Effect of Neutron and Gamma Radiations on Zeolite and Zeotype Materials

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Summary:The influence of γ - and (n, γ)-radiation on the cation exchange and the structure of zeolite and zeotype materials has been studied. Samples were subjected to different doses of γ-irradiation varying between 0.5 and 10 MGy and Neutron irradiation flux varied from 1.14×10^{17} to 3.88×10^{17} n cm^{-2}. Structural effects consequent to γ-irradiation were examined by X-ray diffraction, electron scanning micrograph and FTIR measurements. Neutron and γ-irradiation did not lead any appreciable change in the structure, however, the displacement cations to "locked-in sites results partial reduced barium and caesium uptake. The decrease of the intensities of the absorption bands of the hydroxy-groups reveals that γ-irradiation has a strong dehydrating influence. The effect of γ-radiation on UO_2^{2+} and Am^{3+} uptake into NH_4-L and NH_4-SAPO-34 was also observed. K_d of the uranyl ions increased with increasing pH up to 6.3. At pH> 3.5, the uranyl ions were precipitated, and consequently the K_d values were contained to increase.

Introduction

Zeolites are crystalline aluminosilicate minerals, with open pore structures, widely used as catalysts and sorbents in the chemical industry. Zeotypes are microporous crystalline inorganic materails, analogous with zeolites to some extent, *e.g.*, B-ZSM-5 and SAPO-34. Zeotypes have largely been studied recently by isomorphic substitution of aluminum or silicon by other T-atoms (B, Be, Ga, Fe, Zr, Cr and P) in zeolitic framework [1-3]. Zeolite cation exchange properties have been studied extensively with regard to their utility as potential scavengers in the treatment of aqueous radioactive wastes, [4-5] as a carrier of target elements in nuclear reactors [6], and in facilitating Szilard-Chalmers separations [7-9]. Rees and co-workers have studied the effect of neutron irradiation on Linde Sieve 13X and correlated loss in gas sorption capacity to structural degradation caused by dehydration. γ-Irradiation is stated to create defects [11-12] that play an important role in forming centres of electron acceptors and donors [13]. In oxygen atmosphere, irradiation of zeolite-Y with γ-rays forms superoxide ions, O_2^-, attached to Na^+ cations; however, under vacuum, γ-irradiation forms centres of trapped electron that share among 4 Na^+ at site II position in the large cavities of zeolite-y [14]. γ-Irradiation is also assumed to form Lewis acid sites on dehydroxylating $NaNH_4Y$ zeolite [15]. The effect of gamma irradiation on the crystal structure, thermal stability and sorption characteristics of zeolite NaY has recently been investigated [16]. The present study deals with the sorption of actinide ions (UO_2^{2+}, Am^{3+}) in zeolite-L and SAPO-34 and subsequent the effect of γ-irradiation on the uptake and distribution coefficient (K_d). The influence of γ- and (n, γ)-irradiation on Ba^{2+} and Cs^+ cation exchange process in high silica zeolites and boron-zeotypes has also been studied. An earlier paper gave detailed consideration to self-diffusion of barium and caesium cations in neutron and gamma irradiated zeotype materials [17].

Results and Discussion

Effect of neutron and gamma irradiation

Changes in crystal structure of high silica zeolites and their boron-zeotypes under the influence of neutron irradiation were studied by X-ray diffraction, thermoanalytical methods and FTIR spectroscopy. X-ray diffraction indicated that all the materials retained excellent crystallinity after a mixed gamma/neutron exposure of 1.2×10^{18} n/cm^2. Scanning electron micrographs of unirradiated zeolites and zeotypes are shown in plate 1; the micrographs from the neturon irradiated samples were essentially identical in appearance. The thermograms (TG/DTG) of all materials studied were virtually identical before

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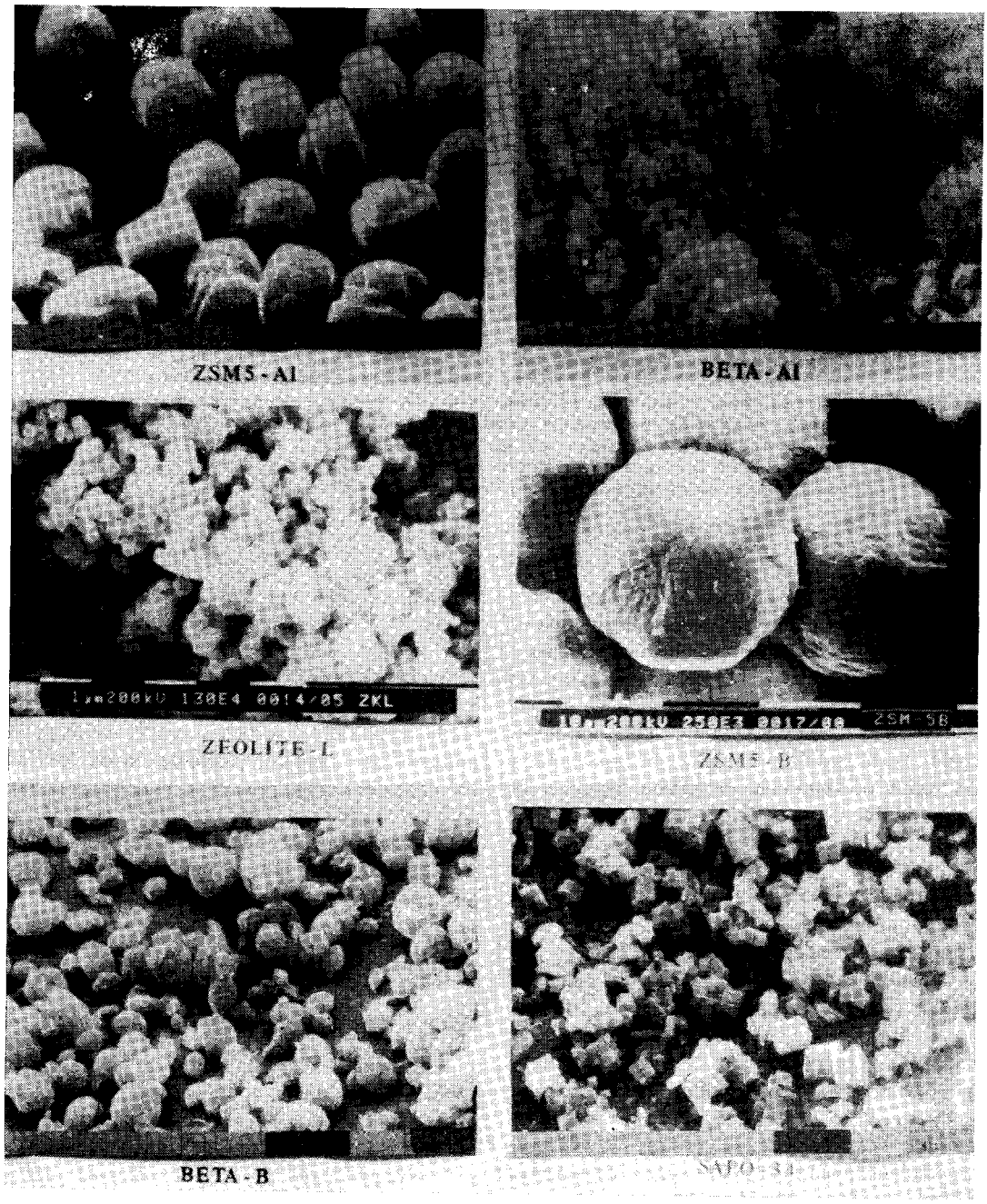


Plate 1. Scanning electron microscope of zeolites and zeotypes

and after gamma irradiations, only minor differences in weight loss being observed, (~10%) those of ZSM5 and BETA being slightly different from their boron-zeotypes. For all samples the effect of γ-radiolysis was only significant at low doses up to 0.5 MGy, little change occurring as the dose was further increased. The gamma protons from ^{60}Co have an average energy of ~1.25 MeV and their absorption therefore occurs largely by way of the Compton process. Energetic scattered electrons mainly displace the mobile cations from their normal positions. The displacement occurs through coulombic interaction with the nuclei [25]. In the case of zeolitic water, the absorption of γ-

radiation eventually brings about its radiolysis and this effect will have much greater importance than the displacement of ions. Radiolysis result in the formation of OH radical and hydrogen atoms (H) and moreover the hydrogen atoms may attach to the oxygen atoms of a Bronsted acid site thus generating equal numbers of Lewis acid and Bronsted base centres, causing further loss of water molecule [26]. This process, if present, obviously reached saturation at low dose. In samples which had received mixed gamma/neutron irradiation again only small effects at low doses were seen. It was perhaps significant that the main initial effect was completed after a neutron exposure which corresponded to a concomitant gamma dose of ~0.5MGy, *i.e.* the same dose as was responsible for the effect in samples which were irradiated with gamma radiation. The weight loss observed while heating from 373 to 1073K might therefore be attributable to dehydroxylation processes of exactly the same type and produced almost entirely by gamma radiation. It was not necessary to invoke effects due to thermal neutron reactions *e.g.*, $^{1}H(n, \gamma)^{2}H$ which has a cross section, ~ (330 mb) and to fast neutron induced recoils. However, in the boron zeotypes doped with ^{10}B changes were observed which depended upon the degree of neutron exposure, these being due to the nuclear reaction $^{10}B(n,\alpha)^{7}Li$ in the framework. It can be concluded that the neutron dose generally had only a small effect in contrast to previous work with zeolite NaY where the water content, and the course of its departure during thermal treatment, was clearly modified by neutron irradiation [8]. The effects produced by gamma irradiation, however, were in agreement. BETA-^{10}B proved an exception and a dose of 10 n cm^{-2} x 10^{17} created a 40% loss in weight. The reason for this was not clear.

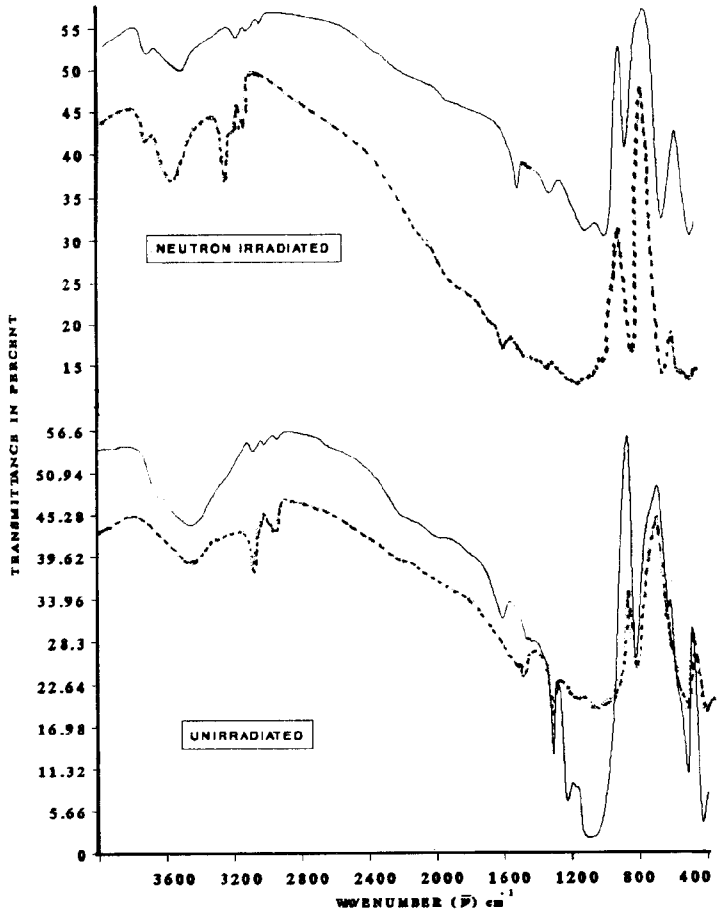


Fig.1: Infrared spectra (KBr pellet) of neutron irradiated and unirradiated zeolite ZSM5 and zeotype ZSM5-B ZSM5(—) ZSM5-B (----). Neutron exposure = 3.88 x 10^{17} n cm^{-2}.

Decreases in intensity of certain i.r. absorption bands were observed in neutron irradiated samples figures 1-2. The bands altered were those characteristic of hydrogen bonded water and may have indicated a crystalline arrangement of water in the irradiated samples [27]. Neutron-irradiation also leads to the appearance of absorption bands in the region of the stretching vibrations of the OH groups (3730, 3655 and 3350 cm^{-1}). In boronzeotypes the increase in vibration frequencies upon irradiation might be due to an increase in (Si, B)-O bond order. An increase in intensity of bands at 580 and 460 cm^{-1} could be attributed to the vibrations of the Si-O bonds in SiO_4 tetrahedra. The infrared spectra of zeolites in the 1300-200 cm^{-1} region appeared to consist of two classes of vibration, (a) those caused by internal vibrations of the framework TO_4, tetrahedron, the primary building unit in all zeolite framework, which tend to be insensitive to vibrations in frameworks structure and (b) vibrations related to external linkages between tetrahedra which were sensitive to the framework structure and to the presence of some SBU (secondary building unit) and building block polyhedra such as double rings and the large pore openings. No vibrations specific to AlO_4 tetrahedra or Al-O bonds are assigned but rather vibrations of TO_4 groups and T-O bonds where the vibrational frequencies represented the average Si, Al composition and bond characteristics of the central T cation [28].

Effect of γ-and (n, γ)-radiation on ion exchange capacities

The influence of gamma and mixed gamma/neutron irradiation upon the capacities for barium and caesium uptake in zeolites and boron-zeotypes is illustrated in Figures 3-4. The exchange

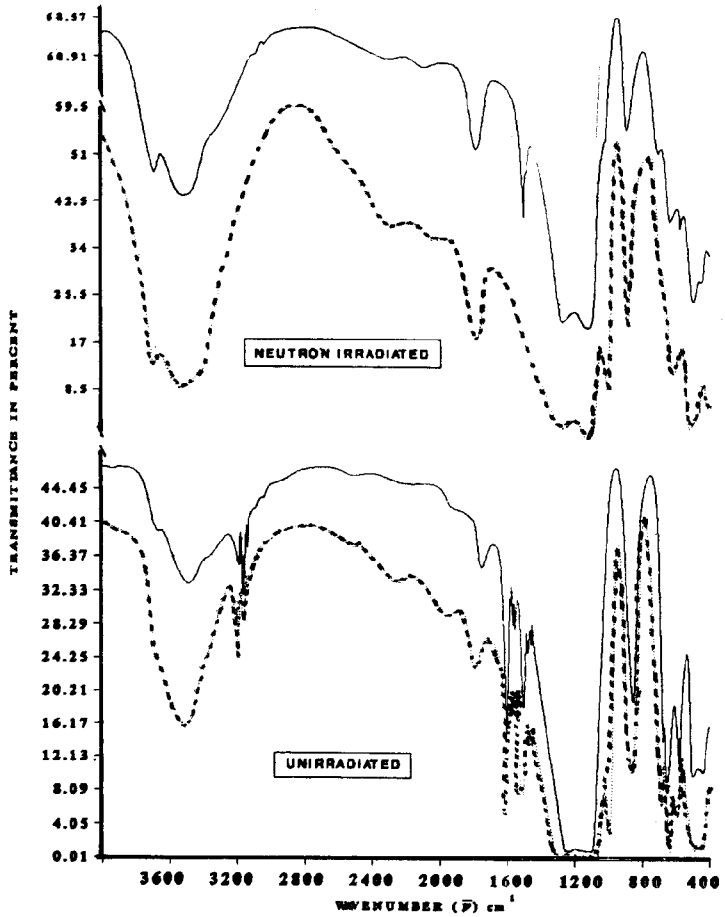


Fig.2: Infrared spectra (KBr pellet) of neutron irradiated and unirradiated zeoliter BETA and zeotype BETA-B (BETA (——) BETA-B(----). Neutron exposure = 3.88 x 10^{17}n cm^{-2}.

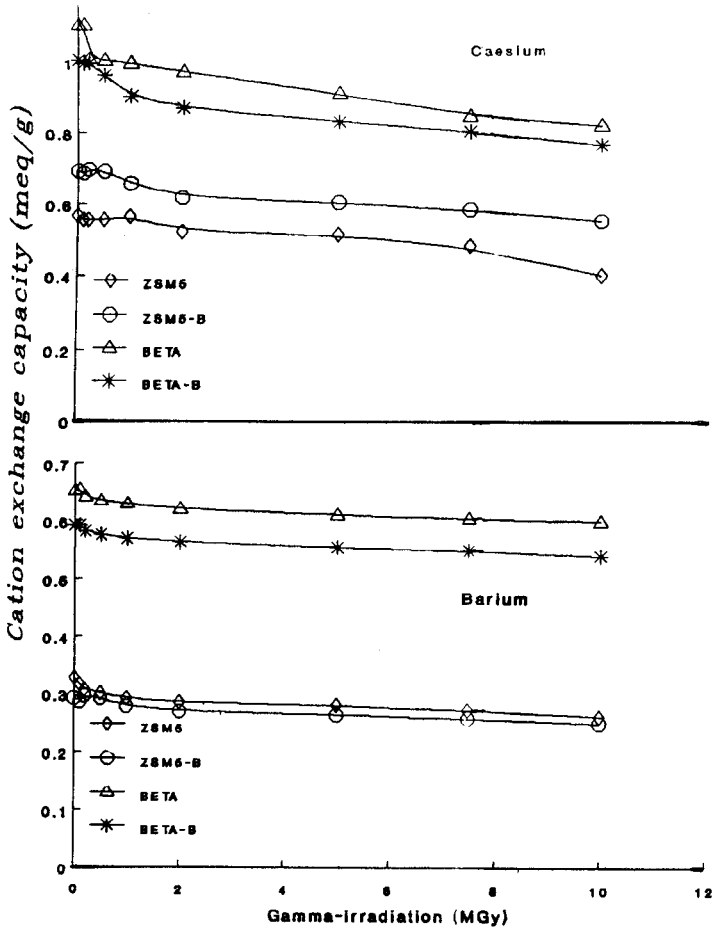


Fig.3: Effect of Gamma irradiation on caesium and barium exchange capacity in zeolites and their zeotypes.

capacity of Ba^{2+} and Cs^{+} was observed to decrease with increasing neutron exposure. This effect was especially pronounced in zeolite BETA. In a zeolite exchange involving large counter ions the extent of uptake may be limited to a certain extent by the available intracrystalline pore volume of the host lattice and to a greater extent by the departure of the window leading to these pores. The zeolite BETA offers large free dimensions topologically similar to the cages and cavities of faujasite (window width 7.4 Å) compared with kinetic diameters of Cs^{+} and Ba^{2+} of 3.3. Å and 2.86 Å respectively. The effect of irradiation apparently restricts the free movement of Cs and Ba cations and suggests that neutron irradiation favours the creation of locked-in sites for Ba^{2+} and Cs^{+} [7-9,29]. The probability of the recoil atom coming to rest in the locked-in site has been shown to be governed by the ratio of free volume associated with these sites to the total free volume in the zeolites [7,8]. When ZSM5, ZSM5-^{10}B, BETA and BETA-^{10}B were irradiated with slow (thermal) neutrons, the most probable changes were due to the (n, γ) recoil of the reaction ^{23}Na (n, γ) ^{24}Na and ^{27}Al(n, γ) ^{28}Al and to the (n, α) recoils of ^{7}Li and ^{4}He from the reaction ^{10}B(n, α) ^{7}Li. All of these would result in displacement damage by primary recoil and "knock on" processes. The energy transfer through elastic collisions of fast neutrons with constituent atoms was expected to disrupt the Si-O and Al-O bonds. Loss of exchange capacity due to radiation damage has been observed in synthetic zeolites 4A and NaX [30].

Data in Figure 4 indicate no change in exchange capacity of Ba^{2+} and Cs^{+} attributable to

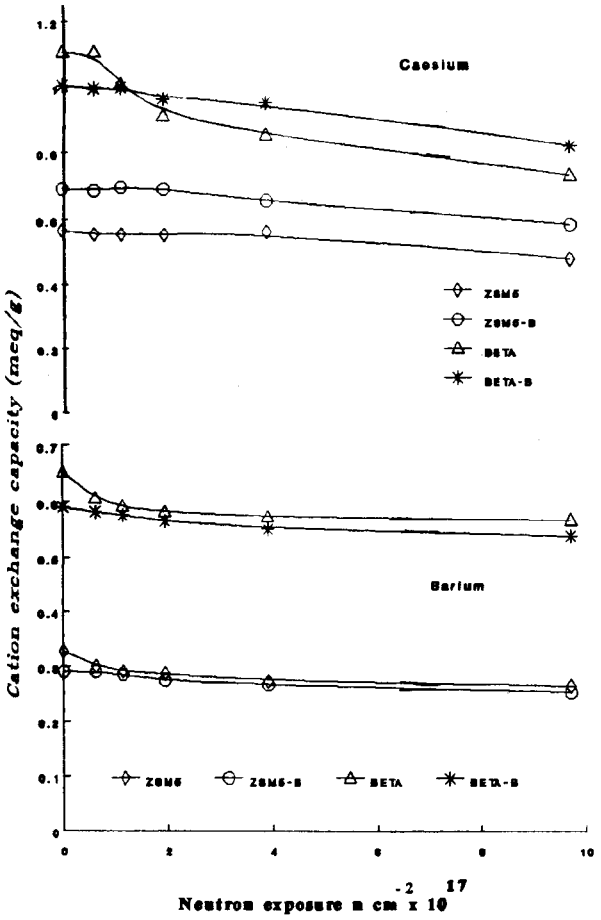


Fig.4: Effect of neutron irradiation on caesium and barium exchange capacity in zeolites and their zeotypes.

γ-irradiation effects on the structure of ZSM5 and ZSM5-B, but some differences in CEC of Ba^{2+} and Cs^{+} at low γ -doses were observed in BETA and its boron zeotype. The low uptake of Ba^{2+} and Cs^{+} ions was the consequence of Na^{+} ions being largely confined within the sodalite cages which were inaccessible for Ba^{2+} and Cs^{+} cations. Radiation had little effect on sodium exchange and therefore it was concluded that radiation induced displacement of cations from the supercage to the sodalite cage and vice versa did not significantly alter the original concentration of the exchangeable cations in the supercage.

Effect of γ-irradiation on pH and K_d values

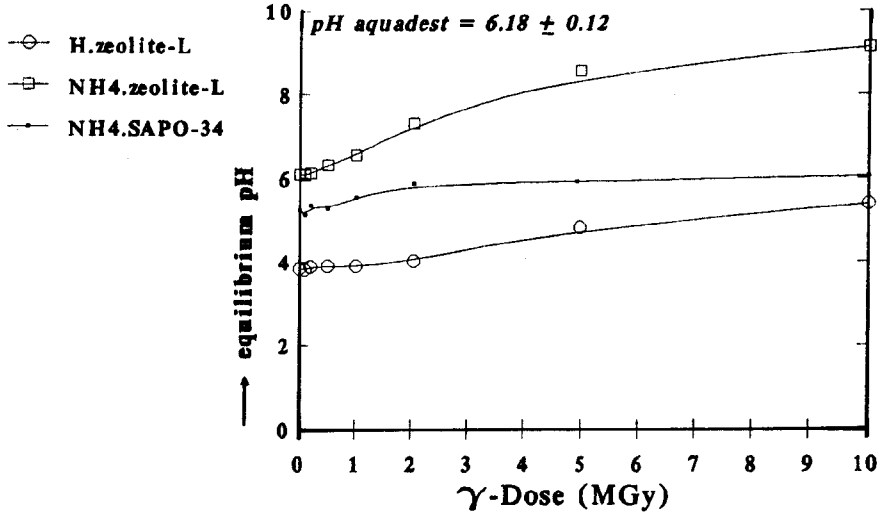
Figure 5 shows the effect of γ -radiation on the pH of the exchanger in aqueous solution. It indicates that increased γ -dose caused increase of pH and was not influenced by the doses higher than 4 MGy. The γ-irradiation caused a tremendous increase in equilibrium pH of NH_4-L; this increase of pH was resulted by deammoniation and dealumination processes which were resulted by the localized heat generated by gamma irradiation [31,32]. Figure 5B indicates the effect of γ-irradiation on the distribution coefficient for Cs^{+} and Sr^{2+} uptake into NH_4-L. Doses up to 2 MGy caused a slight increase of K_d with the increase of pH.

Figure 6 shows the effect of γ-radiation on the UO_2^{2+} and Am^{3+} uptake the similar results were obtained for CO_2^{2+} and Am^{3+} uptake into NH_4-L. K_d of uranyl ions increased with increasing pH up to pH 6.3. At pH > 3.5, the uranyl ions were precipitated, and consequently the K_d values were continued to increase. No significant difference was observed in the K_d values with the increasing equilibrium pH for ^{241}Am uptake. The similar results were obtained for UO_2^{2+} and Am^{3+} uptake into NH_4SAPO-34 (Figure 6B). The uranyl ion exchange had a higher K_d value than for americium ion. The low concentration of Am^{3+} was influenced the equilibrium pH and hence the uptake and K_d values were different.

Experimental

The high silica zeolites and zeotypes (BETA, ZSM5-^{10}B BETA-^{10}B and SAPO-34) were synthesized hydrothermally [18-23]. Boric acid (92% enriched in ^{10}B) was supplied by K.K. Greef (Cambrian Gases U.K) and used for the preparation of ZSM5-^{10}B and BETA-^{10}B. ZSM5, and zeolite-L obtained from Laporte Industries, Widnes, U.K. NH_4 and H-forms of zeolite-L and SAPO-34 were used to observe the uranyl and americium uptake at various pH values (pH 1-5). 50 mg of sample was added to 20 cm^3 of appropriate solutions containing 0.01 M $UO_2(NO_3)_2.6H_2O$ in 0.01M HNO_3, or to Am^{3+} carrier free solutions (5 μCi/cm^3 in 0.01 M HCl) and the pH of the solutions was adjusted by ammonia solution. The samples were batch-exchanged for 2 weeks, centrifuged and analyzed for cation uptake. The UO_2^{2+} and Am^{3+} in the solution were estimated using the liquid scintillation analyzer (1900 CA Tri-Carb). HPGe detector and 4k multichannel analyzer (Canberra 35 Plus) was used to measured the γ-radioactivity

A. Effect of γ-radiation on pH of aqueous solution of zeolite-L and SAPO-34



B. Effect of γ-radiation on Kd of Cs and Sr exchange in NH4.zeolite-L

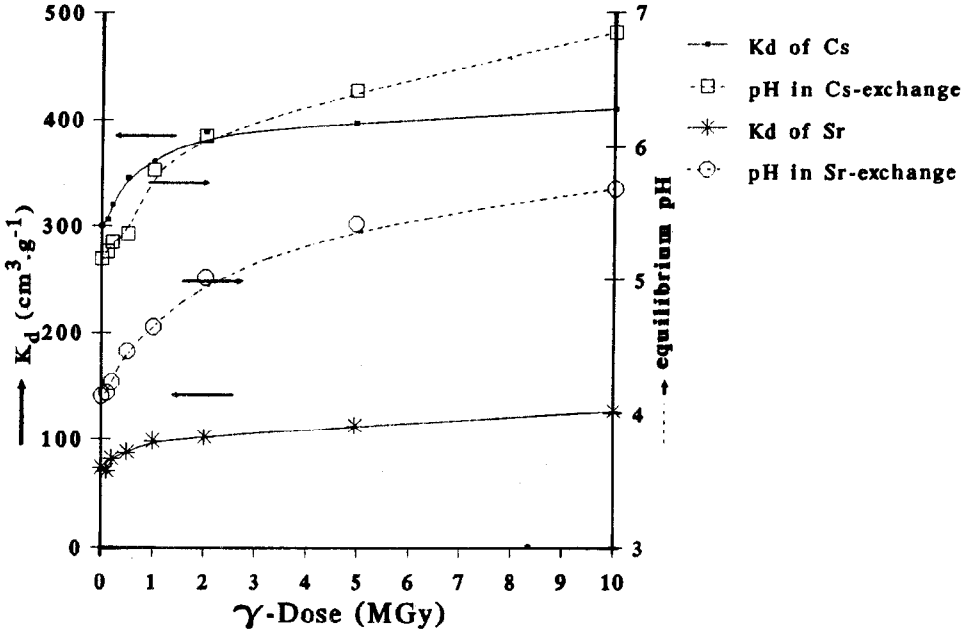


Fig. 5: (a-b) Effect of γ-radiation on pH and K_d values for zeolite-L and sapo-34.

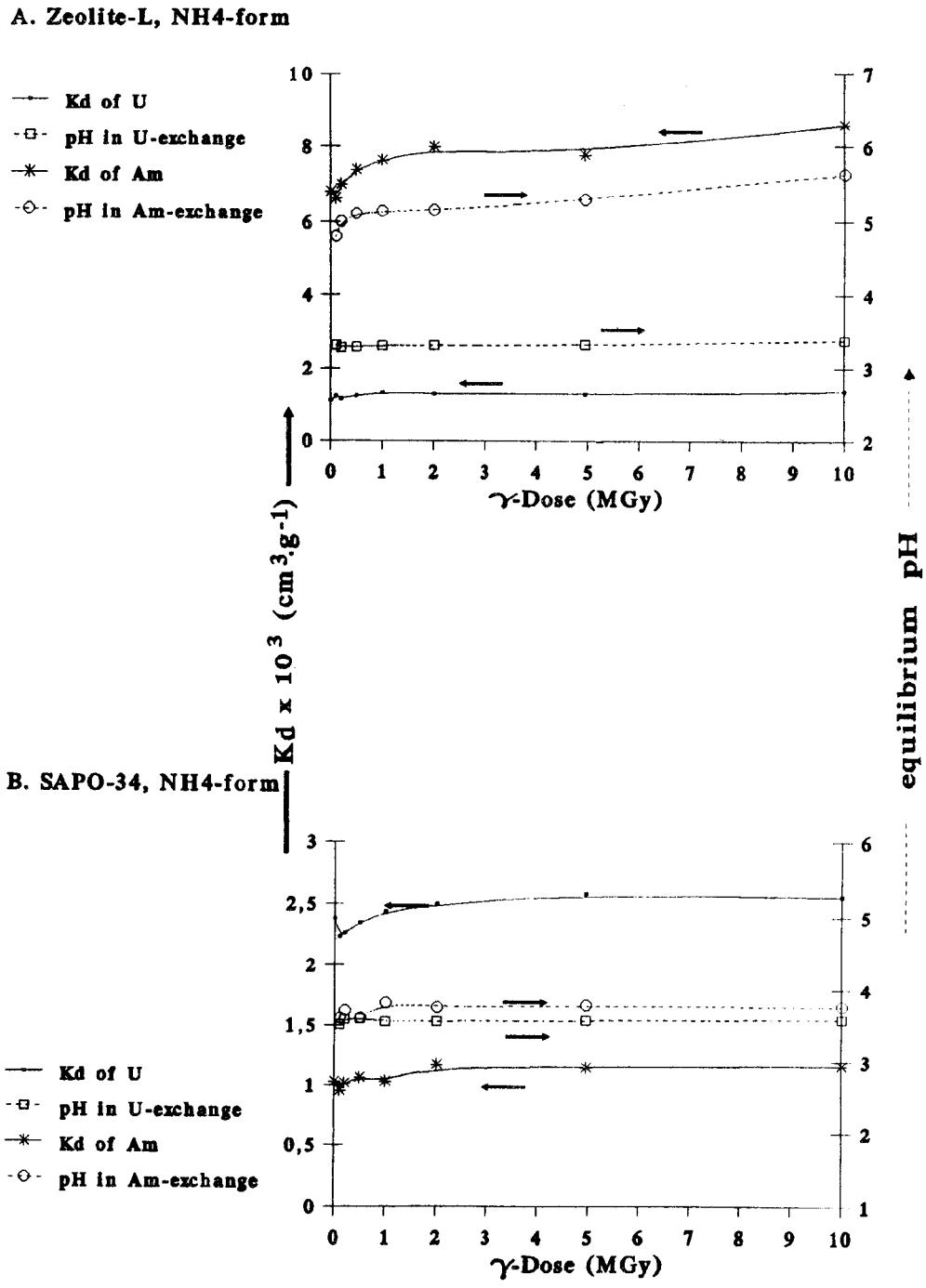


Fig.6: (a-b) Effect of γ-radiation on actinide exchange in zeolite-L and Sapo-34.

from ^{235}U and ^{241}Am in the solid samples, using the emissions: 185.6 kev for ^{235}U and 59.8 kev for ^{241}Am. Caesium was measured by Cerenkov counting.

Gamma irradiations were carried out in the University of Salford type NEL9 ^{60}Co γ-irradiation unit. The dose rate (~40 Gy min^{-1}) at the irradiation position used as determined by ferrous-

ferric (Fricke) chemical dosimetry [24]. Irradiation was carried out, at room temperature to achieve a total dose of 10MGy. Zeolites and boron-zeotypes (100 mg) were neutron irradiated for different time periods in the Universities Research Reactor, Risley, Cheshire, U.K., at a thermal neutron flux of $1.25x10^{12}$ n $cm^{-2}s^{-1}$. This neutron flux was associated with a gamma radiation field, and fast neutron flux for the same magnitude as the thermal flux in the reactor core. The concomitant gamma dose rate was approximately 0.06 MGy per hour. The combined irradiation is refered to as "mixed gamma/neutron". The total gamma dose was less than 0.5 MGy which, although not negligible, was small in comparison with the gamma doses given in the ^{60}Co facility.

The crystallinities and morphologies of irradiated and unirradiated materials were measured using a PW 1710 Phillips X-ray diffractometer (XRD), a Perkin-Elmer Fourier transform infrared spectrometer (FTIR 1710) and a scanning electron microscope (Cambridge S-600). Water contents were observed by thermogravimetry using a Mettler M3-TG50 thermobalance.

Conclusion

The ion exchange and sorption properties of particular ion are very specific for the individual exchanger and sorbent. High silica zeolites and boron-zeotypes were highly selective towards caesium and less so for barium. Zeolite-L with the unique columnar structure like chabazite, could be a promising sorbent for the removal Am^{3+}, but not for UO_2^{+2} in aqueous solution pH 2-4. However, the new zeotype material, SAPO-34 which has two dimensional structure-chabazite type, was found to have potential as an exchanger and sorbent, and tends to exhibit high selectivity for uranyl ions.

Neutron irradiation did not show any detectable effect on the crystal structure and thermal stability of high silica zeolites and boron zeotypes. Gamma radiolysis resulted in the loss of zeolitic water, the loss in weight which occurred at high temperatures and might correspond to a dehydroxylation process. Aluminosilicate high silica zeolites and boron-zeotype materials were both very resistant to both neutron damage and gamma radiation and thus may be useful as gas sorbents or cation exchangers under high fluxes of radiations.

γ-Irradiation dose greater than 1 Mgy decreases the acidity of L and SAPO-34. The non-framework Al may be produced from deammoniation and cause an increase the equilibrium pH of zeolite in water. There was no significant effect of γ-irradiation on either the cation exchange capacity or the actinide uptake into zeolite-L and SAPO-34. Small changes in uptake behaviour of UO_2^{2+} and Am^{3+} were due to change of the equilibrium pH. Which was created by localized heat generated by γ-radiation and annealing process. Radiation induced displacement of exchangeable cation did not have a major affect on the overall ion exchange capacity.

References

1. W. Schwieger, W. Bergk, K.H. Freude, D.M. Hunger and H. Pfeifer, Zeolites Synthesis, ACS Symposium Series, **398**, 274 (1989).
2. P.A. Jacobs and J.A. Martens, Synthesis of high silica aluminosilicate zeolites., Studies in Surface Science and Catalysis., Vol. **33**, Elsevier, Amsterdam, (1987).
3. R. Szostak, Molecular Sieves, Principles of Synthesis and Identification, Van Nostrand Reinhold, New York (1988).
4. W.B. Mercer and L.L. Ames, Natural Zeolites: Occurrence, Properties, Use, p. 451, Pergamon, New York (1978).
5. L. Zsinka, L. Szirtes, J. Mink and A. Kalman, *J. Inorg. Nucl. Chem.*, **36**, 1147 (1974).
6. D.O. Campbell, *Inorg. Nucl. Chem. Lett.*, **6**, 103 (1970).
7. A. Dyer, Qin Guan-Lin and L.V.C. Rees, *Zeolites*, **3**, 108 (1983).
8. P.P. Lai and L.V.C. Rees, *J. Chem. Soc. Faraday Trans., I*, **72**, 1809 (1976).
9. L.V.C. Rees and P.A. Newell, *Am. Chem. Soc.*, **40**, 166 (1977).
10. L.V.C. Rees and C. Williams, *J. Chem. Soc. Faraday Trans. I*, **61**, 1481 (1964).
11. V.N. Kazansky, *Kinet. Katal.*, **18**, 43 (1977).
12. K.I. Aika and J.H. Lunsford, *J. Phys. Chem.*, **81**, 1393 (1977).
13. J. Vedrine, *J. Chim. Phys.*, **67**, 439 (1970).
14. P.H. Kasai, *J. Chim. Phys.*, **43**, 3322 (1965).
15. A. Abou Kaais and N.N. Abou Kais, Actas Sym. Iberoam. Catal., Vol. 2 (Lisbon Protugal) 1667 (1984).
16. G.A. El-Nabarawy, A. El-Shobaky and A.M. Dessouki, *Radiat. Phys. Chem.*, **33**, 23 (1989).

17. S.K. Durrani, A. Dyer and R. Blackburn, accepted for publication in "*Zeolite*" (1992).
18. R.M. Klotz, US Pat. 4, 285 919 (1981).
19. M. Taramasso, G. Manara, Ger. Pat. Offenlegungsschrift 2924915 (1980).
20. M.G. Howden, *Zeolites*, **5**, 334 (1985).
21. L.W. Robert, N.Y. Oneonta and T.K. George, US Pat. 3 308 069 (1967).
22. S. Xiang, Q. Wang and J. Wang, *J. of Chinese Univ.* **10**, 677 (1989).
23. B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan and E.M. Flanigen, United States Patent 4, 440, 871, (1984).
24. H. Fricke, and E.J. Hart, In Radiation Dosimetry, Vol. II (Eds. F.H Attix,. and W.C. Roesch) Academic Press, New York (1961).
25. B.T. Kelly, Irradiation Damage to Solid., Pergamon Press, New York (1966).
26. A. Abou-Kais and N.N. Abou-Kais, *Acta Physica Chim.*, **31**, 109 (1985).
27. J. Lehto and L. Szirtes, *Radiochem. Radioanal. Letters*, **50**, 375 (1982).
28. E.M. Flanigen, H. Khatami and H.A. Szymanski in Molecular Sieve Zeolite-I, ACS Symp. Series 101, 201 (1971).
29. S.K. Durrani, R. Blackburn and A. Dyer, *Zeolites* **12**, 202 (1992).
30. L.V.C. Rees and M.S. Khalid, In "Molecular Sieves" Soc. of Chemical Ind. Conf., London, 319 (1968).
31. P.H. Kasai and R.J. Bishop Jr. in Zeolite Chemistry and Catalysis, J.A. Rabo (Ed), ACS monograph, *Am. Chem. Soc.*, **17**, 350 (1976).
32. Th. El-Nabarawy, G.A. El-Shobaky and A.M. Dessouki, Int. J. Radiat. Appl. Instrum. Part C, *Radiat. Phys. Chem.*, **33** (1), 23 (1989).