PROCEDURE OF CLEANING OF THE LIQUID RADIOACTIVE WASTE BY MODIFIED ZEOLITES OF ARMENIA

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Introduction

The usage of natural zeolites for efficient purification of liquid radioactive waste (LRW) from cesium and strontium is the task of great importance because zeolites exhibit high selectivity with respect to these radionuclides. For this reason thorough geological-petrographical and mineralogical-geochemical investigations have been carried out for classification and characterization of zeolite rocks from different Armenian deposits. A particular attention was drawn to zeolites from Nor Koghb (Noyemberyan region) deposit which is the richest with clinoptilolites. This type of zeolite was selected as base mineral for further investigations.

Results and Discussion

Chemical analysis was shown that K, Ca cations forms of clinoptilolite are dominant and that a linear dependence between water concentration and the sum of Na^+ and Mg^{2+} cations exists.

Experiments on thermal analysis of clinoptilolite samples have shown that dehydration process occurs during thermal treatment up to 700 ^{0}C without destruction of zeolite cage, after which it starts to deteriorate. Hence, temperatures below 700 ^{0}C may be used as optimal temperatures for treatments. Chemical treatments of the samples (in alkali and acid) have been used for increasing the clinoptilolite content in zeolite samples up to 95%. At the same time these experiments allow testing the samples stability in given chemical conditions. Also, the kinetics of some cations leaching initially presented in the zeolite structure is studied.

The adsorption isotherms with respect to the water and benzene vapors for the natural, acid treated and electron irradiated clinoptilolite samples were studied. It is determined that the acid treatment in solutions of some concentrations improves adsorption properties of the samples. The electron irradiation with doses up to 10^{15} e/cm^2 weakly affect the adsorption properties of the clinoptilolites, and at higher doses the collapse of the structure takes place.

The adsorption kinetics of the Cs^+ ions from the solutions of its salt, in which were placed the powder samples of the clinoptilolite (natural untreated, subjected to treated thermal and chemically, irradiated) was studied. It is found that the ion-exchange rate is maximal in the first 60 min, which is slowing later and reaching its saturation. The samples treated above 350^{0}C demonstrate sharp decrease of the ion-exchange capacity, and at lower temperatures the thermal treatment effects appear to be unnoticeable. For the electron irradiated samples the effect of the doses below 10^{15} e/cm^2 is small. The similar results were obtained in the case of γ-irradiation.

For making the mono-cation forms of clinoptilolite the zeolite was treated by ion-exchange in different metal salts. The chemical analysis of exchanged samples was carried out and exchange extent was determined. Absorption and ion-exchange properties (rate and depth) of mono-cationic forms of different clinoptilolite samples were studied depending on type of guest cation and contact time. It is determined that the best removal of Cs^+ cations from the solutions take place in the case of clinoptilolite samples in Na form treated by sodium hypochloride.

Experiments were performed also for investigations of the solution pH (Fig.1), Cs^+ concentration (Table 1) and temperature (Fig.2) on samples ion-exchange properties. The level of ion extraction is expressed by distribution coefficient $K_d = \frac{A_0 - A_f}{A_f} \cdot \frac{V}{m}$, were A_0 is concentration of cesium ions in initial solution, A_f is the concentration in purified final solution, V is solution volume, and m is the mass of solid absorbent-exchanger in solution.

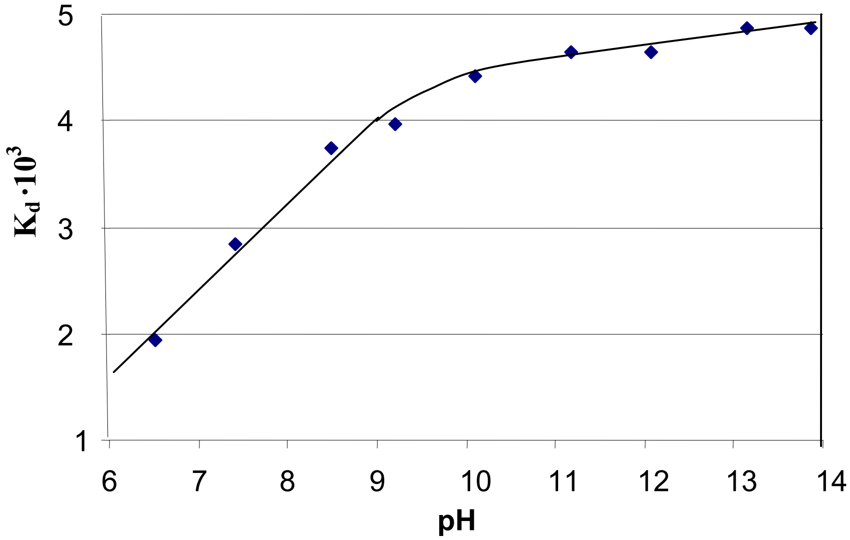

Fig. 1. Dependence of K_d for Na-clinoptilolte on pH of CsCl solutions

Table 1. Dependence of distribution coefficient for clinoptilolite on cesium concentration in solution

Concentration of Cs^+, g/l	Distribution coefficient K_d, ml/g
10^{-2}	$5 \cdot 10^3$
0.2 -1	$2 \cdot 10^3$
5-10	$5 \cdot 10^2$

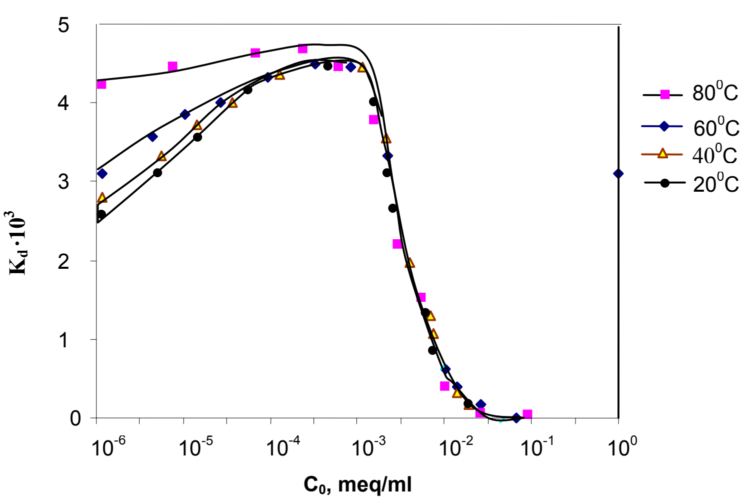

Fig.2. Temperature dependence of distribution coefficient for Na-clinoptilolte at different concentrations.

The influence of binder on zeolite granules preparation, their stability in static and dynamic conditions, and ion-exchange properties of clinoptilolite with respect to different cations in model solution was studied. The optimal characteristics as well as mechanical and chemical stability had the samples prepared with polyvinyl butyral as a binder.

Base on performed experiments the laboratory plant for extraction of metal cations from solutions in dynamic regime is designed and developed. This plant was used for successful experiments on Cs^+ removal from model solution and water cleaning.

Conclusions

The efficient technology is developed for preparation of chemically modified samples of Armenian clinoptilolite as ion-exchange absorber for treatment of Cs containing solution. These samples were studied with respect to their ion-exchange properties in model solutions in specially developed plant.

The results of experiments allow suggesting these sorbents for future treatment of liquid radioactive waste, particularly in Armenian Nuclear Power Plant.

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