THE USE OF COMPOSITE FERROCYANIDE MATERIALS FOR THE TREATMENT OF HIGH SALINITY LIQUID RADIOACTIVE WASTES RICH IN CESIUM ISOTOPES

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Introduction. Several factors affecting the removal of cesium from LRW, namely total salt content, pH and organic matter content, were also investigated. High concentrations of complexing organic matter significantly reduced the sorption capacity of ferrocyanide sorbents.

Materials and methods. 15 ferrocyanide composites were synthesized for study, based on copper, nickel and cobalt ferrocyanide precipitated onto five different mineral sorbents - zeolite from the deposit "Bagration", clays (red clay, yellow clay and green clay) from the "Semeytau" deposits, and montmorillonite from the "Akzhar" deposit. These natural sorbents differ substantially in their mineral and chemical compositions.

For modeling the effects of different parameters on the sorption of cesium (pH, salinity, organic matter content): pH was adjusted with concentrated solutions of nitric acid and sodium hydroxide; salinity was modified by varying the concentration of the main component of salt content, sodium nitrate; and organic matter was introduced in the form of the complexants Na_2-EDTA and oxalic acid, which are used as decontaminating agents in nuclear power plant operation and which may reduce sorptive efficiency.

Results and discussion.

Cesium sorption capacity for the various sorbents decreases in the following order: montmorillonite (60.7) > red clay (39.3) > green clay (39.1) > yellow clay > (31.9) > zeolite (21.3) (all values in mg g^{-1}). Differences in adsorption capacity reflect the mineralogical and geochemical characteristics of the different sorbents, and are strongly controlled by specific surface area. Copper and nickel ferrocyanides performed better than cobalt ferrocyanide by an order of magnitude. Composites in the experiment extracted 96¬ 99% of the total content of cesium in solution. The distribution coefficient Kd ranged from 910^3 to 510^4. Kinetic data for cesium sorption from solutions modelling liquir radioactive waste showed that the selected sorbents reach sorption equilibrium in relation to Cs within one hour from the beginning of the experiment. The adsorption isotherms are described by Langmuir-type dependence. Over the remaining 2-6 hours of the experiment the amount of cesium adsorbed did not change. The dependence of the adsorption capacity on waste pH is most closely described by a second-degree polynomial equation (the value of the approximation R^2 = 0.92-0.98). At pH > 10, the adsorption capacity of composite sorbents and pure ferrocyanides begins to decline, being more noticeable for the latter. Adsorption capacity at pH 12 is decreased by 15-20% compared to lower pH values. The change of the sorption capacity of the composites is less marked, which may be due to their higher chemical stability in alkaline solutions. The data obtained show a decrease in adsorption capacity with increasing salinity in the model solution. However, even at very high salinities (ca. 500 g L^{-1}) sorbents are able to adsorb over 400 mg of cesium per gram.

Conclusions. The use of composite materials based on metal ferrocyanides combined with natural mineral sorbents for treatment of high salinity Cs-containing liquid radioactive waste (LRW) was investigated. Among the investigated composites, the best sorption characteristics for Cs were shown by materials based on copper ferrocyanide.