The Exchange of Tritiated Water Between Zn-A Zeolite and the Surrounding Water

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Zeolites are considered as adsorbents for tritiated waste water. The sorption capacity of 4A zeolite is increased, and the speed of tritium release, as THO, decreased if sodium ions in 4A zeolite are replaced with small divalent cations. The exchange kinetics THO/H_2O between Zn—A zeolite containing tritiated water and the surrounding water was investigated at 30—60 °C, using zinc--exchanged 4A zeolite beads of 0.8 and 1.6 mm radius. The kinetics was controlled by the diffusion of water in the solid particle and interpreted in terms of the Boyd — Reichenberg diffusion model. Effective self-diffusion coefficients of water in the zeolite beads were obtained and the kinetic data are discussed from the point of view of using zeolites as sorbents and storage material for tritiated waste water.

INTRODUCTION

The escape of tritiated water into the environment is a potential hazard in nuclear facilities. Zeolites have been proposed as sorbents for tritiated waste water,[1,2] but their storage after use requires careful consideration since they release tritium by exchange when in contact with water vapour or liquid water.[3,4]

In our previous papers[5-7] we investigated the kinetics of THO release from zeolite beads into the surrounding water, using 4A and 13X zeolites and the ion-exchanged Cs—A and Co—A forms.[7] Experimental data revealed that the half-life of THO/H_2O exchange is almost two orders of magnitude longer when 67% of sodium ions in 4A zeolite are replaced by divalent cobalt cations. In the present work we investigate the release of THO from Zn—A zeolite into the surrounding water, in order to get more information about the influence of cations in the lattice upon the diffusion of water in zeolite pores.

EXPERIMENTAL

Preparation of Zn—A zeolites

Commercial Linde 4A beads of 1.6 and 3.2 mm nominal diameter were used as starting material. According to manufacturer's specification they contain up to 20 w.% of a mineral clay binder. Sodium in the zeolite beads was replaced by zinc according to the ion-exchange procedure described elsewhere.[8] The exchanged beads were thoroughly washed with distilled water, dehydrated by prolonged heating at 350 °C, then placed in a dessicator vessel over a saturated aqueous solution of ammonium chloride containing $3.7 \cdot 10^6$ Bq of tritium per gram of water. After 14 days of equilibration at 25 °C, samples attained constant weight and were taken and analzed for Zn, Na and H_2O (+THO) contents as described previously.[8,9] The following results were obtained:

1.6 mm beads: 14.90 w.% Zn, 0.61 w.% Na, 20.68 w.% H_2O.

3.2 mm beads: 12.80 w.% Zn, 1.40 w.% Na, 20.44 w.% H_2O.

Using the same procedure for pure 4A zeolite crystals (without binder), the formula of the unit cell obtained[9] was: $Zn_{5.55} Na_{0.90} (AlO_2)_{12} (SiO_2)_{12}$; hence the molar ratio Zn/Na was 5.55/0.90. That ratio in our samples, including, of course, the binder, is 5.67/0.66 for the 1.6 mm bead and 5.20/1.60 for the 3.2 mm bead. The difference between the two beads is most probably due to a slight difference in the content of binder (which varies in different batches).

Experimental Technique

Zeolite samples of about 1 g, saturated with tritiated water were transferred into a thermostatted vessel containing 50 g of water. The rate of exchange of THO in the solid phase and H_2O in the liquid phase was measured by taking, after suitable time intervals, liquid aliquots of 0.05 g for tritium determination. During the exchange, the liquid phase was constantly agitated. The aliquot and 5 cm³ of the scintillation mixture were placed in a vial and tritium measured in a »LKB« liquid scintillation counter.

RESULTS AND DISCUSSION

According to Hellferich[10], the isotopic exchange of an uncharged sorbate molecule between a solid and liquid phase can be interpreted, in principle, by the diffusion models developed for isotopic ion-exchange if the basic assumptions relevant to the model are satisfied. In the present case, spherical particles are in contact with a vigorously stirred liquid phase. The ratio of bulk watter and the water content in the solid is about 250, and at any elapsed time the ratio of THO/H_2O in the liquid phase is extremely low. The above experimental conditions satisfy the simple Boyd — Reichenberg solid phase diffusion model for »infinite solution volume«:[11]

$$F_t = 1 - 6/\pi^2 \sum_{n=1}^{\infty} 1/n^2 \exp(-n^2 \tau) \tag{1}$$

Here F_t is the extent of exchange, τ is a dimensionless function which depends on the elapsed time t and on the self-diffusion coefficient D of the exchanging species in the solid phase:

$$\tau = D \pi^2 (t - t_o)/r^2 \quad \text{for} \quad t \geq t_o \tag{2}$$

Eq. (2) is valid for a general case when the induction time t_o precedes the diffusion process. In the case of Co—A, the induction time t_o is related to the establishment of a steady state at the solid — liquid interface, when the release of THO is negligible.[7] In Eq. (2), r is the radius of the solid particles.
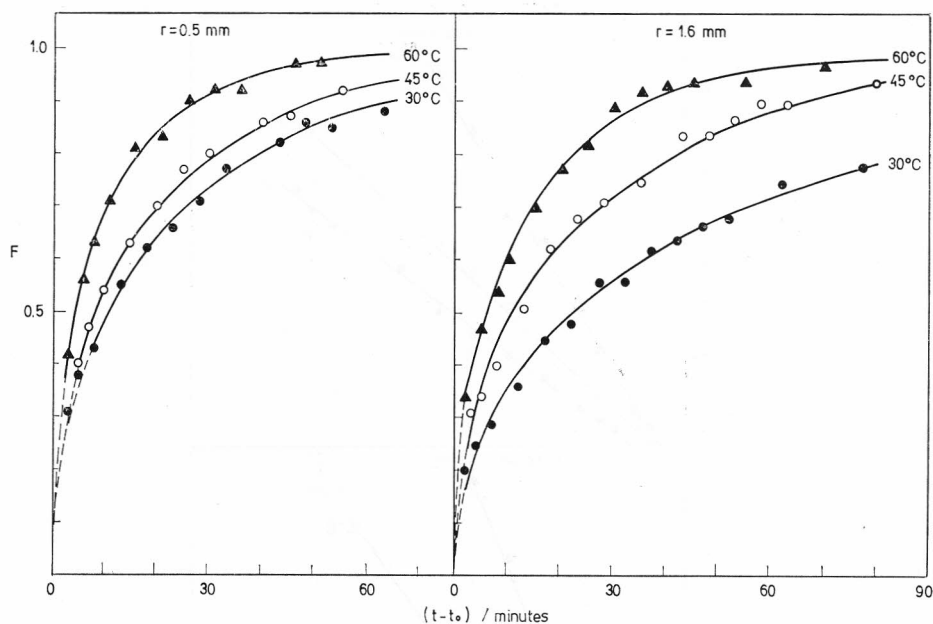
Figure 1. The extent of THO/H$_2$O exchange (F_t) against the elapsed time (t).

The experimental results are presented in Figure 1, as F_t *vs.* t curves for both bead sizes at three temperatures. Equations (1) and (2) were applied to our experimental data. From the F_t values the corresponding values of τ were obtained using the numerical table of Reichenberg.[11] Figure 2 presents τ *vs.* t plots according to Eq. (2). From the straight lines in Figure 2 the values of D and t_o were computed using the least-squares linear regression. With the Arrhenius type of equation for the diffusion coeficients:

$$D = D_o \exp (-E_D/RT) \tag{3}$$

the activation energy for diffusion, E_D, has been obtained. The calculated values of t_o, D, E_D and D_o are listed in Table I.

A comparison of the exchange kinetics is presented in Figure 3. Points are experimental measurements, the lines are Eqs. (1) and (2) fitted to the experimental data. The influence of cations in the lattice framework is striking. When sodium ions are replaced by small divalent cations (Co^{++}, Zn^{++}), the exchange THO/H$_2$O is much slower. Comparing cations with the same charge, no simple rule can be formulated. The exchange is faster when the larger Cs$^-$ replaces Na$^+$, but the opposite is true in the case of smaller Zn^{2+} ions compared to Co^{++}. The effect of ionic size for cations with the same charge is probably combined with the extent of exchange, and even more with the position of cations in the crystal lattice. To elucidate such combined effects, a study of the exchange on heteroionic zeolite forms might be necessary (for example, Zn—Na—A, stepwise from pure Na—A to pure Zn—A).
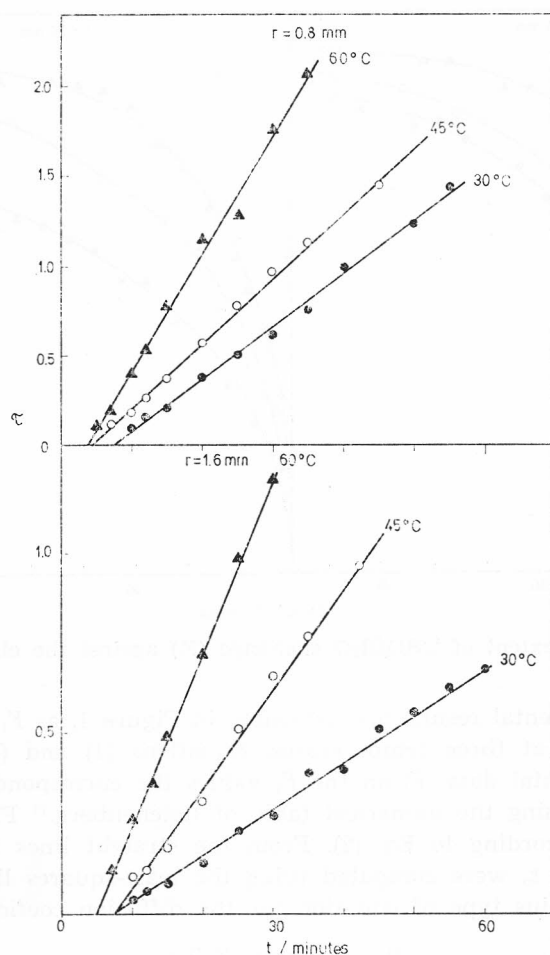
Figure 2. Plots of τ *vs.* t (eq. (2)).

TABLE I

Effective Self-Diffusion Coefficients (D), *Induction Time* (t_o) *and Activation Parameters*

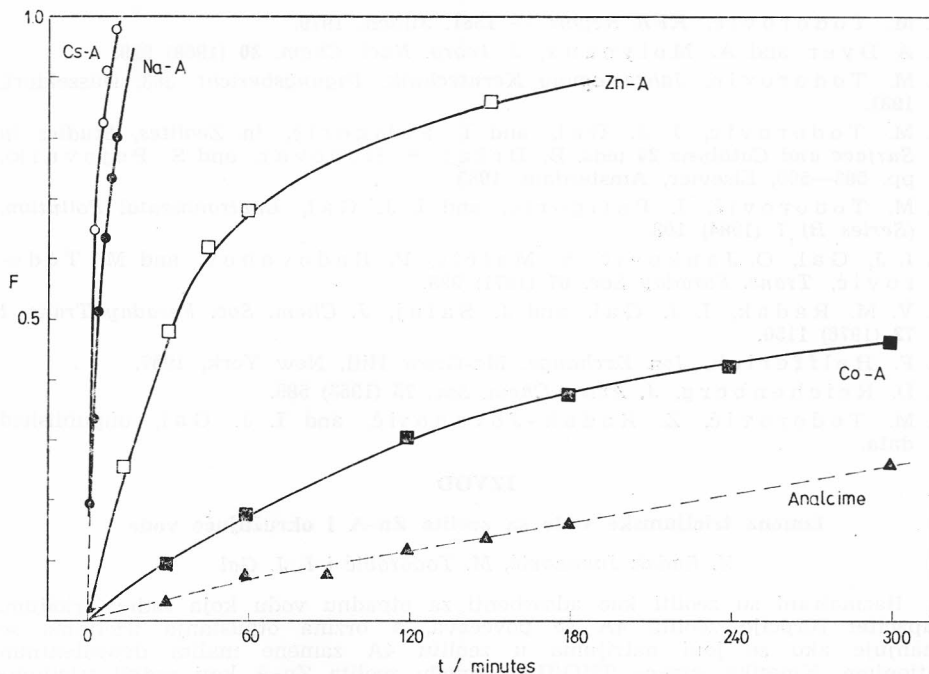| Nominal radius r/mm	Temp./°C	t_o/min	$10^{10}\,D/\text{m}^2\,\text{s}^{-1}$	E_D/kJ mol^{-1}	$10^5\,D_o/$ $/\text{m}^2\,\text{s}^{-1}$
	30	7.3	0.311 ± 0.008		
0.8	45	4.6	0.394 ± 0.008	25.0 ± 8	0.06 ± 0.01
	60	3.7	0.720 ± 0.013		
	30	7.9	0.571 ± 0.021		
1.6	45	7.2	1.180 ± 0.040	35.5 ± 1	7.73 ± 0.40
	60	4.8	2.070 ± 0.060		

Figure 3. F_t vs. t (eq. (1) and (2)). Na-A (ref. 5), Cs-A and Co-A (ref. 7), Zn-A (this work), Analcime (ref. 12). All A-zeolites in the form of Linde 4A beads of 1.6 mm radius with binder. Analcime is synthetic, pure crystals without binder, average radius $1.1 \cdot 10^{-5}$ m.

Zeolite 4A, in the form of commercial beads is a powerful drying agent with a sorption capacity of water of about 20 w. %. It is available in large quantities at a reasonable price. Therefore, it can be used as a sorbent and a temporary storage material for tritiated waste water, provided that after use it is well isolated from the environment. However, it is hardly suitable as a permanent storage material for tritiated water. By exchanging cations, the diffusion coefficient of water in the solid beads can be reduced to about $1 \cdot 10^{-12}$ m^2 s^{-1}, but this is still too high for permanent storage.[7]

Among the many synthetic zeolites now available ,it seems that an interesting material for storing concentrated tritiated waste water might be analcime, whose kinetics of THO/H$_2$O exchange is shown in Figure 3. In our next paper we shall report further on the release of tritiated water from analcime.

REFERENCES

1. F. A. K o e h l e r, B. D. C r a f t, B. D. A s h e, and H. A. W o l t e r m a n n, *Nucl. Technol.* **25** (1975) 497.
2. H. B r ü c h e r, D. T h i e l e, and M. T o d o r o v i ć, *Trans. Am. Nucl. Soc.* **31** (1979) 530.

3. M. Todorović, *KFA Report* — **1581**, Jülich, 1979.

4. A. Dyer and A. Molyneux, *J. Inorg. Nucl. Chem.* **30** (1968) 829.

5. M. Todorović, *Jahrestagung Kerntechnik, Tagungsbericht*, 363, Düsseldorf, 1981.

6. M. Todorović, I. J. Gal, and I. Paligorić, in *Zeolites, Studies in Surface and Catalysis* **24** (eds. B. Držaj, S. Hočevar, and S. Pejovnik), pp. 563—569, Elsevier, Amsterdam, 1985.

7. M. Todorović, I. Paligorić, and I. J. Gal, *Environmental Pollution, (Series B)* **7** (1984) 193.

8. I. J. Gal, O. Janković, S. Malčić, P. Radovanov, and M. Todorović, *Trans. Faraday Soc.* **67** (1971) 999.

9. V. M. Radak, I. J. Gal, and J. Salaj, *J. Chem. Soc. Faraday Trans. I* **72** (1976) 1150.

10. F. Helfferich, *Ion Exchange*, Mc-Graw Hill, New York, 1957.

11. D. Reichenberg, *J. Amer. Chem. Soc.* **75** (1953) 589.

12. M. Todorović, Z. Radak-Jovanović, and I. J. Gal, unpublished data.

IZVOD

Izmena tricijumske vode sa zeolita Zn-A i okružujuće vode

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Razmatrani su zeoliti kao adsorbenti za otpadnu vodu koja sadrži tricijum. Kapacitet sorpcije zeolita 4A se povećava, a brzina otpuštanja tricijuma se smanjuje ako se joni natrijuma u zeolitu 4A zamene malim dvovalentnim katjonima. Kinetika izmene THO/H_2O između zeolita Zn-A koji sadrži tricijumsku vodu i vode koja ga okružuje ispitivana je na 30—60 °C korišćenjem zrna zeolita 4A izmenjenih cinkom čiji su poluprečnici 0,8 i 1,6 mm. Kinetiku kontroliše difuzija vode u zrnu, a za interpretaciju je korišćen model difuzije Boyda i Reichenberga. Dobijeni su efektivni koeficijenti samodifuzije vode u zrnima zeolita, a kinetički podaci se razmatraju sa stanovišta korišćenja zeolita kao sorbenata i materijala za odlaganje otpadne tricijumske vode.