J Radioanal Nucl Chem (2010) 283:379–384
DOI 10.1007/s10967-009-0377-z

Treatment of low level radioactive liquid wastes using composite ion-exchange resins based on polyurethane foam

S. V. S. Rao · R. Lekshmi · A. G. S. Mani · P. K. Sinha

Received: 7 July 2009 /

Abstract Composite ion-exchange resins were prepared by coating copper-ferrocyanide (CFC) and hydrous manganese oxide (HMO) powders on polyurethane (PU) foam. Polyvinyl acetate/Acetone was used as a binder. The foam was loaded with about five times its weight with CFC and HMO powders. The distribution coefficients of CFC-PU foam and HMO-PU foam for cesium and strontium respectively were estimated. Under similar conditions the HMO-PU foam showed higher capacity as well as better kinetics for removal of strontium than CFC-PU foam for Cs. The pilot plant scale studies were conducted using a mixed composite ion-exchange resin bed. About 1000 bed volumes could be passed before attaining a DF of 10 from an initial value of 60–80. The spent resin was digested in alkaline $KMnO_4$ and the digested liquid was fixed in cement matrix. The matrices were characterized with respect to compressive strength and leach resistance.

Keywords Polyurethane foam · Cesium · Strontium · Polyvinyl acetate

Introduction

Treatment of radioactive liquid wastes, particularly low level wastes assumes importance as considerable volumes of these wastes are generated in nuclear fuel cycle. These wastes contain mainly radioactive cesium-137 and strontium-90. Low level wastes are classified as category I, II and III wastes. The category I wastes are potentially active and generally diluted and discharged. The Category-II and III radioactive liquid wastes are treated either by chemical precipitation or by ion-exchange techniques. The decontamination factors obtained in the chemical treatment process are low especially when the total dissolved solids of the wastes are greater than 500 ppm. A great deal of literature is available on the treatment of radioactive wastes using inorganic ion-exchangers for the removal of above radionuclides [1, 2]. A comparison of inorganic ion exchangers for the removal of cesium and strontium has been reported [3].

Generally, inorganic ion-exchangers in the powder or bead form will affect the flow rates and also choke the column in large scale operations. To avoid these problems they are coated on some other materials to improve the column characteristics. Polyurethane foams (PU foams) are used with or without loading reagents in the separation and pre concentration of metals [4]. In case of loaded PU foam, the foam acts as a supporting material. The PU foam can find an excellent application in the treatment of low level radioactive wastes as it possesses high porosity, chemical durability and radiation resistance. In our centralized waste management facility (CWMF) studies were conducted on the unloaded PU foam for the removal of *n*-tributyl phosphate [5] and radioactive cobalt-60 [6]. Copper ferrocyanide (CFC) coated PU foam was used for the removal of radioactive cesium [7, 8] as the copper ferrocyanide has low solubility and high capacity for Cs [7, 9]. The removal of radioactive strontium (Sr-90) from low level radioactive wastes is equally important as the abundance and half life of it are similar to that of Cs-137. For the removal of radio active strontium hydrous manganese oxide (HMO) is selected in the present studies as the HMO has higher affinity and exchange capacity for strontium compared to that of other oxides [10].

S. V. S. Rao (✉) · R. Lekshmi · A. G. S. Mani · P. K. Sinha
Centralised Waste Management Facility, BARC (F),
Kalpakkam 603 102, India
e-mail: svsrao@igcar.gov.in

The scope of the present work comprises preparation of a composite ion-exchange resin CFC-PU foam and HMO-PU foam by coating PU foam with copper ferrocyanide and hydrous manganese oxide respectively using polyvinyl acetate/acetone binder; Testing of the resins to find out their absorption capacity with respect to Cs-137 and Sr-90; Conducting experiments in the pilot plant scale with the actual waste containing radioactive cesium and strontium; Digestion of spent resin in alkaline potassium permanganate and fixing the digested liquid in cement matrices and characterization of matrices to evaluate their compressive strength and leach resistance.

Experimental

Materials

1. Copper sulfate, L.R, Sarabhai M Chemicals, Baroda.
2. Potassium ferrocyanide, G.R, Sarabhai M Chemicals, Baroda.
3. PU foam, DP foam Ltd; Pondichery, India.
4. Radioactive cesium, Cs-137, BRIT, India.
5. Radioactive strontium, Sr-90-Y-90, BRIT, India.
6. Polyvinyl acetate, Laboratory Reagent, Rolex.
7. Acetone, L.R Reachem Chemicals, Chennai.
8. Manganese Sulphate, G.R Merk Limited, Mumbai
9. Potassium Permanganate L.R, Fischer Chemicals, Madras, India.
10. Sodium Hydroxide L.R, Fischer Chemicals, Madras, India.

Methodology

Preparation of PU foam

Polyurethane foam sheets of 5 mm thickness having a density of 20 kg m^{-3} were cut into cubes of 5 mm length for the purpose of estimating the capacity of the resin. These PU foam pieces were washed in 1 N HCl followed by deionized water. However, for the purpose of pilot plant scale studies the PU foam pieces of size about $50 \times 50 \times 5$ mm (l×b×h) were used.

Preparation of copper ferrocyanide powder

Solutions of copper and ferrocyanide were mixed in such a way that their molar concentrations were in the ratio of 2.2:1. The precipitate formed was filtered and dried at ambient temperature. After drying, the lumps were ground and sieved to obtain the powder having a particle size of <75 μm.

Preparation of hydrous manganese oxide powder

Solutions of potassium permanganate, manganous sulphate, and sodium hydroxide were mixed in such a way that their molar concentrations were in the ratio of 1:1.4:2.8. The HMO powder was prepared in the similar manner as described above for CFC.

Characterization of copper ferrocyanide powder

The copper ferrocyanide was characterized with respect to true density, surface area and X-ray patterns. The density of CFC was determined using pycnometric method. The instruments used for the surface area and X-ray analysis were surface area analyzer (Quanta Sorb Junior), and X-ray diffractometer (Siemens Model D-500) respectively.

Characterization of hydrous manganese oxide powder

The hydrous manganese oxide was characterized in the similar way as described for CFC for true density, surface area and X-ray patterns.

Preparation of CFC-PU foam and HMO-PU foam

The PU foam pieces were coated with CFC and HMO using polyvinyl acetate/acetone binder. About 125 g of CFC or HMO powder was coated on 25 g PU foam using 250 mL of acetone containing 4.4 g of polyvinyl acetate. The PU foam, CFC/HMO powder and the binder were stirred in a container to ensure a uniform coating. The coated foam pieces were dried at room temperature.

Determination of distribution coefficients of CFC-PU foam and HMO-PU foam

About 0.1 g of PU foam coated five times of its weight with CFC or HMO powder was kept in contact with 100 mL of solution containing stable cesium/strontium and trace amount of radioactive cesium-137 or strontium-90 for the determination of distribution coefficients. The temperature and pH of the solution were 30 °C and 8.3 respectively. The initial specific activities of cesium and strontium were 74 and 29 Bq/mL respectively. The contents were stirred for two minutes and left without any further stirring. After 24 h, an aliquot of 2 mL was collected in a test tube and the radioactive cesium and strontium were estimated using gamma counter and GM counter (supplied by M/S Pla, Mumbai) respectively. The distribution coefficients (K_d) in L kg^{-1} were calculated using the following equation

$$\% \text{ of extraction} = E = \frac{[(A_{\text{initial}} - A_{\text{final}})]}{[A_{\text{initial}}]} \times 100$$

$$K_d = \frac{E \times \text{Volume of the solution}}{(100 - E) \times \text{Weight of the CFC-PU foam or HMO-PUfoam}}$$

Kinetics of removal of cesium and strontium on CFC-PU foam and HMO-PU foam

About 0.1 g of PU foam coated with five times of its weight with CFC powder was kept in contact with solution containing 10^{-3} M stable cesium and trace amount of radioactive Cs-137. Similarly, in another set about 0.1 g of PU foam coated with five times of its weight with HMO powder was kept in contact with 100 mL of solution containing 10^{-3} M stable strontium and traces of Sr-90. The temperature and pH of the solution were 30 °C and 8.3 respectively. The initial specific activity of cesium and strontium was 74 and 29 Bq/mL respectively. The contents were stirred for 2 min and left without any further stirring. An aliquot of 2 mL sample was taken at 2 min, 1, 3, 5, 6 and 24 h. The radioactivity of cesium and strontium was estimated using gamma counter and the GM counter respectively.

Column operation in pilot plant scale studies

A stainless steel ion-exchange column having diameter and height 150 and 700 mm respectively was set up for pilot plant scale studies. The CFC-PU foam and HMO-PU foam were packed in a perforated nylon bag and loaded in the column. In this arrangement the spent foam can be easily taken out from the column for digestion and fixation. About 0.9 kg of CFC-PU foam and 0.9 kg of HMO-PU foam was loaded in the bag. The volume of packed bed was about 8 L. The Stainless steel column and the cartridge containing CFC-PU and HMO-PU foam are shown in Figs. 1 and 2 respectively.

Digestion of CFC-PU foam

The CFC-PU foam and HMO-PU foam weighing about 12.5 g each were kept in contact with radio active liquid waste. The activity absorbed was estimated. The foam was then digested in 125 mL of 2 M NaOH solution containing 16.25 g of $KMnO_4$. The initial temperature was 30 °C and during the course of digestion the temperature raised to 60 °C in 30–45 min. The digestion process was carried out for 2 h.

Fixation of digested liquid in cement matrix

About 40 mL of digested liquid containing traces of radio active cesium was added to 100 g of cement. The contents were stirred and transferred to a mould. The temperature during cementation process raised from 30 to 40 °C. After allowing for curing for about a month the specimens were tested for compressive strength and leach resistance.

Characterization of cement matrices

Compressive strength

The cement specimens were tested for their compressive strength on a FIE (Fuel Instruments and Engineers Pvt. Limited) machine conforming to a grade ‘A’ of BS:1610:1964.

Leaching experiments

Ground water was used as a leachant and its conductivity, pH, hardness as $CaCO_3$ and chloride content were 338 μS/cm, 8.3, 74 and 36 ppm respectively. The leaching studies were carried out with the cement matrix according to the American Nuclear Society standard leach test method (ANSI 16.1) as reported in the literature [11]. The radioactive cesium leached out was estimated using the gamma counter and the Beta activity was estimated using GM counter. The volume of the sample taken for the estimation of cesium in leaching experiments was 4 mL. Leach rate (LR) in cm day^{-1} was calculated using the following equation.

$$LR = (\Sigma A/A_0) \times (V/S) \times 1/\Sigma t$$

Where $\Sigma A/A_0$ = cumulative leach fraction

A_0 = initial activity of cesium
A = activity of cesium at any time t (days)
V = volume of the specimen (cm^3)
S = surface area of the specimen (cm^2)
Σt = cumulative time (days)

Fig. 1 Stainless steel ion-exchange column

The Leach Indices (LI) were also calculated using the following equation

$$\mathrm{LI} = 1/\mathrm{n}\sum_{n=1}^{n}\log(\beta/\mathrm{D})$$

Where n is number of leaching intervals, β is a defined constant (1 cm^2/s), and D is the effective diffusivity of radionuclide and the computation procedure of it is given elsewhere [11].

Results and discussion

Characterization of HMO and CFC powder

The true density and surface area of the hydrous manganese oxide were observed to be 2900 kg m^{-3} and 1020 m^2 kg^{-1} respectively. Hydrous manganese oxide (HMO) was also characterized with respect to X-ray diffraction. The X-ray pattern of HMO prepared in the laboratory was compared with that of the commercially available manganese dioxide powder. Unlike MnO_2, the HMO has showed amorphous nature.

The above results obtained from the characterization of CFC have been reported elsewhere [7]. The X-ray patterns obtained were similar to that of $Cu_2Fe(CN)_6{\cdot}7H_2O$.

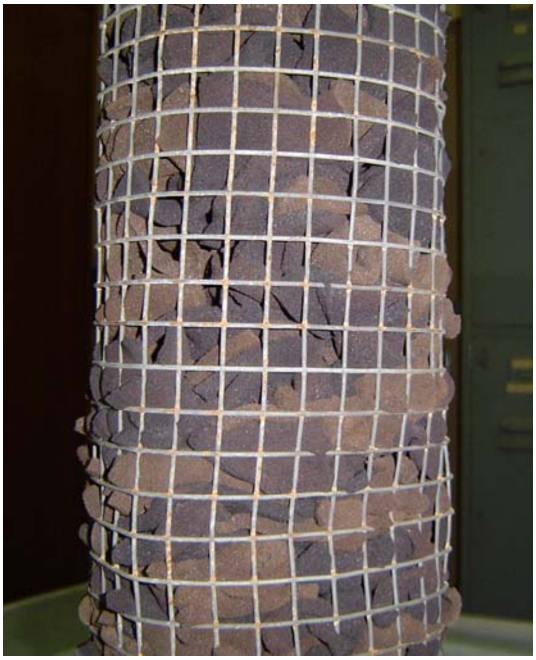

Fig. 2 Cartridge loaded with CFC-HMO PU foam

Determination of distribution coefficients of HMO and CFC

In order to optimize the loading of CFC and HMO on PU foam, the coated resins were kept in water for three days and the adhesiveness of the powder was tested by physical observation. The optimized loading of CFC and HMO was about five times of the weight of the PU foam. The distribution coefficients (K_d) of CFC-PU foam and HMO-PU foam are given in Table 1 and the coefficient of variation in these measurements is about 10.5. It is observed that the HMO-PU foam has shown higher exchange capacity for strontium compared to that of CFC-PU foam for cesium. The comparison of the capacities helps in selecting the amounts of CFC-PU foam and HMO-PU foam for the column studies. Since the CFC-PU foam has shown lower capacity, the amount of resin needed in column studies would be more than that of HMO-PU foam resin.

Table 1 Distribution coefficients (L kg^{-1})

	0.1 mM	1 mM	10 mM
Cesium			
CFC-PU foam	25337	8200	80
HMO-PU foam	190	–	–
Strontium			
CFC-PU foam	–	–	–
HMO-PU foam	>55000	33165	3660

Kinetics of removal of cesium and strontium on CFC-PU foam and HMO-PU foam

The kinetics of uptake of cesium and strontium by CFC-PU foam and HMO-PU foam respectively is given in Fig. 3. It is evident from the figure that the kinetics of removal of strontium is higher on HMO-PU foam compared to that of cesium on CFC-PU foam. In two minutes the CFC-PU foam removed about 73% of cesium from 10^{-3} M solution where as the HMO-PU foam removed about 96.6% of strontium. As the kinetics of uptake of cesium by CFC-PU foam is lower than that of HMO-PU foam, the CFC-PU foam resin bed height should be more than that of HMO-PU foam for better removal of cesium.

Pilot plant scale studies

Pilot plant scale experiments were carried out by passing the radio active liquid waste having an initial activity of about 70 Bq/mL. The pH and total dissolved solids of the waste were 9 and 2600 ppm respectively. The major cations in the waste solution were calcium, sodium and the anions were chloride and nitrate. The temperature during the column experiments was observed to be around 30–32 °C. The flow rate of the waste solution was about 2.7 L min^{-1}. The decontamination factor (DF) is a ratio of initial activity (before the treatment) to the final activity (after the treatment). After passing the liquid waste through the column the effluent sample was collected at regular intervals and analyzed for its radioactivity. The DF obtained was plotted against the volume of the liquid passed and it is given in Fig. 4. Initially the DF was about 80 with respect to beta and gamma activity. However, the DF was reduced with passing of waste solution. The column studies were terminated after passing 1000 bed volumes of waste solution even though the column was not utilized to its capacity and at that time the DF was observed to be about 10. In all these experiments the treated effluent was collected in a tank. In the end for determining the average DF an aliquot of 4 mL sample drawn form the tank was analyzed for its radioactivity. The average DF was observed to be about 20. The initial activity of Sr-90 was about 22 Bq mL^{-1} and after the treatment the activity was below 1 Bq mL^{-1} in the effluent.

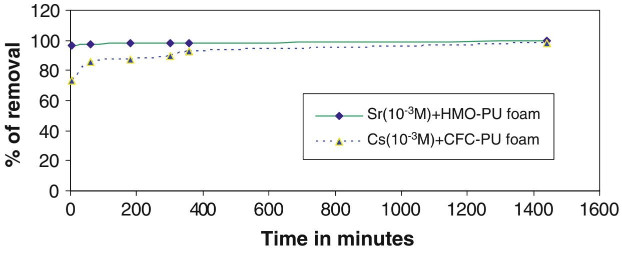

Fig. 3 Uptake of cesium and strontium

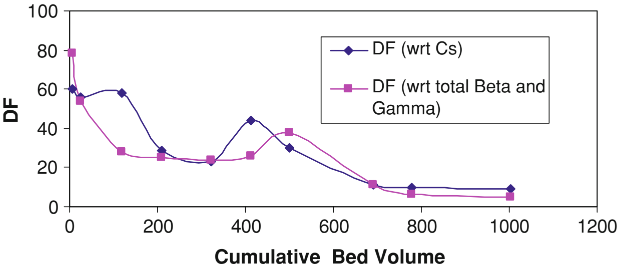

Fig. 4 Cumulative bed volume of the radioactive liquid passed through the column against decontamination factor

The surface dose on the column at the lower, middle and top portion was observed to be 180, 240 and 24 mR h^{-1} respectively. The spent foam was taken out and kept in 20 L mild steel drum and cement grout was poured around that. After the setting of cement the drum was disposed of. The total volume of the liquid passed through the column was 8,000 L and the volume of the final waste form after cement fixation was 20 L. The volume reduction factor is a ratio of the initial volume of the waste to the final volume. Therefore, the over all volume reduction factor obtained was about 400.

Leaching studies

As an alternate and better method of disposal of spent resin is digesting the resins before its fixation in cement matrix. To find out the feasibility of this process the coated CFC-PU foam and HMO-PU foam were digested according to the procedure given in the experimental session. The digested liquid was fixed in cement matrix. The cement matrices were allowed for curing for about a month and then they were subjected to leaching studies, according to ANS 16.1 standard leach test method. The leachant samples were analyzed periodically for radio active cesium and total beta activity. It was observed that the leach rates were around 5×10^{-3} cm day^{-1} after 73 days in both cases. The cumulative leach fraction of cesium leached out was 0.07. The results are shown in Fig. 5. The leach indices

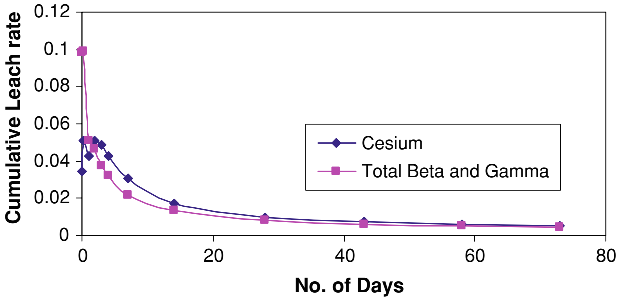

Fig. 5 Cumulative leach rate vs time

(LI) for cesium and beta were also estimated to be around 7 which are greater than the stipulated value 6. During the curing of cement matrix the pH of it will be around 12. At this pH copper ferrocyanide is not stable. Therefore, the cesium which is absorbed in CFC will be released from the cement matrix. In our studies it was found that most of the cesium was leached out from the cement matrix [12]. In the present studies even after 73 days of leaching the cumulative fraction of cesium leached out was around 0.07. This is due to the fact that the hydrous manganese oxide formed during the digestion of foam acted as an adsorbent and there by reduced the leach rates. The compressive strength of the matrices was 21 MPa. It is also much higher than stipulated value 0.4 MPa.

Conclusion

A complete process for the treatment of low level radioactive liquid wastes using composite resins based on polyurethane foam was developed. The radioactive waste containing 70 Bq/ml activity was treated in pilot plant scale level. The radio active strontium in the waste could be removed to <1 Bq/mL. The spent resin after digestion was fixed in the cement matrix. The leach indices were about 7 which are higher than the stipulated value 6. The over all volume reduction factor is around 400 in this process. If digestion of spent foam followed by fixation of digested liquid process is followed the volume reduction factor would be around 230.

Acknowledgments The authors express their thanks to Shri. Kanwar Raj, Head, WMD and Shri S.D. Misra Director, NRG, BARC for their support during these studies. Thanks to Shri C. Desingh for his technical assistance

References

1. Technical report series N0 408 (2002) Application of ion-exchange process for the treatment of radioactive waste and management of spent ion ion-exchangers. International Atomic Energy Agency, Vienna
2. Naushad Mu (2009) Inorganic and composite ion-exchange materials and their applications. Ion Exch Lett 2:1–14
3. Sipos-Galiba I, Lieser KH (1980) Comparison of the properties of inorganic ion-exchangers with respect to the separation of the fission products cesium and strontium. Radiochem Radioanal Lett 42(4–5):329–340
4. Braun T, Navratil JD, Farag AB (1985) Polyurethane sorbents in separation science. CRC press, Boca Raton
5. Rao SVS, Raj SS, Lal KB, Srinivasan MP, Narasimhan SV, Panicker PK (1996) Removal of n-tributyl phosphate from synthetic intermediate level wastes. Sep Sci Technol 31(7): 1011–1017
6. Rao SVS, Lal KB, Narasimhan SV, Ahmmed J (1997) Separation of cobalt from synthetic intermediate and decontamination radioactive wastes using polyurethane foam. Sep Sci Technol 32(18):3007–3026
7. Rao SVS, Lal KB, Narasimhan SV, Ahmmed J (1999) Copper ferrocyanide-polyurethane foam as a composite ion-exchanger for removal of radioactive cesium. J Radioanal Nucl Chem 240(1):269–276
8. Rao SVS, Narasimhan SV, Lal KB (2003) Composite CFC-PU foam ion-exchanger in the removal radio active cesium-pilot plant scale studies using simulated and actual plant waste. J Radioanal Nucl Chem 256(1):137–141
9. Paul AH (1993) A review of information on ferrocyanide solids for removal of cesium from solutions. Sep Sci Technol 28(17&18):2479–2506
10. Trivedi P, Axe L (1999) A comparison of strontium sorption to hydrous aluminum, iron, and manganese oxides. J Colloid Interface Sci 218:554–563
11. Moghissi AA, Godbee HW, Hobart SA (1986) Radioactive waste technology. The American Society of Mechanical Engineers, New York
12. Rao SVS, Lal KB, Panicker PK, Narasimham SV (1995) Fixation of copper ferrocyanide cake in the urea-formaldehyde matrix. Waste Manage 15(7):501–505