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Study in Changes of Physico-Chemical Parameters in Deolite C-20 Resin After γ-Treatment

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Ion-exchanger materials have been an integral part of the radiochemical process application and in clean-up operation of low level aqueous waste streams. They are widely used in various purposes including in nuclear power plants. Therefore an attempt is made to understand the effect of γ-treatment on the physico chemical parameters of the resin Deolite C-20.

INTRODUCTION

Resins used[1] throughout the nuclear power industry are strong acid-cation exchanger containing sulphonic acid functional group and strong base exchanger containing quaternery ammonium ion functional group. Nuclear grade resin under irradiation would perhaps give smaller amout of gas and other decomposition products due to their smaller contents of soluble organic impurities. The attention has not been paid to the study of radiation damage to the ion exchanger and hence this work is undertaken in continuation to our earlier work. The radiation effects, physical and chemical properties of resin, phenomenon like de-cross linking, loss of exchange capacity etc. are focussed in this work.

EXPERIMENTAL

The investigation reported in this paper is confined to industrial grade polystyrene based cation exchanger supplied under the brand name Deolite C-20 by Henkel Chemicals, Mumbai, All chemicals used during studies are analytical reagent grade. γ-treatment was accomplished by Co-60 2.5kCi (Normal), 4000-A γ-chamber. The dose rate of the source was 0.25 Mrad/h.

Sample Irradiation: 500 g of air dried exchanger was suspended in 5 cm^3 double distilled water in a stoppered pyrex tube without applying grease and tube was exposed to Co-60-γ at room temperature for the required dose. Similarly some chemicals were irradiated by placing them in pyrex tube but without water. The dose rate at the sample position was determined from time to time by using fricke-dosimeter. Properties of ion-exchange resin like exchange capacity, moisture content and weight loss were determined.

Exchange-capacity Measurement[2]: Ion exchange capacity of resin in K^+, Cu^{2+} and Fe^{3+} form was determined by eluting known amount of sample by an excess volume of sodium sulphate solution. This was done by keeping the sample in micro-column. The column was specially designed for capacity measurement of sample less than 1 g. Fixed volume of effluent was used to estimate K^+, Cu^{2+} and Fe^{3+} ions by flame-photometer and colourimeter respectively. From the relation,

$$\text{capacty} = \frac{2BV}{W}$$

The exchange capacity was determined. Here V is expressed in cm^3, B in molar sodium sulphate required by W g of resin.

Moisture Content Measurement: The exchanger was equilibrated with water by submerging it over night in distilled water. It was then transfered into sintered glass tube of porocity G_3 and centrifused at 2000 rpm for 10 min. to remove unbound water from the resin sample. It was then quantitatively transferred into stoppered bottles and weighed (TW) After keeping over in P_2O_5 for 10–15 days. It was re-weighed as air dried sample (Td) from this the water regain (WR) of an exchanger was calculated.

$$WR = \frac{0.97(TW-TD)}{Td}$$

where 0.97 is the correction factor interstial moisture content at 2000 rpm for the spin time of 10 min. From the value of water regained the perient moisture content of an exchanger was calculated as

$$\% \text{ M} = \frac{WR}{(1 + WR)} \times 100$$

Weight Loss Measurement: Known amount of air dried sample after irradiation were washed thoroughly with distilled water to remove degradation products, dried over P_2O_5 in dessicator, for long period ensuring complete dryness by the re-weighing. The difference between weights is considered as measure of degradation.

Additional weight loss measurements were carried out by heating the resin sample thermogravimetrically in an inert atmosphere. Thermoanalyser STA-780 series manufactured by Stanton-Redcraft was employed for this. The heating rate was maintained 10°C/min. chart speed 200 mm/h. Sample holder was platinum crucible attached with Pt/Rd thermocouple which was coupled with C.P.C.-706 temperature programme.

RESULTS AND DISCUSSION

At very low doses of irradiation ion-exchange resins did not give any changes in degradation and cross-linking of the macro-molecular structure along with the scission of ion-exchanging groups. Colour changes of resin matrix also did not result with increasing doses upto 12 Mrad. Bead fracturing and agglomerisation of the resin were not found. As no such changes were observed, the resin samples were irradiated at high doses like 1 to 12 Mgy. In order to see the radiation effects on the capacity of resins in different cationic forms the resin was irradiated in the virgin state.

The capacity values for industrial grade resin (unirradiated) under air dried conditions are presented in Table-1. It is seen that capacity values with respect to cations are in increasing order for the exchanger used. It is revealed that the Fe^{3+} salt form of the resin is more stable than the K^+ form of resin. Ionic radius and values are also given in the Table-1 for the camparision with the exchang capacity values. It is observed that among the different forms of resins, the bonding in Fe^{3+} form of resin is strongest, this can be explained on the basis of nature of hydration shell of cation, which is observed by Dasent[3]. The Li^+ form is more hydrated indicating the hydration shell is much larger as compared with the other forms. Small hydration shell will in stronger contact pair formation between Fe^{3+} ion and the functional group. It is indicative that the ion exchange capacity depends upon various factors namely valence-state cation, ratio of relative charge and size of ion, nature of hydration shell, ionic radius and length of metal-oxygen bond. Similar observations are reported by others on resins[4, 5] with code name KU-2 and Dowex-50.

TABLE-1
CAPACITY VALUES AND MOISTURE CONTENT FOR INDUSTRIAL GRADE RESIN (UNIRRADIATED) UNDER AIR DRIED CONDITION

	K^+	Cu^{2+}	Fe^{3+}
Capacity/meq g^{-1}	2.10	2.60	4.20
Moisture content	42.20	44.80	46.20
Ionic Radius	1.51	0.71	0.64

Moisture Content: It is observed that ion exchanger swelled owing to the diffusion of water molecules into them when immersed in water. Values expressed on the basis of weight percentage for the resin are presented in Table-2. It is observed that the water content in cation exchanger is in the order of capacity, with respect to cations Fe^{3+}, Cu^{2+}, K^+. It is usually said that the water content of the resin is governed by nature of the cation. In case of Fe^{3+} form of resin because of entry of more water in hydration shell, it will diminish the active position resulting into more water content as compared to Cu^{2+} and K^+ forms.

TABLE-2
EFFECT OF γ-IRRADIATION OF THE MOISTURE CONTENT OF POLYSTYRENE CATION EXCHANGER DEOLITE C-20

Absorbed dose	K^+	Cu^{2+}	Fe^{3+}
1	2.2	1.6	1.5
3	6.2	5.2	3.1
7	13.4	12.4	11.1
11	18.4	13.1	12.0
12	24.2	20.1	18.1

Loss in Exchange Capacity: The effect of radiation on the exchange capacity of resin is shown in the Table-3. It is seen that upto 12 mgy, there is a steady decrease in a exchange capacity with increasing γ-dose. The radiation effect is observed to be minimun for Fe^{3+} form whereas it is maximum for K^+ form. Also decrease in capacity is always less for dry samples of resins than for resin samples suspended in water. The decrease in exchange capacity in case of resin suspended in water, is almost double as compared to that of air-dried resin. These results have been summerised in the Table-3.

TABLE-3
EFFECT OF IRRADIATION ON THE EXCHANGE CAPACITY OF EXCHANGER DEOLITE C-20 DURING AIR DRY AND WATER SUSPENDED CONDITIONS

Dose/MGy	Decrease in capacity		
	K^+	Cu^{2+}	Fe^{3+}
1	2.1 (5.7)	1.5 (3.7)	1.5 (1.6)
2	5.4 (11.2)	2.3 (7.9)	2:3 (6.4)
3	7.4 (14.2)	3.1 (10.9)	3.1 (9.8)
5	13.1 (17.6)	5.1 (13.9)	4.1 (12.1)
7	15.3 (20.4)	6.5 (17.1)	6.1 (16.2)
9	17.9 (23.2)	7.4 (19.1)	7.2 (17.1)
11	17.9 (27.2)	8.5 (22.4)	8.2 (19.5)
12	19.1 (28.9)	9.2 (24.1)	8.1 (20.2)

About 7% loss of exchange capacity was reported by Ichikava, in cases using Dowex-50 resin when exposed to dose of 6.1×10^7 Rad.

Dedgaonker[6] and others find out that loss of exchange capacity was about 7.1% in H^+ form and 5.8% in Sr^{2+} form of the resin. Tulsion-T-42-MP when exposed to dose of 3.6 mgy. In the present study Fe^{3+} form was found more stable towards the radiation dose.

Weight Loss Measurement: Water trapped in resin matrix diminishes in the irradiation processes. Effect of radiation on the moisture content of Deolite C-20 is presented in Table-4. 0.5 g of dessicator dry resin was irradiated under water and air dried before weighing. Radiation causes steady decrease in moisture content of all ionic forms. The order of stability with respect to cations observed as $Fe^{3+} > Cu^{2+} > K^+$. It is seen that the order of stability on the basis of exchange capacity is exactly the same. These data summerised in Table-4 shows that radiation brings about 24.2, 20.1 and 18.1 percentage decrease in K^+, Cu^{2+}, and Fe^{3+} cationic forms respectively in Deolite C-20 resin. In the case of polystyrene KU-20 resin, it is reported[7] that the moisture content decrease progressively with the dose upto 3 mgy to the extent 75% and then remained constant and after 12 mgy dose a complete break down of the resin occured[8]. Dedgaonkar[6] and others have reported 25% decrease in Sr^{2+} form of polystyrene resin.

TABLE-4
EFFECT OF RADIATION ON THE WEIGHT OF POLYSTYRENE RESIN MATRIX-DEOLITE C-20

Absorbed Dose/MGy	Decrease in weight percentage		
	K^+	Cu^{2+}	Fe^{3+}
1.0	2.1	2.1	1.6
2.0	4.4	3.8	3.6
3.0	6.6	5.7	5.1
5.0	11.1	9.4	8.1
7.0	15.4	13.4	12.2
9.0	22.1	17.4	15.1
11.0	24.1	22.1	17.9
12.0	26.9	20.2	19.7

In order to find out the weight loss in resin itself, another series of experiments is carried out. Resin samples were dried for 15 days by keeping them in a dessicator over P_2O_5 and weighed as 0.5 g. After irradiation under water, these were dried in a dessicator and weighed. It is expected that the contribution to loss due to the breakage of micro-structure of resin should be observed by these experiments give these loss, together with water loss. The data on weight loss with respect to observed dose are presented in Table-4. The stability trend with respect to cations is same being $Fe^{3+} > Cu^{2+} > K^+$.

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