

Radiation Stability of Inorganic Exchangers—I

K. L. N. RAO^a, R. N. VARMA^a, K. R. BALASUBRAMANIAN*^a and T. S. MURTHY^b

^aIsotope Division, Bhabha Atomic Research Centre, Bombay-400 085

^bConsultant, Bhabha Atomic Research Centre, Bombay-400 085

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The inorganic exchangers ammonium molybdophosphate and hydrous manganese dioxide were subjected to gamma doses of 10^6 and 10^7 Gy to study the radiation stabilities of these compounds. Investigations were made on the chemical composition, infrared absorption patterns and also distribution ratios and total exchange capacities. It was found that there were no significant changes between the control and irradiated samples, showing that these exchangers are stable up to the levels of irradiation under investigation.

In recent years many insoluble inorganic compounds have come into prominence as useful ion-exchange materials. In the nuclear field these inorganic exchangers find a wide variety of applications mainly because of their radiation and thermal stabilities¹. These have been employed in the purification of coolant and moderator water in pressurised reactors and in several radiochemical separations². Gill and Tandon³ reported the effect of γ -radiation on some ferrocyanides, antimonates and ceric tungstate and compared the results with those obtained on Dowex-50 X 8 and Amberlite IR-120. Szirtes *et al.*^{4,5} evaluated the properties of zirconium phosphate, chromic phosphate and zirconium tellurate after subjecting them to γ -radiation. Inoue and Tsuji⁶ examined the properties of hydrous TiO_2 after irradiating the material. An interesting observation has been made recently by Szirtes⁵ while studying the effects of γ -radiation on inorganic exchangers wherein some compounds like cerium arsenate and cerium phosphate do undergo some radiation damage. The present authors have evaluated the effects of gamma radiation on inorganic exchangers ammonium molybdophosphate (AMP), polyantimonic acid (PA), zirconium antimonate (ZrA) and hydrous manganese dioxide (HMD) and the preliminary results have been reported earlier⁷. This paper describes the results of further detailed investigations carried out on AMP and HMD for their radiation stability characteristics.

Results and Discussion

Table 1 gives the distribution ratio values obtained for the elements cesium on AMP and zirconium on HMD, control and irradiated to 10^7 Gy wet. As seen from the results, there is only marginal variation in the values before and after irradiation. Similar results were obtained in the case of irradiation up to 10^6 and 10^7 Gy (dry). The observed variation appears to be well within experimental limits. This could possibly indicate that the exchangers did not undergo significant changes during irradiations.

The percentages of manganese in HMD before and after irradiation upto 10^7 Gy in the presence of 2M nitric acid are in the range $49.6 \pm 1.6\%$, showing that there is no significant change in chemical composition due to irradiation. The total exchange capacities of these exchangers (AMP and HMD) for the respective elements (Cs and Ce) from simulated fission product waste solution (Type-1), are not much different before and after irradiation.

TABLE 1—DISTRIBUTION RATIOS— 10^7 GY WET

Sl. no.	HNO ₃ M	AMP-Cs		HMD-Zr	
		Control	Irradiated	Control	Irradiated
1.	0.2	3 208	2 647	37 674	34 639
2.	0.5	3 125	2 389	14 533	18 187
3.	1.0	2 554	2 171	4 530	4 736
4.	2.0	1 880	1 593	2 881	2 975
5.	4.0	1 071	917	650	577
6.	6.0	644	548	303	298
7.	8.0	375	320	194	191
8.	10.0	228	188	165	162

In Fig. 1 are given some typical breakthrough curves obtained from simulated fission product solution type-I for elements Cs on AMP and Ce on HMD before and after irradiation of the respective exchangers to a dose of 10^7 Gy under wet conditions. The curves show a general sigmoid pattern almost similar to each other. A similar observation was made in cases of irradiation to 10^6 Gy and to 10^7 Gy (dry). The X-ray diffractograms for control and γ -irradiated (10^7 Gy) AMP samples under wet conditions are identical, showing that there is no perceptible change in the crystal structure due to irradiation. The diffractograms under other conditions of irradiation lead to similar observations. Ir spectra of AMP before and after irradiation to γ -dose of 10^7 Gy under wet conditions, of the exchanger show practically no difference between the control and irradiated samples. The ir spectra of AMP irradiated to 10^7 Gy under both dry and wet conditions were also similar. Thermograms of AMP obtained before and after irradiation

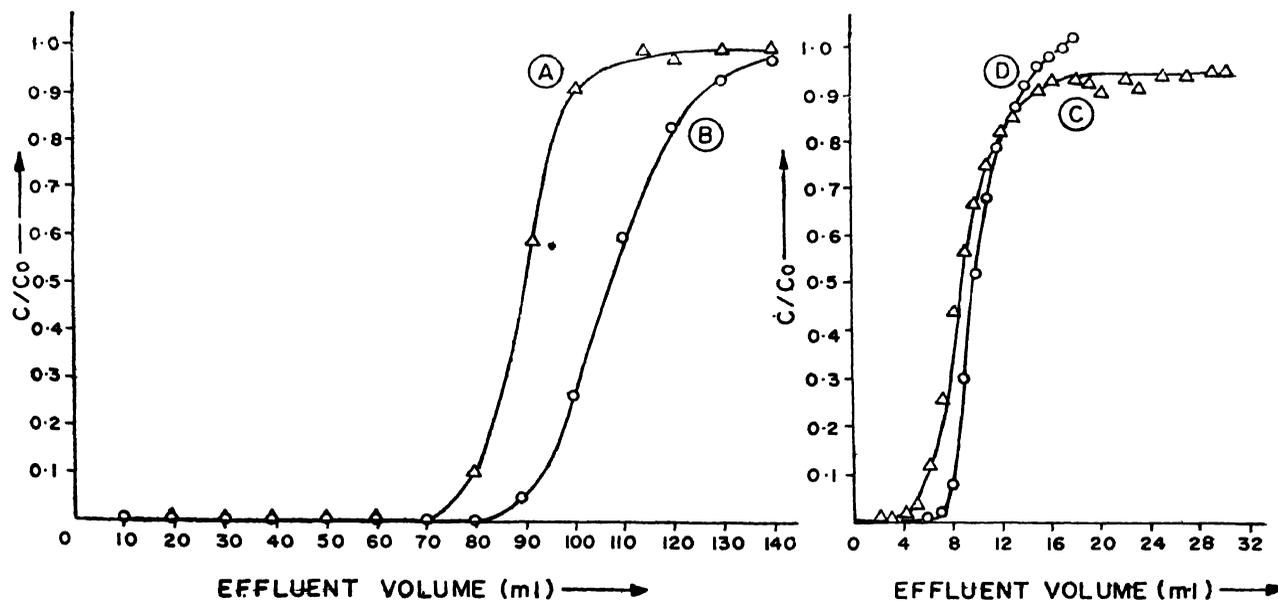


Fig. 1. Breakthrough curves of samples irradiated to 10^7 Gy with $2M$ HNO_3 : (A) AMP and (C) HMD; (B) and (D) controls.

to 10^7 Gy indicate that the weight-loss characteristics are the same in both control and irradiated samples.

X-Ray diffractograms of HMD samples before and after irradiation (10^7 Gy) under wet conditions show that there is no significant change in the amorphous nature of the material due to irradiation. The infrared absorption spectra for HMD samples control and irradiated to 10^7 Gy under wet conditions, are almost the same indicating that there is no significant change in the chemical composition due to irradiation. Samples irradiated to 10^6 Gy also show a similar behaviour. The thermograms of HMD samples control and irradiated to 10^7 Gy with $2M$ nitric acid, are close to each other indicating that the control and irradiated samples have similar weight-loss characteristics.

Conclusion: The observations suggest that the basic properties of the materials examined do not change as a result of irradiation upto 10^7 Gy of gamma radiation.

Experimental

AMP (Hopkin & Williams) and HMD (Central Salt and Marine Chemicals Research Institute, India) were used. All the reagents used were of G.R. (E. Merck) or AnalaR grade. All the tracers used were available with B.A.R.C.

Irradiation: Irradiation was carried out using either a Gamma Chamber-900 or Panoramic Batch Irradiator (PANBIT) depending on the dose to be imparted—3 and 45 $kGy\ h^{-1}$ respectively.

The exchanger samples (15–20 g) either in the dry form or slurried with $2M$ nitric acid were

irradiated to a total dose of 1 or 10 MGy. Wherever necessary, control samples were treated with nitric acid for the same period under identical conditions.

Distribution ratio was determined by equilibrating each exchanger (0.2 g) with appropriate tracer in presence of nitric acid of various molarities for 4 h.

Manganese in hydrous manganese dioxide (HMD) was determined using standard analytical methods⁸.

Breakthrough pattern and exchange capacity:

The exchangers were loaded in glass columns of appropriate dimensions (i.d. 5–12 mm \times 15 cm) and were conditioned with 1 or $2M$ nitric acid depending on the feed. Simulated fission product solution Type-I with or without dilution and spiked with the radioactive tracer of the element under investigation was passed through the column at a rate of 0.1 or 0.25 $ml\ min^{-1}$. 1 ml fractions were collected till the ratio C/C_0 was about 0.9–1.0, where C_0 is the original concentration of the feed and C the concentration of the effluent from the column. The columns were washed with nitric acid or water and the amount of the element held per g of the exchanger was evaluated. The breakthrough curves were obtained by plotting C/C_0 against the effluent volume.

X-Ray diffraction studies were carried out in Fuel Chemistry Division of B.A.R.C. using a Siemens diffractometer with copper- K_{α} radiation of wave length 1.54184 Å. Ir spectra (KBr) were obtained on a Perkin-Elmer 577 spectrophotometer. TGA analysis was done using a Mettler TA-1 thermoanalyzer.

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