

## Copper ferrocyanide – polyurethane foam as a composite ion exchanger for removal of radioactive cesium

S. V. S. Rao,<sup>1</sup> K. B. Lal,<sup>1</sup> S. V. Narasimhan,<sup>2</sup> Jaleel Ahmed<sup>1</sup>

<sup>1</sup> Centralized Waste Management Facility, N. W. M. G.,

<sup>2</sup> Water and Steam Chemistry Laboratory, B.A.R.C. (F), Kalpakkam, 603 102, India

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A method has been developed for the removal of cesium from the aqueous radioactive waste using a composite ion-exchanger consisting of Copper-Ferrocyanide Powder (CFC) and Polyurethane (PU) Foam. Polyvinyl acetate has been used as a binder in the preparation of CFC-PU foam. The physical properties of CFC such as density, surface area, IR stretching frequency and lattice parameters have been evaluated and also its potassium and copper(II) content have been estimated. Optimization of loading of CFC on PU foam has been studied. The CFC-PU was viewed under microscope to find out the homogeneity of distribution. Exchange capacities of the CFC-PU foam in different media have been determined and column studies have been carried out. Studies have been undertaken on extraction of cesium from CFC foam and also on digestion of spent CFC-PU foam and immobilization of digested solution in cement matrix. The cement matrices have been characterized with respect to density, bio-resistance and leaching resistance.

### Introduction

Radioactive <sup>137</sup>Cs is one of the important fission products with a long half-life (30 years) and high fission yield (6%). It is present in significant amounts in reactor as well as in reprocessing plant wastes. Generally the reactor wastes are low level wastes having a specific radioactivity in the range of 37 to 3.7·10<sup>4</sup> Bq/l and specific conductance about 360 μS/cm. The reprocessing wastes, however, contain low, intermediate and high level wastes. Since the volumes of high level wastes are low, they are calcined and immobilized in a glass matrix. The low and intermediate level wastes are treated in order to separate the radionuclides into a small and concentrated volume and immobilized in a suitable matrix. The techniques<sup>1</sup> generally employed are evaporation, chemical precipitation, ion-exchange and sorption. The ion-exchange and sorption methods offer better volume reduction factor (VRF), which is the ratio of initial volume to the final volume, compared to that of chemical treatment methods and are more economical than evaporation methods.

A good deal of literature is available on inorganic ion-exchangers,<sup>1–4</sup> organic ion-exchangers<sup>1,5,6</sup> and composite ion exchangers.<sup>7,8</sup> Since the inorganic ion-exchangers are more selective and radiation resistant they are used in the removal of radionuclides. The common inorganic ion-exchangers used in the removal of cesium are ammonium molybdo phosphate (AMP),<sup>9</sup> zirconium phosphates<sup>10,11</sup> and ferrocyanides of transition metals.<sup>12,13</sup> Even though all these materials have good retention capacity for radioactive cesium their use is limited in the column operations owing to their

high flow resistance and low mechanical strength of granules often leading to clogging of the column. These problems can be circumvented by the use of composite ion-exchangers, which can be prepared by incorporating inorganic exchanger in a polymer matrix during the preparation of polymer beads,<sup>14</sup> loading on an inert support<sup>15–17</sup> or incorporating on an anion exchange resin.<sup>18,19</sup> It is reported<sup>12</sup> that generally the non reactive supports such as fiberglass, paper pulp, carbon and clay generally did not give good packed beds for column operations. Fine solids either plugged the bed pores or were lost to the effluent solution.

The selective removal of cesium from radioactive waste using ferrocyanide solids is a well known technique as these compounds have low solubility and high capacity for Cs. Among other ferrocyanides, copper ferrocyanide (CFC) offers better elution and mechanical characteristics and radiation stability.<sup>12</sup> Yet another advantage is that the composition of copper ferrocyanide product fairly remains constant and does not vary with change in mole ratios of the reactants.<sup>20</sup> Polyurethane (PU) foam sorbents supporting various organic and/or inorganic reagents have been successfully prepared and used for the separation process. PALÁGYI and BRAUN have made an excellent review<sup>21</sup> on the polyurethane foam sorbents. These materials, in addition to offering excellent hydrodynamic properties, are amenable for acid digestion at ambient temperatures, thus simplifying the disposal of spent PU foams. Chemically the PU foams are rather stable and inert<sup>22</sup> but they are dissolved by concentrated sulfuric acid and destroyed by concentrated nitric acid. Polyvinyl acetate (PVA) has been selected as a binder in our studies because of its hydrophobic nature.

The studies reported in this paper include preparation and characterization of CFC with respect to density, composition, surface area, infrared spectroscopy and X-ray diffraction; loading of CFC on PU foam using PVA as a binder; microscopic viewing of CFC–PU foam; optimization of weight percentage of CFC on PU foam; determination of distribution coefficient of cesium for CFC–PU foam in different media; column studies; finding the distribution of radioactive cesium on PU foam in the column; extraction of cesium from spent PU foam and digestion of spent CFC–PU foam in nitric acid and fixation of nitric acid waste resulting from the digestion in cement matrix.

## Experimental

### Materials

- (1) PU foam, DP foam Ltd; Pondichery, India, and
- (2) radioactive cesium,  $^{137}\text{Cs}$ , carrier-free cesium chloride in HCl solution; BRIT, India.

### Methodology

**Preparation of copper ferrocyanide:** Solutions of copper(II) and ferrocyanide were mixed in such a way that their molar concentrations are in the ratio of 2.2:1. The precipitate was allowed to settle for 24 hours and filtered and dried at 110 °C to constant weight. The powder was sieved to obtain a particle size between 75 and 100  $\mu\text{m}$ .

**Characterization of copper ferrocyanide powder:** The CFC was characterized with respect to true density, copper(II) and potassium content, surface area, infrared spectroscopy and X-ray diffraction. The density of CFC was determined using a pycnometric method. For the estimation of copper(II) and potassium content, CFC powder was dissolved in a mixture of concentrated nitric acid and sulfuric acid and the solution was evaporated to dryness. The residue was dissolved in deionized water. The estimation of copper and potassium were carried out using atomic absorption spectrophotometer (G B C Model 902). The instruments used for the surface area, IR and X-ray analysis were surface area analyzer (Quanta Sorb Junior), infrared spectrometer (Hitachi Model No. 270-30) and X-ray diffractometer (Siemens Model D-500).

**Preparation of CFC–PU foam:** PU foam (density 20  $\text{kg/m}^3$ ) was cut in to 5 mm cubes and washed with 1M HCl, deionized water and acetone. The foam pieces were dried at room temperature and the open pore content of the foam was estimated to be 97%.

To prepare CFC–PU foam, about 1 g of PU foam was added to the 3 ml of polyvinyl acetate-ethyl alcohol solution (density 780  $\text{kg/m}^3$ ) containing the required amount of CFC and the contents were stirred well and

kept for over night for drying. In order to verify the uniform distribution of CFC on PU foam, the CFC–PU foam was observed under a microscope.

### Determination of distribution coefficients and exchange capacity of CFC–PU foam

For the determination of distribution coefficients about 0.1 g CFC–PU foam was kept in contact with about 100 ml of solution containing inactive cesium spiked with radioactive cesium ( $^{137}\text{Cs}$ ). The contents were stirred for two minutes and left without any further stirring. To find out the extent of removal of cesium, an aliquot of 2 ml was collected in a test tube and radioactive cesium was estimated using a gamma-counter supplied by M/S Electronics India Limited, India. The distribution coefficient,  $K_d$ , in ml/g was calculated using the following equation

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

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

The exchange capacities were computed and reported in terms of milliequivalents per gram of CFC–PU foam.

### Kinetics of removal of cesium

To find out the percentage removal of cesium with time, experiments were conducted by keeping about 0.271 g of CFC–PU foam in contact with 100 ml of solution containing 1 mM cesium spiked with radioactive cesium. The percent removal of cesium was estimated at various time intervals. In another set of experiments inactive cesium was not added and the concentration of radioactive cesium was 2.4  $\cdot 10^5$  Bq/l.

### Column experiments

A 'U' shaped column having a diameter of 15 mm was loaded with about 2.75 g CFC–PU foam and the volume of the packed bed was 29 ml. In order to calibrate the packed column, the pressure drop was measured against flow rate. Low level and synthetic intermediate level wastes were passed through the column and eluate was collected to find out the decontamination factor (DF), which is a ratio of initial and final activity of the solution. The spent CFC–PU foam pieces were collected and the radioactivity present on them was measured using the gamma counter. A column having a diameter of 10 mm was loaded with 0.5 g inactive and 0.038 g of radioactive CFC–PU foam. The specific activity of radioactive foam was 2.6  $\cdot 10^6$  Bq/kg. The volume of the bed was 3 ml and the

flow rate of the eluant, i.e., ammonia solution, was  $9.6 \text{ ml}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ . Concentrated nitric acid (16M) was added to the wet spent CFC–PU foam, and allowed for over night digestion. The weight of dry CFC–PU foam and the volume of wet CFC–PU foam were 2.75 g and 29 ml, respectively. The volume of the nitric acid added was 16 ml.

#### *Immobilization in cement matrix and characterization*

About 100 g of cement, 8.5 ml digested solution and 26.5 ml of water were mixed well and transferred into a mould for curing. The diameter and height of the cement specimen used in the characterization of cement matrices were 44 and 45 mm, respectively. 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.

The cement specimens were kept in a medium containing nutrient salts such as potassium dihydrogen orthophosphate, potassium monohydrogen orthophosphate etc.,. This medium for bacterial growth was prepared according to the procedure recommended by American National Standard ANSI/ASTM G 22-76. The bacterium used in these studies was *Pseudomonas Aeruginosa* which was isolated from the fresh water. The cement specimens were exposed to the bacteria by semi continuous fermentation method for 90 days and subsequently were tested for their compressive strength.

#### *Leaching experiments*

The leaching experiments were conducted in accordance with the American Nuclear Society (ANS) 16.1 standard leach test method. Ground water was used as a leachant and its specific conductance and pH were  $338 \mu\text{S}/\text{cm}$  and 8.3, respectively. The radioactive cesium was determined using the gamma counter. The volume of the sample taken for the determination of cesium in leaching or in all other experiments was 2 ml.

Leach rate (LR) was calculated using the following equation.

$$\text{LR} = (\Sigma A/A_0) \cdot (V/S) \cdot 1/\Sigma T \quad (1)$$

where  $\Sigma A/A_0$  – cumulative leach fraction,  $A_0$  – initial concentration of cesium,  $A$  – concentration of cesium at any time  $T$  (seconds),  $V$  – volume of the specimen ( $\text{m}^3$ ),  $S$  – surface area of the specimen ( $\text{m}^2$ ),  $\Sigma T$  – cumulative time (seconds).

#### *Diffusion coefficients*

The diffusion equation employed in these studies is derived by assuming cylindrical plane source model with the surface concentration as zero at the leachant/solid interface at time  $>0$ .<sup>23</sup>

$$D = \pi/4 \cdot (V/S)^2 \cdot M^2 \quad (2)$$

where  $M$  is the slope of the plot of cumulative leach fraction (CLF) of cesium against the square root of days.  $V$  and  $S$  are the volume and surface area of the matrix, respectively.

## **Results and discussion**

#### *Characterization of CFC powder*

The physical properties of copper ferrocyanide such as density, surface area, infrared stretching frequency of  $\text{C}\equiv\text{N}$  ( $\nu_{\text{C}\equiv\text{N}}$ ) and crystal parameters obtained from XRD studies are given in Table 1. The XRD spectrum of CFC was compared with that of some of the possible compounds like  $\text{K}_2\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$ ,  $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  and  $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$  and observed that it matched better with that of  $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$ . Figure 1 shows the XRD spectrum of CFC and the vertical lines in it show the peak positions and relative intensities of  $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$ . From the analysis of potassium and copper(II) content of CFC and the X-ray patterns, it was inferred that the CFC might be a mixture of potassium copper ferrocyanide and copper ferrocyanide. It is reported in the literature<sup>20,24</sup> that the compounds formed during the precipitation of copper ferrocyanide may be copper ferrocyanide or potassium copper ferrocyanide or mixture of these two. From the estimation of potassium and copper(II) content and assuming the structural formula of potassium copper ferrocyanide and copper ferrocyanide as  $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$  and  $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$  respectively, the percentage of these compounds in the CFC solid was calculated to be 7% and 93%, respectively.

#### *Characterization of CFC–PU foam*

When viewed under a microscope the PU foam showed a honeycomb like network of structure. The CFC loaded on it actually bonded to the hexagonal rings. Visual observation indicated a uniform loading of CFC on PU foam, but under microscope in some places an agglomeration of CFC particles was observed. Figure 2 shows the microscopic view of CFC–PU foam. The block spots on the rings indicate the agglomerated CFC.

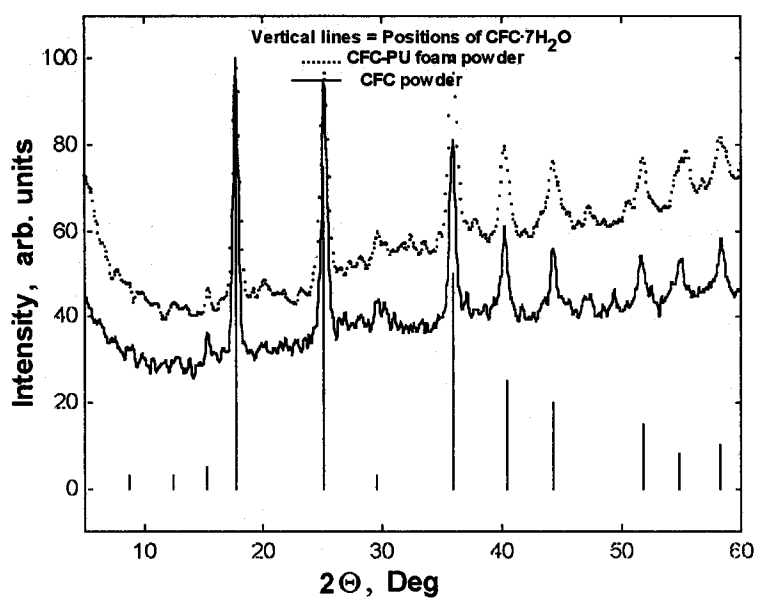


Fig. 1. XRD pattern of CFC powder



Fig. 2. Microscopic view of CFC-PU foam (58x magnification)

Table 1. Physical properties of copper ferrocyanide powder

Size, $\mu\text{m}$	75–100
Density, $\text{kg/m}^3$	2010
Surface area, $\text{m}^2/\text{kg}$	10, 850
Crystal structure	Ortho rhombic
Lattice parameters	
<i>a</i>	11.5567
<i>b</i>	5.5369
<i>c</i>	3.5314
$\text{C}\equiv\text{N}$ Stretching frequency, $\text{cm}^{-1}$	2072

Table 2. Distribution coefficients (in ml/g) of CFC–PU foam

Medium	Concentration of cesium		
	10 mM	1 mM	0.1 mM
Ground water	143	4242	–
3M sodium nitrate	70	451	3320

XRD pattern of CFC –PU foam is also given in Fig. 1. The dotted lines show the XRD spectrum of CFC–PU foam, which was same as that of  $\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$  indicating that there is no change in the structure of CFC after loading on PU foam.

#### Optimization of CFC loading on PU foam

In order to optimize the loading of CFC on PU foam, the PU foam was loaded with different amounts of CFC and the CFC–PU foam was kept in contact with 10 mM cesium solution for 24 hours and the exchange capacities were determined as described in the experimental section. The exchange capacities of CFC–PU foam having 45, 55 and 65% (w/w) of CFC were found to be 0.51, 0.66 and 0.53 meq/g, respectively. The loading of CFC beyond 55% (w/w) did not help much in the removal of cesium as excess addition of CFC might be leading to agglomeration of CFC particles. Unless otherwise stated, further experiments were carried out with PU foam containing 55% (w/w) of CFC.

#### Determination of distribution coefficients in different media

The distribution coefficients ( $K_d$ ) of CFC–PU foam for cesium in the ground water as well as in a solution containing 3M sodium nitrate were estimated and the values are reported in ml/g in Table 2. The  $K_d$  values were observed to be low in 3M sodium nitrate solution.

#### Kinetics of removal of cesium

Figure 3 shows the percentage removal of cesium against time. The rate of removal is higher from solution containing radioactive cesium alone.

#### Column studies

The experimental setup used in the column studies is given in Fig. 4. A ‘U’ shaped column was selected in these studies because if there are any loosely bound CFC particles present in the CFC–PU foam, the ‘U’ tube facilitates the gravitational settling of these particles on either side of the tube and will be held in the pores of PU foam. Short circuiting of flow, air entrapment and bottom support are also avoided in ‘U’ tube. Before starting the column experiments the ‘U’ tube was calibrated and the slope of curve plotted between pressure drop and flow rate was observed to be  $0.37 \text{ cm/ml}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ . The pressure drop observed in these experiments to attain a flow rate of  $8 \text{ ml}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$  was 2 cm whereas the reported pressure drop value for the AMP polymer beads to get the flow rate of  $4.5\text{--}8 \text{ ml}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$  was 20 cm.<sup>16</sup> The low pressure drop obtained with PU foam facilitates higher flow rates in actual plant scale operations, which is a tremendous advantage.

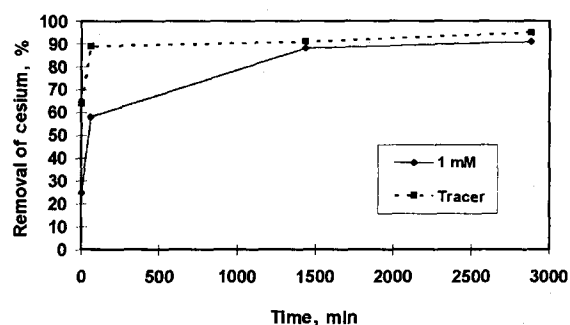


Fig. 3. Kinetics of cesium removal

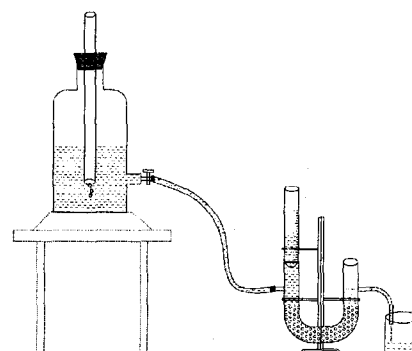


Fig. 4. Experimental setup of column studies

### Low level waste

The dimensions of the packed bed column were discussed in the experimental section. Low level radioactive waste (generated at Madras Atomic Power Station) having a specific radioactivity of  $1.1 \cdot 10^4$  Bq/l, pH 8.7 and conductance  $340 \mu\text{S}/\text{cm}$  was passed through the column at a flow rate of  $26 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ . The contact time was 1.1 minute. Even after passing 345 bed volumes of waste solution the final activity of the treated effluent was found to be 33 Bq/l and the decontamination factor (DF), which is the ratio of initial specific activity to the final specific activity of the waste solution was observed to be better than 300.

### Intermediate level waste

In the Purex process the first cycle raffinate is treated as high level waste. The nitric acid waste resulting from the second and third cycles is either concentrated and treated as high level waste or neutralized with the alkaline waste arising from the alkaline washing of n-tributyl phosphate (TBP) in the purex process.<sup>25</sup> Hence the neutralization of acidic waste is not a problem and implementable even in industrial scale. CFC-PU foam treatment is not going to be used for high level waste. Instead of concentrating the nitric acid to high level waste, it can be neutralized and treated as ILW. Since the CFC-PU foam process needs the pH around 8–9 care must be taken to maintain the pH during the neutralization process. The main chemical constituent in the ILW is sodium nitrate. The concentration of sodium nitrate in the ILW would be in the range of 3–4M. The

synthetic ILW containing 4M sodium nitrate and  $4.4 \cdot 10^5$  Bq/l radioactive cesium was prepared and passed through the column with a flow rate of  $4 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ . The DF obtained was around 10. Different flow rates and different concentrations may be improve the DF obtained.

### Distribution of radioactivity on the spent CFC-PU foam

The spent PU foam pieces obtained from the column studies of low level waste were collected and determined for the radioactive cesium. The relative cumulative percentage of radioactivity along the column is given in Fig. 5. It is evident from the figure that more than 80% of the activity is retained in the first 6 ml of volume of the column. The specific activity of spent CFC-PU foam pieces in the inlet side were measured and the maximum specific activity was found to be  $7 \cdot 10^8$  Bq/kg.

### Recovery of cesium from spent PU foam

In order to extract the cesium from CFC-PU foam, ammonia solution was taken for elution because it provides the required pH for destabilizing the copper ferrocyanide complex and also forms a complex with copper(II) ion. Figure 6 shows the percentage of cesium eluted against the volume of the solution passed. It is seen from the figure even after passing of about 5 bed volumes, the recovery was only 70%, which indicates that neat polyurethane foam also absorbs radioactive cesium. Later the distribution coefficient of cesium on neat PU foam in  $10^{-7}\text{M}$  cesium solution was observed to be 639 ml/g.

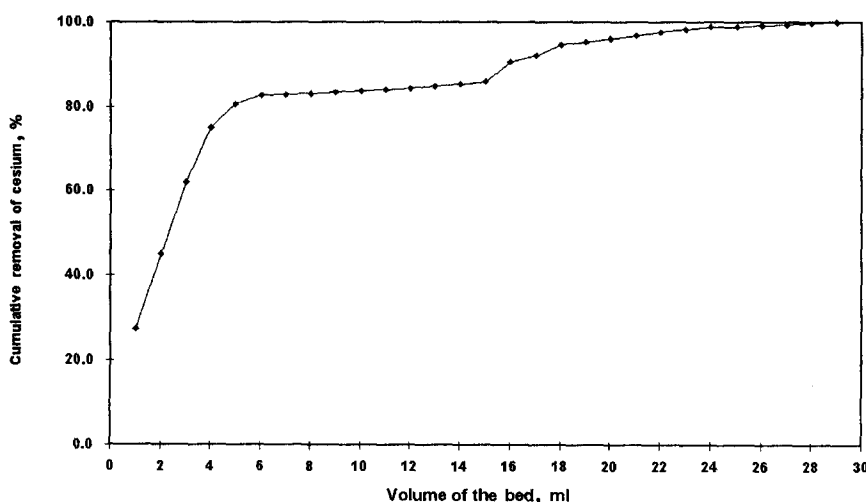


Fig. 5. Distribution of cesium on CFC-PU foam

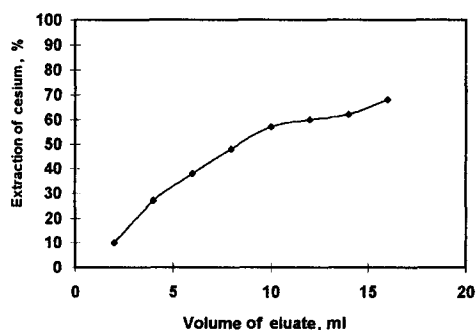


Fig. 6. Extraction of cesium from CFC-PU foam

#### Digestion of CFC-PU foam

Digestion of the CFC-PU foam was carried out as described in the experimental section. When the nitric acid was added, brown vapors of nitrogen oxides were evolved. The nitric acid was estimated by titrating it with sodium hydroxide using phenolphthalein as an indicator. From the estimation of nitric acid, the consumption of acid during digestion of CFC-PU foam was only 30% and the volume of the digested liquid was 33 ml. The estimation of unreacted nitric acid gives an idea about the amount of excess cement required for the neutralization during the immobilization of digested liquid in the cement matrix.

#### Immobilization of digested solution in ordinary Portland cement (OPC)

The digested solution was immobilized in the ordinary portland cement matrix and characterized as per the procedure given in the experimental section. The physical properties of cement specimen such as density, compressive strength, and diffusion coefficient of cesium are given in Table 3. The density of the specimens was higher than that of the copper ferrocyanide sludge containing cement specimen<sup>25</sup> and it may be due to the formation of fine silica grains during the neutralization reaction between cement and nitric acid. The compressive strengths of the specimens were much higher than the stipulated values (0.4 MPa) of 10 CFR 61 (US Code of Federal Regulations). After 90 days of exposure to bacteria, there was no apparent bacterial growth on the cement specimens. Figure 7 shows cumulative leach fraction against square root of time. The leaching results were compared with those of 18% (w/w) copper ferrocyanide containing cement specimens.<sup>26</sup> The diffusion coefficients obtained in this process were observed to be two times lower.

Table 3. Physical properties of cement specimen

Density, kg/m <sup>3</sup>	2200
Compressive strength, MPa	
After one day	12.1
After 90 days immersion in water	14.5
After exposure to bacterial attack for 90 days	14.0
Bio degradation	No growth
Leach Resistance (after 43 days)	
Leach rate, m/s	$8.6 \cdot 10^{-10}$
Diffusion coefficient, m <sup>2</sup> /S	$2.0 \cdot 10^{-12}$

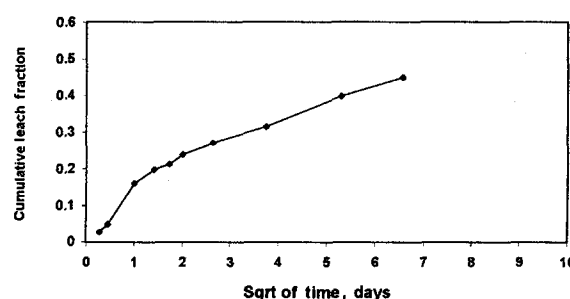


Fig. 7. Cumulative leach fraction vs. sqrt of time

Generally, the specific activity of low level waste will be around  $3.7 \cdot 10^3$  Bq/l. In our experiments the specific activity of spent CFC-PU foam was observed to be  $7 \cdot 10^8$  Bq/kg. Therefore  $1.9 \cdot 10^5$  l could be treated using 1 kg of CFC-PU foam. The volume of the digested liquid after 1 kg CFC-PU foam digestion will be 5.8 l. After fixing the digested liquid in cement the volume of cement matrix becomes 48 l considering the amount of cement required for neutralization and solidification. Therefore this process yields an overall volume reduction factor of about 3958.

#### Conclusions

The above studies indicated that the CFC-PU foam can be used for the treatment of low level radioactive waste. Since the flow rates obtained with CFC-PU foam are quite high, this process can be used to treat large volumes of waste. The disposal of CFC-PU foams is not a problem, compared to normal organic ion-exchangers since the PU foams are amenable for wet digestion and the digested liquids can be safely disposed of in the cement matrix. The volume reduction factors in this process are in the range of 2000–4000 for low level wastes of  $1.8$ – $3.7 \cdot 10^3$  Bq/l and it is two orders higher than the ones generally obtained in the Copper-Ferrocyanide precipitation process about  $30$ <sup>27</sup> without immobilization in cement.

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