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Sorption behavior of tritiated water on Armenian natural zeolites

Y. Keheyan,^{1*} S. Khachatryan,¹ G. Christidis,² D. Moraetis,² R. Gevorkyan,³ H. Sarkisyan,³ H. Yeritsyan,⁴ S. Nikoghosyan,⁴ A. Hovhannisyanyan,⁴ A. Sahakyan,⁴ N. Kekelidze,⁵ L. Akhalbedashvili⁵

¹ CNR, ISMN, Chemistry Department, University of Rome "La Sapienza", p.le Aldo Moro, 5, 00185 Rome, Italy

² Technical University of Crete, Laboratory of Petrology and Economic Geology, 73100 Chania, Crete, Greece

³ Mineralogy Petrography Department, Yerevan State University, Alek Manukyan Str. 1, 375025 Yerevan, Armenia

⁴ Yerevan Physics Institute, Solid State Radiation Physics Department, Alikhanian Bros. Str. 2, 375036 Yerevan, Armenia

⁵ Tbilisi State University, Department of Materials, Chavchavadze ave. 1, 380028 Tbilisi, Georgia

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The sorptive behavior of tritiated water on natural, irradiated, chemically treated and heated at high temperatures Armenian zeolites was studied and their capacity for the separation and enrichment of tritiated water was evaluated. The distribution coefficients from the batch experiments were calculated for different zeolites and vary between 0.23 and 3.01. The influence of temperature, acidity, basicity, specific activity, electron and gamma-irradiation on sorption has been studied.

Introduction

Tritium (T or ³H) is a relatively short living nuclide with half-life of 12.3 years and is present in all nuclear reactors and reprocessing plants as a fission product.¹ Tritium, the heaviest and only radioactive isotope of hydrogen, is increasing in importance in environmental considerations. The naturally occurring levels of this isotope are the result of cosmic ray interactions in the atmosphere. Additional sources are from fallout from weapons and by waste products of nuclear power reactors. The possible use of tritium as fuel for fusion reactors may result in an additional source of tritium.² This isotope may be present in a number of chemical forms, but frequently a large fraction occurs as tritiated water (HTO), which is found in the gaseous and liquid effluent streams of many nuclear installations.¹ The vapour of HTO is formed readily. PRICE³ has determined that in the range of 25 to 80 °C, the vapour pressure of HTO is less than that of H₂O and that HTO has a higher boiling point than H₂O (100 °C).

The removal of fission products from waste water is an important problem nowadays. Many organic and inorganic adsorbents have been used to remove tritiated water from nuclear waste. Among the adsorbents molecular sieves are most commonly used in tritium recovery systems and tritiated water is usually adsorbed and retained on them.^{4–6} The capability of many molecular sieves; 3A, 4A, 5A, 13X synthetic zeolites,⁷ alumina pillared group IV phosphates,^{8,9} clay minerals,⁹ silica gel, activated alumina,¹⁰ boro-silicate glasses,¹¹ natural mesolite¹² and others to provide sorption of tritiated water in its liquid and gaseous state is well known in the literature.

The selective separation of HTO and H₂O on molecular sieves from tritiated water is based on the

difference of interaction forces between adsorbent and adsorbed molecules. These interaction forces include dispersion and short-range repulsion energies, polarization energy and components due to electrostatic interactions.¹³ They are different for HTO and H₂O molecules as a result of the large isotopic effect. This leads to fractionation of HTO between sorbed and equilibrated water.

Studies on the removal of tritiated water using difference in adsorption characteristics between HTO and H₂O on synthetic 3A, 4A, 5A, 13X zeolites and alumina-pillared group IV phosphates have shown their great potential for the separation HTO and H₂O. A distribution coefficient of HTO greater than unity has been calculated. The distribution coefficient of alumina-pillared group IV phosphates is two times greater than that of synthetic zeolites.⁸

Sorptive behavior of tritiated water on natural zeolites is less thoroughly studied.

Clinoptilolite is a zeolite of the heulandite group with typical monoclinic unit cells. The void volume of clinoptilolite is 0.34 cm³/g and the mineral is, therefore, known as compact zeolite. Clinoptilolite-rich zeolites are used for the removal of ammonium from municipal sewage and radionuclides, i.e., Cs and Sr, from wastes of nuclear power plant stations.¹⁴

The water molecules have an effective radius of 1.3 Å, and the tritiated water molecules have a radius of 1.41 Å.

The sorption of tritiated water in zeolites could vary if the original cation in the zeolite lattice is replaced by other cations, like Ba²⁺, etc. Ion-exchange can be accompanied by some changes in the Si–O framework.¹⁵

The aim of this work was to study the sorptive behavior of HTO on Armenian natural zeolites and evaluate their potential for the separation of HTO from HTO/H₂O mixtures.

* Author for correspondence.

Experimental

The clinoptilolite-rich zeolite tuffs used in this study were collected from the Noyemberyan deposit, Nor Kokhb region, Republic of Armenia. The geological, mineralogical-petrographical and geochemical description of Noyemberyan zeolite deposit was presented in Reference 16.

X-ray diffraction (XRD) analyses show that the clinoptilolite content in used tuffs varies between 70–85%. Tuffs contain also a minor quantity of feldspar, quartz, montmorillonite, mica, calcite and other rock materials.

The chemical composition of clinoptilolites is given in Table 1. The content of SiO₂ varies between 65.44–75.00% and the Si/Al ratio between 3.56–5.42 which shows that they belong to high silicon containing zeolites of the heulandite family. In our experiments we have used zeolites chemically treated (activated, treated by BaCl₂, H₂SO₄, NH₄OH, NaOCl, HCl). To estimate the irradiation effect on zeolite sorption capacity electron- and gamma-irradiated samples have been used. The particle and pore size of used zeolites were 10–75 nm, and 3.6–4.4 Å, respectively.

A number of zeolite samples were exposed in air to doses of gamma-ray irradiation, namely 200, 700 kGy at 293 K using a ⁶⁰Co γ-cell (Atomic Energy of Canada, Ltd.) and the irradiated samples have been contacted with HTO. The distribution coefficients¹ were calculated for all samples.

Batch experiments were carried out in 50-ml Erlenmeyer flasks. Each type of clinoptilolite was contacted with a known volume (such that volume to weight ratio be 10:1) of tritiated water (Amersham) of initial activity 45 μCi/ml for different contact times at ambient temperature. The mixture was stirred with a magnetic stirrer (500 rpm). The solution was then filtered using 0.22 μm syringe filters (cellulose acetate membranes with porosity of 0.22 μm). The radioactivity of initial and final solutions were counted by a Packard Tri-Carb 2260 XL spectrometer using an Optiphase "HiSafe 3" as liquid scintillator. The tritium counting efficiency (25%) and background (30–40 cpm) in the energy region used for tritium were measured periodically. One, two and ten minutes countings were carried out for each sample. Some of the samples before contact with tritiated water were activated at 350 °C and 1.332 Pa for 5 hours to enhance the surface and channels in zeolites. The zeolite cavities can be partially occupied by water, nitrogen, oxygen and other molecules, and these impurities can disturb the HTO sorption. Thus, drying of samples results in a partial release of these

impurities from the micropores and then more sorption sites become available for tritiated water. Indeed drying rises the HTO/H₂O ratio of the sorbents.¹ For a batch experimental system, K_d has been expressed as:⁶

$$K_d = \frac{C_i V_i - C_e (V_i - m w)}{m w C_e}$$

where C_i and V_i are the initial specific activity and volume of the tritiated water, respectively, C_e is the specific activity of equilibrated tritiated water, m is the water adsorption capacity of zeolites, w is the weight of zeolites. In the used Armenian zeolites the adsorption capacity varied from 13 to 16 ml/g.

Results and discussion

The experimental results are shown in Table 2. The distribution coefficient varies between 0.23 and 3.01 indicating the different capacities of the zeolites for sorption of HTO. The difference in the K_d values could be attributed to the type of treatment of the zeolite. The raw materials contain K⁺, Na⁺, Ca²⁺, Mg²⁺, while chemically treated zeolites also contain Ba²⁺, H⁺. They are present in the cavities of the zeolites due to their specific location, charge and size. They affect the adsorption selectivity of the zeolites for HTO and H₂O molecules by different electrostatic interaction forces.

There is a dependence between K_d and contact time. The amount of sorbed tritium increased with contact time until 48 hours, after which K_d slightly decreased (Table 2) probably due to a desorption process.

At room temperature HTO can penetrate into the zeolite framework gradually through micropores. Desorption, probably takes place only on the surface because insidely sorbed HTO is more stably kept by strong framework charge because once sorbed it could not easily be desorbed.¹¹

The adsorption characteristics of H₂O and HTO on molecular sieve 5A, as well as on silica-gel and activated alumina, were studied by TANAKA and YAMAMOTO.¹⁰

The investigations of radiation effects in zeolites are very scarce, although radiation modifications of these materials can play a significant role in changing the sorption and other properties.^{17–20} By irradiation of zeolites with γ-rays or with high energy particles it is possible to change the atom charge states, creating lattice point defects and their accumulation creates disordered areas, etc. The irradiation induces radiation defects with controllable concentration and type without changing the stoichiometry of the irradiated material.

Table 1. Chemical analysis of Noyemberyan clinoptilolite

Oxides	Composition, wt%	Element	Atomic composition
SiO ₂	68.75	Si	30.9
Al ₂ O ₃	11.92	Al	6.31
MgO	0.96	Mg	0.58
TiO ₂	0.30	Ti	0.18
CaO	4.37	Ca	3.12
Na ₂ O	0.65	Na	0.48
K ₂ O	2.20	K	1.82
H ₂ O	13.06	H ₂ O	13.06
Fe ₃ O ₄	1.63	Fe	1.18

Table 2. Variation of the distribution coefficient in Armenian zeolites

No.	Name	Dominating cation	Contact time, h	K_d
1	Raw	K ⁺ , Na ⁺ , Ca ²⁺	0.5	0.30
2	Raw	K ⁺ , Na ⁺ , Ca ²⁺	2	0.30
3	Raw ^a	K ⁺ , Na ⁺ , Ca ²⁺	2	0.48
4	Raw	K ⁺ , Na ⁺ , Ca ²⁺	24	0.90
5	Raw ^a	K ⁺ , Na ⁺ , Ca ²⁺	48	1.01
6	Raw ^b	K ⁺ , Na ⁺ , Ca ²⁺	48	1.12
7	Raw	K ⁺ , Na ⁺ , Ca ²⁺	60	0.98
8	Raw	K ⁺ , Na ⁺ , Ca ²⁺	240	0.94
9	Raw	K ⁺ , Na ⁺ , Ca ²⁺	1 month	0.90
10	Treated by BaCl ₂	Ba ²⁺	0.16	0.77
11	Treated by BaCl ₂	Ba ²⁺	0.5	1.16
12	Treated by BaCl ₂	Ba ²⁺	2	1.6
13	Treated by BaCl ₂	Ba ²⁺	24	1.50
14	Treated by BaCl ₂	Ba ²⁺	48	0.89
15	Treated by BaCl ₂ ^a	Ba ²⁺	48	1.16
16	Treated by BaCl ₂	Ba ²⁺	240	0.90
17	Treated by H ₂ SO ₄	H ⁺	0.5	0.23
18	Treated by H ₂ SO ₄	H ⁺	2	0.64
19	Treated by H ₂ SO ₄	H ⁺	48	1.50
20	Treated by H ₂ SO ₄ ^a	H ⁺	48	1.60
21	Treated by H ₂ SO ₄ ^a	H ⁺	60	1.58
22	Treated by HCl ^a	H ⁺ , K ⁺	48	3.01
23	Treated by HCl ^a	H ⁺ , K ⁺	60	1.3
24	Treated by NaOCl	Na ⁺ , K ⁺	3	0.48
25	Treated by NaOCl	Na ⁺ , K ⁺	24	0.50
26	Treated by NaOCl	Ag ⁺ , Na ⁺	3	0.85
27	Treated by NaOCl	Ag ⁺ , Na ⁺	24	0.90
28	Treated by NH ₄ OH	Na ⁺ , K ⁺ , H ⁺	3	0.77
29	Treated by NH ₄ OH	Na ⁺ , K ⁺ , H ⁺	48	0.80
30	Treated by NH ₄ OH	Na ⁺ , K ⁺ , H ⁺	60	0.80

The concentration of clinoptilolite in zeolites varies in the range of 85–90%.

^a Before contact outgassed at 350 °C and at 10⁻² torr for 5 hours.

^b pH 1, acid added to the solution.

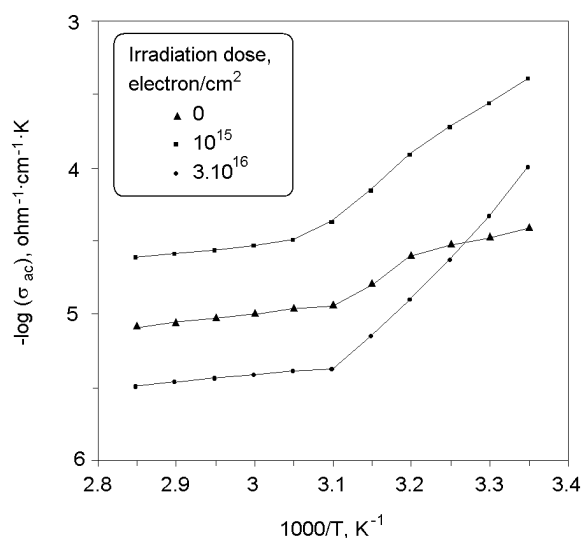
The overall uncertainty of the measured values of K_d values was estimated to be ±5–6%.

Table 3. Activation energies (in eV) of natural clinoptilolite (raw) before and after electron irradiation as a function of the temperature

Irradiation dose, electron/cm ²	$T \leq 310$ K	$310 \leq T \leq 322$	$T \geq 322$ K
0	0.3	0.66	0.08
10 ¹⁵	0.64	1.0	0.08
3·10 ¹⁶	1.4	1.0	0.08

Table 4. Variation of K_d in gamma- and electron-irradiated zeolites

Treatment	Dominating cation	Irradiation dose, e/cm ²	Contact time, h	K_d
Treated by BaCl ₂	Ba ²⁺	10 ^{14a}	48	0.77
Treated by BaCl ₂	Ba ²⁺	3·10 ^{13b}	48	0.90
Raw	K ⁺ , Na ⁺ , Ca ²⁺	1·10 ¹⁷	48	0.77
Raw	K ⁺ , Na ⁺ , Ca ²⁺	3·10 ¹⁰	48	0.90
Raw ^c	K ⁺ , Na ⁺ , Ca ²⁺	700 kGy	48	1.08
Raw ^c	K ⁺ , Na ⁺ , Ca ²⁺	200 kGy	48	1.08
Heated at 700 °C	K ⁺ , Na ⁺ , Ca ²⁺	200 kGy	48	1.10
Heated at 700 °C	K ⁺ , Na ⁺ , Ca ²⁺	—	48	0.56

^a Irradiated after chemical treatment (treated by BaCl₂).^b irradiated before chemical treatment (treated by BaCl₂).^c Gamma-irradiated.Fig. 1. Arrhenius dependence of the a.c. conductivity (σ_{ac}) measured at 1 kHz on the temperature of natural clinoptilolite for different irradiation doses

Thus, by irradiation it is possible to control the sorption and other properties of the zeolite. References 18 and 19 have reported that the irradiation of US-HY zeolite by ionizing γ -rays induces contrasting effects. A low dose irradiation assists the protonic conduction by increasing proton mobility whereas a high dose resists the protonic conduction due to increasing loss in the assisting role of water on dehydration. A nonlinear dependence of adsorption properties of zeolite NaA was observed^{21,22} after γ and neutron irradiation with doses of 0–1200 kGy. At small doses (5–50 kGy) there is an ordering structure whereas at higher doses disordering of the crystal lattice takes place. The observed ordering of structure after irradiating with small doses is explained by the annihilation of initial (sometimes named biographic) defects while the disordering of structure is explained by the accumulation of radiation defects. At some doses of the electron irradiation with an energy of 8 MeV an increase of sorption property of natural clinoptilolite is observed.²⁰ Authors suggested that this

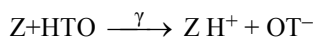
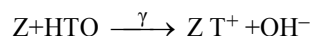
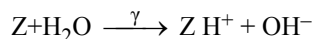
is due to the variation of the charge states of zeolite atoms with electron irradiation but not to structural changes at the cell level. Sorption properties of Armenian natural clinoptilolite in relation to water and benzene vapors after their irradiation by electrons with an energy of 8 MeV have shown that the sorption of water vapors increases with increase of the dose, and that of vapors of benzene decreases. The sorption and migratory behavior of heavy water in Armenian, Georgian and Greek clinoptilolites having various sizes of granules and chemical modification was also investigated.

Among natural zeolites the clinoptilolite represents great interest mainly because it is widespread in nature, has a high Si/Al>4 molar ratio and a nanoscale porous system.¹⁷ The study of radiation effects of Armenian natural clinoptilolite after electron irradiation and electrophysical and optical properties was performed.²³ Here, at initial irradiation doses the dielectric constant increases monotonously more than three times up to a dose of 10¹⁵ electron/cm². However, at a dose of 3·10¹⁶ electron/cm² the dielectric constant sharply decreases and this dose is critical for the zeolites. Figure 1 illustrates the Arrhenius dependence for some samples of natural clinoptilolite before and after electron irradiation. One can see that the activation energy has a different behavior depending on the irradiation dose. The comparison of these experimental data shows that for all samples at a temperature of 322 K (and higher) the activation energies are the same, i.e., 0.08 eV. At lower temperatures different activation energies were observed (Table 3).

The influence of electron and gamma-irradiation on the sorption capacity of zeolites has also been studied and reported in Table 4.

From the comparison of non irradiated samples with irradiated ones it is evident that irradiation does not affect significantly sorption capacity. However, an increase of electron irradiation decreases sorption capacity. Under high dose of electron irradiation the structure of zeolite can deform until destruction (amorphization). Gamma-irradiation slightly increases

the sorption capacity of raw materials, however, a dependence between K_d and irradiation dose effects was not observed. Gamma-irradiation generates in general a loss due to dehydration and a specific loss due to gamma-assisted contraction of the zeolite channels. The influence of γ -radiation is shown schematically in the following reaction scheme:



where Z is zeolite.

The results are in coincidence with previous similar ones²² where the influence of γ -irradiation on the IR absorption of zeolite showed dehydroxylation of the zeolite surface and formation of water molecules which increases with the γ -irradiation dose.

The action of high-energy radiation on solids is important in the design of materials for use in the nuclear industry. Large irradiation doses (MGy, 1 Gy = 1 J/kg) can lead to observable atom displacements in the crystal lattice. Irradiation of SiO_2 yields colour centres that absorb in the UV.^{24–28} These coloured centres are called E centers and are associated with trapped electrons.

The studies on the radiolysis of SiO_2 , $\gamma-Al_2O_3$ and Si-Al gels suggest that the prime action of the radiation on these oxides is the formation of positive cavities and electrons. When heated at 700 °C zeolites show significantly low sorption capacity. Previous studies have shown that Armenian zeolites are not affected when heated upon to 700 °C, even heating up to 750–800 °C does not modify its basic physical-chemical parameters.¹⁶ This suggests that temperatures up to 700 °C do not influence significantly sorption capacity.

Clinoptilolite has been investigated by BARRER and MAKKI²⁹ as a source of porous, largely crystalline, molecular sieve sorbents.

By treating the zeolite with acid of different strengths a range of high area sorbents has been produced, in which all the original cations have been replaced by hydronium ions, and in which the aluminium has been progressively removed from the frameworks (Fig. 2). From water, a polar molecule, the sorbed volume did not vary greatly among all the sorbents. (H_2O content in original zeolite is 13.5 cm³/100 g at $p/p_0=0.5$ and 0.25, 14 cm³/100 g at $p/p_0=0.5$ and 15).

It has been shown that at 5M HCl only the molar ratio of $Al_2O_3:SiO_2$ becomes 0.00:10.8 with composition of $[Si_{5.4}O_{8.8}(OH)_4]_n \cdot H_2O$. The elimination reaction produces nests of four hydrogens in number equal to the Al removed when in the original this ratio

was 1:10.8. In our experiments the treatment with 2M HCl has given an approximate composition of crystalline product $H_3O^{+}_{0.08}[Al_{0.08}Si_{5.4}O_{9.1}(OH)_{3.7}]_n \cdot H_2O$.

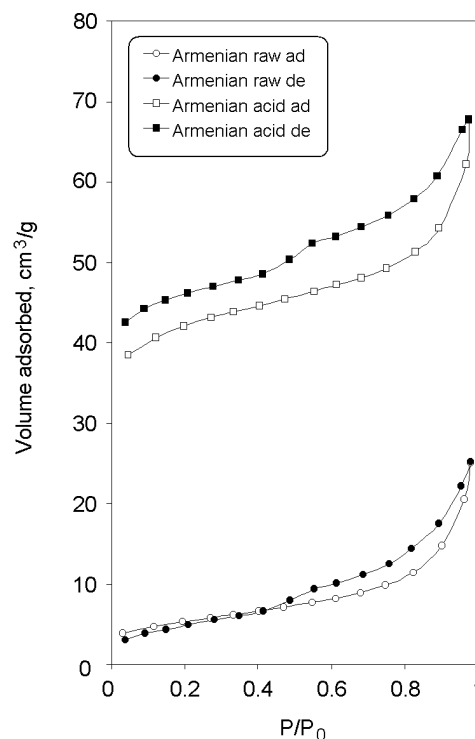


Fig. 2. Thermogravimetric curves of the Armenian original clinoptilolite and clinoptilolite treated with 2N HCl

When aluminosilicates are treated with mineral acids there may be an exchange of their cations by hydronium ions and hydrolysis of Al–O–Si bands occurs (silica gel and aluminium salts are formed) (Fig. 3).

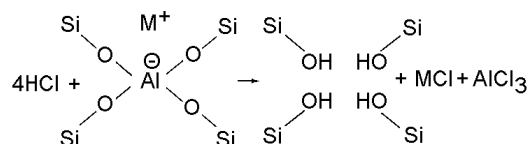
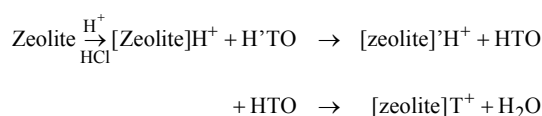


Fig. 3. Dealumination process

Steady state dissolution rates are observed proportionally to the mineral surface area under the influence of acid. A Langmuir-type dependence on the dissolved concentration of the reactive species is also observed. This observation is consistent with the involvement of surface complexes as radiation intermediates.^{30,31}



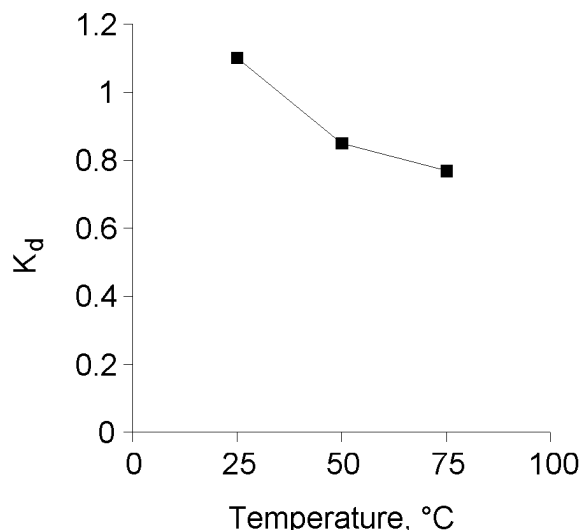
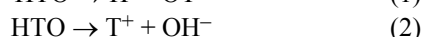
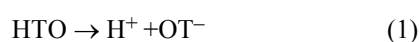


Fig. 4. Dependence of K_d from temperature

In Reference 32 it has been found that the dependence of K_d on temperature in the range of 5–70 °C and on initial activity of the solution in the range of 10^{-2} to 10^1 $\mu\text{Ci/ml}$ was not significant and authors explained that by the fact that the dimension of water molecule is significantly smaller when compared to the pore sizes of the molecular sieves, thus the sorption process does not involve activated diffusion. To evaluate the temperature effect, additional experiments were carried out also at $T=50$ °C and $T=75$ °C, taking into consideration only one sample (85% clinoptilolite rich raw material) (Fig. 4).

An increase of temperature slightly decreases the K_d . This can be explained by the dissociation of HTO. The HTO dissociates as:



Equation (2) predominates at high temperatures.^{33,34}

BRECK et al.³⁵ examined the adsorption of water vapor on silica gel and type A zeolites. Temperature dependence of adsorption capacity of zeolites was favorable when compared with that of silica gel. The temperature change from 25 to 100 °C caused the former to reduce by a factor of 1.6 while the latter by a factor 20. On the other hand, molecular sieves are superior to other adsorbents at higher temperatures and lower water vapor pressures, because their adsorption capacity has much smaller temperature and vapor pressure dependences.

These trends are in accordance with the results of NAKASHIMA and TACHIKAWA.³⁶

Conclusions

The sorption behavior of HTO on irradiated raw and chemically treated zeolites was studied and distribution coefficients were determined. The distribution coefficient varies between 0.23 and 3.01. These variations of K_d suggest that Armenian zeolites have different sorption capacities, which can be explained by the nature of cations, due to their size, charge, and location in the zeolite structure.

Different cations can display different interaction with HTO and H_2O molecules, consequently these zeolites have different distribution coefficients.

Contact time plays a significant role on sorption ability. However, the equilibrium between different zeolites and HTO/ H_2O mixtures is achieved after a minimum of 2 hours. The sorption behavior of zeolite depends on the nature of the cation species, their size and charge, as well as, the structure of the zeolite.

The temperature has a negative effect on sorption. An increase of the temperature apparently results in a decrease of sorption. This phenomenon depends on HTO dissociation.

Electron irradiation significantly decreases sorption capacity. With an increase of the irradiation dose from $3 \cdot 10^{10}$ to 10^{17} e/cm^2 sorption apparently decreases. This can be explained by the zeolite framework destruction (amorphization) under high dose irradiation.

Gamma-irradiation does not affect sorption significantly. Zeolites heated at 700 °C and gamma-irradiated zeolites display slightly higher sorption.

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