Cleaning of liquid radioactive wastes using natural zeolites

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Abstract

Natural zeolite, clinoptilolite, was used to eliminate liquid radioactive wastes (LRW) ^{137}Cs and [90]Sr. The influence of several factors (pH of solution, grain size of the zeolite, etc.) on the process effectivity was studied. It was shown that clinoptilolite is an effective filter of the nuclides above. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Natural zeolites, clinoptilolites, have been successfully used to eliminate several types of LRW. Thus, a porous clinoptilolite was applied to eliminate ^{137}Cs, ^{90}Sr and ^{60}Co in the Institute of Atomic Energy of Japan. The elaborated method was recommended for industrial use (Breek, 1974). Several zeolitas, in particular, clinoptilolite, were used by Nikashina and Zaborskaya (1977) and Zaitsev et al. (1984) (Russia) to elucidate a sorption mechanisms of ^{137}Cs and [90]Sr.

Clinoptilolite (Fig. 1, Table 1) belongs to family of the most widespread zeolites (Barrer, 1985), so, its wide use in enviromental protection as a 'filter' could be inexpensive and simultaneously ellective. An ideal composition of clinoptilolite is $Na_6[Al_6Si_{30}O_{72}] \cdot 24H_2O$. A pore volumen (in cm^3 of H_2O per cm^3 of the crystal) is approximately 0.34 (Barrer, 1985).

In this work we studied dependence of cleaning of LRW by this zeolite on several experimental conditions.

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2. Experimental part

Study of sorption properties of clinoptilolite was carried out in static and dinamic conditions. According to the strict norms of LRW contents, their activity should not exceed 3×10^{-10} Ci/L. Taking into account that LRW have a small activity, the radionuclides are in a small concentration ($< 3 \times 10^{-9}$ mg/L) and a distribution coefficient K_d is the main measured value

$$K_d = (K_w - 1)V/m,$$

where K_w is a cleaning coefficient, V is a solution volume (mL) and m is a sorbent weight. K_d is convenient value, since its magnitude is a constant and it does not depend on concentration of adsorbing ions in the range of their low concentrations at static conditions.

The system utilized to carry out the experiments contained the following parts: a column for the adsorbent, hydrocharge system, and neumatic system of hydrocharge entrance. It was prepared for use as follows. Clinoptilolite was put into the system through the hydrocharge system. A pulverized adsorbent was cleaned by portions with demineralized water (in counter-current) during the periods of 15 min before the
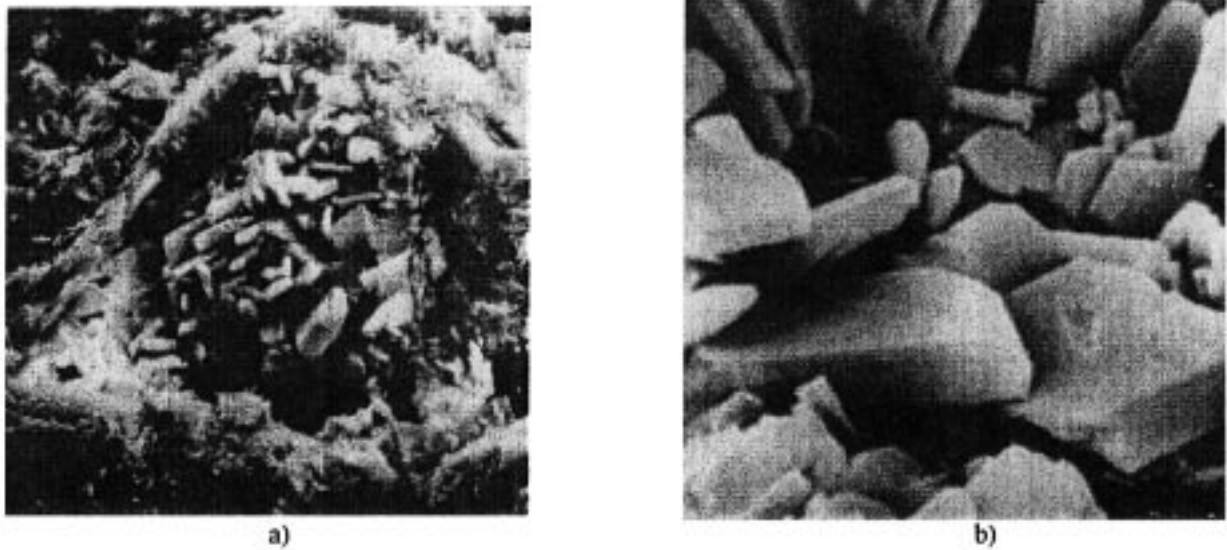
Fig. 1. Clinoptilolite crystals: (a) ×600, (b) ×2000.

moment when the solution used for cleaning of the adsorbent is almost transparent. Then the adsorbent was cleaned in direct current before the moment when the liquid phase becomes clear.

After this procedure, a cleaning of LRW of small activity was carried out. A flow rate of the solution was varied in a range of 5 to 5.5 column volumes per hour in dinamic conditions.

A series of six samples of natural zeolites clinoptilolites was studied in the experiments in static conditions and a series of three different samples of clinoptilolites was used in dinamic experiments.

3. Results and discussion

The following values can be criterions to choose the most suitable adsorbents: distribution coefficient, cleaning coefficient of passing of the liquid through the column, and a solution volume passed through a unit of
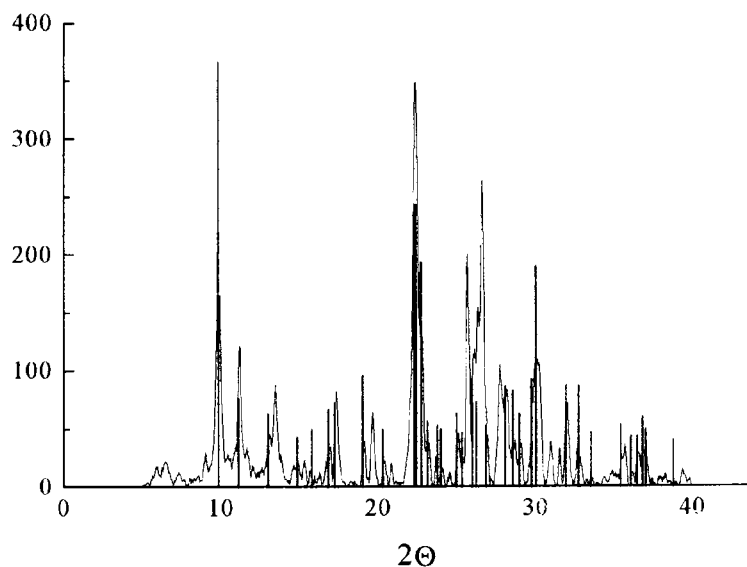

Fig. 2. X-ray powder data of the natural zeolite (static conditions experiment) after its regeneration.

Table 1
Chemical analysis data of clinoptilolite[a]

Components	Wt %	Ion contents in the elemental cell
SiO_2	62.36	Si 28.18
TiO_2	0.39	Ti 0.13
Al_2O_3	13.14	Al 7.01
Fe_2O_3	1.63	Fe 0.55
FeO	–	–
MgO	0.92	Mg 0.62
CaO	2.72	Ca 1.32
Na_2O	3.99	Na 3.50
K_2O	1.20	K 0.69
H_2O[b]	8.32	H_2O 20.57
H_2O[c]	5.33	O 72.0

[a] Clinoptilolita
$Na_{3.50}K_{0.69}Mg_{0.62}Ca_{1.32}[(Al_{7.01}Fe_{0.55})(Si_{28.18}Ti_{0.13})O_{72}] \cdot 20.57$-$H_2O$.
[b] Crystallization water.
[c] Extra water which is present in clinoptilolite mineral and does not form its crystal structure.

volume of the adsorbent before achievement of good cleaning coefficient.

In case when it is possible ($K_w = 10^2 – 10^4$ times) to pass through the column a volume of solution some thousands greater in comparison with adsorbent volume, a regeneration of the adsorbent is purposeless due to its low cost. So, studies on clinoptilolite use for above objectives have a considerable interest.

Because of a variability of LRW of small activity, all sorption experiments in static conditions have been carried out in a solution of the only background electrolyte (sodium nitrate, 1.5 g/L or 17.6 mg-equiv./L on sodium ion). Its use allowed to decrease a sorption of the radionuclides on the system walls and contributed to an exactness of measurements.

During the cleaning process, the pH varied from 7 to 8.5. After regeneration of clinoptilolite with NH_4^+ ions, it was washed with distilled water, filtered and exposed to the following thermal treatment. Heating was begun starting from 50°C, increasing 10°C every 30 min to attain 300°C. Then clinoptilolite was maintained at this temperature during 3 h and again heated gradually 10°C every 30 min to attain 550°C (in air flow passing through the clinoptol015te). After 5 h of maintaining at this temperature, the product was cooled to room temperature. The data of X-ray powder diffraction of heated product showed an absence of structural changes (Fig. 2).

The obtained results in static conditions are presented in Table 2.

Table 2
Sorption of ^{137}Cs and ^{90}Sr in clinoptilolite

No. of clinoptilolite sample	^{137}Cs		^{90}Sr	
	K_d, mL/g	Final pH	K_d, mL/g	Final pH
1	16,000	8.1	3700	8.5
2	10,000	7.5	–	–
3	6000	7.4	2750	7.4
4	6350	7.7	5500	7.5
5	–	–	1200	7.0
6	16,500	7.0	–	–

Table 3
^{137}Cs sorption by clinoptilolite (Na^+ concentration = 17.6 mg eq/L)

Clinoptilolite (sample 1D)				Clinoptilolite (sample 2D)			
Grain size 0.5–2.0 mm, flow velocity 5.6 column vol./h		Grain size 0.25–1.0 mm, flow velocity 2.7 column vol./h		Grain size 0.2–2.0 mm, flow velocity 4.9 column vol./h		Grain size 0.25–1.0 mm, flow velocity 5.4 column vol./h	
$V_{soln}/V_{sorb.}$	K_w	$V_{soln}/V_{sorb.}$	K_w	$V_{soln}/V_{sorb.}$	K_w	$V_{soln}/V_{sorb.}$	K_w
193	255	456	1640	337	12400	492	6300
467	317	1083	1290	637	8600	1050	7200
991	329	1834	1190	1018	4860	1634	4490
1275	326	2578	970	1480	3450	2250	4070

Table 4
Cleaning coefficient of ^{90}Sr (flow of the solution is 5.0–5.3 column volume/h; clinoptilolite grain size is 0.25–1.0 mm)

Clinoptilolite (sample 3D)

$V_{soln}/V_{sorb.}$	K_w	$V_{soln}/V_{sorb.}$	K_w
272	18000	1058	370
404	10500	1400	340
740	5000	1830	340
900	4500	1940	380

The distribution coefficient (K_d) was used, since its value is constant and does not depend on a concentration of absorbed ion, when the ions are present in low concentration.

The dinamic conditions of elimination of ^{137}Cs and ^{90}Sr are the following for both cases: the solution contained 1.5 g/L of $NaNO_3$ (17.6 mg·eq/L), the pH value in the exit place of the solution was 7–8. The results of ^{137}Cs and ^{90}Sr sorption in clinoptilolite in dinamic conditions are presented in Tables 3 and 4.

As it is seen from Table 3, use of larger size of sorbent grains (0.5–2.0 mm) leads to decrease of cleaning grade. Moreover, a difference in effectivity of use of big and small grains is decreased, if the experiment is carried out at lower velocities. The results presented in Table 4 show the effective cleaning of ^{90}Sr solutions.

4. Conclusions

Clinoptilolite having grain size 0.25–1.0 mm is recommended to use to eliminate LRW of low activity containing ^{137}Cs and ^{90}Sr. The pH of used solutions should be aproximately 8 and flow velocity should not exceed 5 column volumes per hour. The present result demonstrate the effectivity of natural zeolites with high silicium contents (clinoptilolites) as filters for above LRW.

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