculated prediction of isolating capacity of engineered safety barriers with inclusion of 10 wt.% of AgCl-containing bentonite (10^{th} Khutor, 0.5 % wt. by Ag) for 2000 years after the beginning of ^{129}I migration was carried out using PhreeqC software.

The provisions to be defended:

1. New methods of bentonites modification with Ag, Ag_2O and AgCl.

2. Sorption properties of Ag-, Ag_2O- and AgCl-containing bentonites towards anionic species of iodine in aqueous media with various compositions.

3. The results of the investigation of Ag and AgCl stability on a selected modified bentonite (10^{th} Khutor deposit) under the impact of solutions corresponding to the most possibly aggressive and approximated to the real operating conditions of the obtained materials.

4. Regularities of change in surface characteristics of the bentonite of 10^{th} Khutor deposit when modifying Ag and AgCl

5. I^- diffusion properties in the samples of natural and Ag and AgCl-containing compacted bentonite of 10^{th} Khutor deposit.

6. Calculated prediction of isolating capacity of engineered safety barriers based on bentonite of the 10th Khutor deposit with addition of 10 % wt. AgCl-containing bentonite, towards radioactive iodine for 2000 years.

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