



Removal of radioactive caesium from low level radioactive waste (LLW) streams using cobalt ferrocyanide impregnated organic anion exchanger

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ABSTRACT

The volumes of low level waste (LLW) generated during the operation of nuclear reactor are very high and require a concentration step before suitable matrix fixation. The volume reduction (concentration) is achieved either by co-precipitating technique or by the use of highly selective sorbents and ion exchange materials. The present study details the preparation of cobalt ferrocyanide impregnated into anion exchange resin and its evaluation with respect to removal of Cs in LLW streams both in column mode and batch mode operations. The K_d values of the prepared exchanger materials were found to be very good in actual reactor LLW solutions also. It was observed that the exchanger performed very well in the pH range of 3–9. A batch size of 6 g l⁻¹ of the exchanger was enough to give satisfactory decontamination for Cs in actual reactor LLW streams. The lab scale and pilot plant scale performance of the exchanger material in both batch mode and column mode operations was very good.

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1. Introduction

Radioactive LLW is generated during operation and maintenance of a nuclear reactor, vitrification of HLW and ion exchange treatment of ILW. The major contaminants of these wastes are the fission products. Among the fission products ¹³⁷Cs is of special concern due to its long half life and biological hazards. So its removal from the waste streams before their discharge to the environment is necessary. Because of the high volumes and the presence of significant quantities of non-radioactive constituents of these wastes a concentration step before suitable matrix fixation is required. Generally this is achieved by either precipitation or ion exchange or evaporation techniques [1]. By these methods the activity in the waste stream is getting redistributed in two phases, one dilute and the other concentrated. The dilute phase is discharged after providing necessary dilution, in order to meet the regulatory limits for radioactive discharge. The concentrated phase with all most all of the total activity will be conditioned by fixing in cement or polymer matrices [2].

Co-precipitation of Cs from the waste stream using metal ferrocyanides is well studied [3,4] and is currently in use at many

plants. The process though efficient has certain disadvantages. The over all efficiency of the process depends on the uptake of the radionuclide by the precipitate and separation of the solid and liquid phases. The precipitates formed should have favourable coagulation, flocculation and separation characteristics. This calls for a precise optimisation of the process parameters to ensure a complete phase separation. Also the precipitate (sludge) separated will contain maximum activity and has to be treated separately by fixing in cement matrix.

Removal of radio Cs from LLW can also be achieved by use of highly selective ion exchange materials. It is well known that transition metal ferrocyanides are selective for Cs uptake [5–8] and a great number of them have been studied for their prospective use in the separation of radioactive Cs from nuclear waste streams [9,10]. One of the most promising Cs selective ferrocyanide is Potassium cobalt ferrocyanide [11,12]. However the microcrystalline nature of these materials renders them useless for use in column mode operations. To prepare ion exchanger of convenient particle size for column mode operations, several types of support materials and binding materials were tried by various scientists [13–16]. Some researchers have also tried the loading of these ferrocyanides on organic ion exchange resins [17,18]. More recent literatures are not available on this direction.

Present study gives the preparation of cobalt ferrocyanide loaded anion exchange resin and its evaluation with respect to ion

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exchange properties. The distribution coefficients of the prepared exchangers were determined in Cs spike solution and in actual reactor LLW solutions. The optimum pH and the optimum amount of exchanger required to get sufficient decontamination for Cs were determined. Batch and column mode operations for the removal of Cs were conducted with actual LLW both in lab scale and pilot plant scale.

One of the waste streams studied was the low level liquid waste generated in the power plant. The major radionuclides present in this waste stream are ^{137}Cs and ^{60}Co . The pH adjustment and ferrous sulphate treatment of this waste at the power plant removes most of the Co present in the waste as sludge. The clear decant is then transferred to the waste management facility for conventional chemical treatment to remove Cs by co-precipitation with copper ferrocyanide. This method produces large volumes of chemical sludge having appreciable radioactivity and is being fixed in cement for its safe disposal. To reduce the sludge volume produced with out affecting the decontamination factor, use of cobalt ferrocyanide loaded anion exchanger powder in repeated batch mode operation was tried.

The other waste stream studied was the effluent of the LLW after its chemical treatment. This waste is discharged to the sea after proper dilution. Although this liquid waste contains very small concentrations of radionuclides, over a long period its can cause accumulation of radioactivity in the water body. Later these radionuclides may enter in to the aquatic food chain and ultimately reach the human environment. To avoid radionuclides entering environment, it is essential to remove them from the waste solution to the maximum extent before its discharge. In this connection ion exchange polishing of the treated effluent in column mode operation was tried to reduce the activity discharged to the sea.

2. Experimental

All the chemicals used for the experiments were of AR grade. Strong base anion exchange resin ($-\text{N}(\text{CH}_3)_3^+$) in chloride form having polystyrene divinyl benzene polymer back bone and iso-porous structure (Indion FPIP) was used for loading cobalt ferrocyanide. To remove any water-soluble residue or undesired anions remaining in the resin, the resin samples were subjected to a preconditioning process. Pretreatment was carried out by treating the resin with 2 M hydrochloric acid and 2 M sodium hydroxide solutions with distilled water washing in between. Finally the resin was equilibrated with 1 M NaCl solutions and washed thoroughly with distilled water. The resin was then air-dried. The anion exchange capacity of the resin was determined by conventional method [19]. ^{137}Cs spike solution used was containing only ^{137}Cs isotope, which was confirmed from the gross β activity measurement and γ -spectrometry. All the experiments were carried out in duplicate to ensure the repeatability of the measurements.

2.1. Preparation of anion exchanger loaded cobalt ferrocyanide

Preparation of the ion exchangers was carried out as explained elsewhere [20]. Anion exchanger beads of size $-16 + 25$ ASTM mesh were first converted into ferrocyanide form. For this 5 g anion

Table 1
Activity spectrum of waste streams.

Isotopes	Activity (Bq ml^{-1}) RLLW waste	ERLLW waste
Gross β	100–120	25–35
^{137}Cs	80–100	20–30
^{134}Cs	5–10	1–2
^{60}Co	1–2	BDL
^{131}I	2–5	<1

BDL, Below detection limit.

exchanger was equilibrated with 100 ml of 0.1 M potassium ferrocyanide solutions for about 5 h by shaking continuously on a mechanical shaker. The ferrocyanide loaded resin was then washed with distilled water to free it from excess ferrocyanide ions. The residue was then equilibrated with 0.1 M cobalt nitrate solution (100 ml) for 24 h shaking continuously on a mechanical shaker to precipitate $\text{Co}_2\text{Fe}(\text{CN})_6$ on the anion exchanger. The $\text{Co}_2\text{Fe}(\text{CN})_6$ loaded resin was then washed with distilled water to free it from excess cobalt nitrate, filtered and dried. The removal of excess electrolyte was ensured by checking the washings for the presence of ferrocyanide ions using cobalt nitrate solution, and vice versa. These exchangers were used for the column mode operations. The amount of cobalt ferrocyanide precipitated on the resin is 5% (w/w).

Anion exchanger in powder form ($-25 + 60$ ASTM mesh) was loaded with cobalt ferrocyanide in the same way as explained above, for using in batch mode operations. The adhering fine particles were removed by repeated washing of the loaded exchanger powder. The amount of cobalt ferrocyanide precipitated on the resin is 13% (w/w).

As the kinetics of uptake of potassium cobalt ferrocyanide is faster than cobalt ferrocyanide [20], the loaded cobalt ferrocyanide was converted into potassium cobalt ferrocyanide by treating with 0.1 M KCl solution.

2.2. Waste solutions studied

In addition to ^{137}Cs spike solution, actual low level waste solutions were also used for the studies. One of the waste streams studied was the LLW generated during the operation of Tarapur Atomic Power Plant (TAPP). All the system leakages from the power reactor are collected as floor drain waste. Also the regenerants from ion exchange columns are collected as chemical regenerant waste. These two streams are the LLW from the reactor (RLLW). This waste is presently managed by conventional chemical treatment method [3,4]. The other waste stream was the effluent of the above LLW after its chemical treatment (ERLLW). The activity spectrums of these waste solutions are given in Table 1.

2.3. Evaluation of ion exchange properties

2.3.1. Determination of Kd

The distribution coefficient, Kd, for Cs uptake by the ion exchanger was determined in batch mode experiments using ^{137}Cs spike solution and actual waste solutions at pH 9.

The values are given in Table 2.

Table 2
Distribution coefficient (Kd) with respect to Cs uptake.

S. No.	Exchanger form	Exchanger weight (mg)	Waste solution	Waste volume (ml)	Kd (ml/g)
1	Beads	40	^{137}Cs Spike	50	9688
2	Beads	40	RLLW	50	3688
3	Beads	40	ERLLW	50	3051
4	Powder	100	^{137}Cs Spike	100	11493
5	Powder	100	RLLW	100	7460

2.3.2. Determination of optimum pH

To optimise the pH of the feed solution for getting maximum decontamination factor (DF), a set of experiments were carried out. 1 g samples of exchanger powder were equilibrated with 25 ml of RLLW waste for 1 h. The pH of the solution was adjusted, using dilute nitric acid or sodium hydroxide as required, to the required value (1–12). The supernatant solution was filtered and analysed for ^{137}Cs activity using NaI(Tl) scintillation counter. From the initial and final ^{137}Cs activity of the solution, DF was calculated.

$$\text{DF} = \frac{A_i}{A_f}$$

where A_i and A_f are initial and final specific activities (Bq ml^{-1}) of the waste solution.

2.3.3. Optimum amount of the exchanger required per batch

The optimum amount of the exchanger required for getting maximum DF was also determined. For this, varying amounts of exchanger powder were equilibrated with 25 ml of RLLW waste solution at pH 9 for 1 h. In each case the DF was calculated.

2.3.4. Settling characteristics of the exchanger powder

The settling characteristics of the cobalt ferrocyanide loaded powdered anion exchanger was determined. 50 ml of cobalt ferrocyanide loaded powdered anion exchanger was taken in a transparent glass measuring jar having diameter 5.2 cm. The measuring Jar was filled with water up to 500 ml. The content was then mixed well and allowed to settle. The settling characteristic of the exchanger was observed by noting the volume of the exchanger getting settled at different time intervals. Percentage settling was calculated from the ratio of the volume of the settled exchanger at a given time and the initial volume of the exchanger (50 ml). The experiment was repeated with powdered virgin anion exchanger also.

2.3.5. Batch mode performance evaluation

2.3.5.1. Lab scale study. Lab scale study was carried out to visualize the repeated batch mode/cascade mode performance of the powdered ion exchanger. 0.5 g of exchanger powder was equilibrated with 100 ml of RLLW waste solution for 1 h. The exchanger was then allowed to settle and the supernatant solution was decanted and analysed for ^{137}Cs activity. The residue from the first set of experiment was again equilibrated with fresh batch of (100 ml) waste and the supernatant solution was analysed for ^{137}Cs activity. This cascade mode of operation was continued up to 13 batches. In each batch the DF was calculated.

2.3.5.2. Pilot plant scale study. The pilot plant scale cascade mode study was carried out in a plastic bucket of 200 l capacity. 500 g of exchanger powder was equilibrated with 50 litres of RLLW waste and stirred for 1 h using a mechanical stirrer. The exchanger was allowed to settle for 30 min and the supernatant was separated from the exchanger using peristaltic pump. The supernatant was analysed for ^{137}Cs activity. The exchanger was repeatedly treated with fresh batches of waste solution. This cascade mode of operation was continued up to 18 batches. In each batch the DF was calculated.

2.3.6. Column mode performance evaluation

2.3.6.1. Lab scale study. Two glass columns of 30 ml capacity (1.3 cm diameter) were filled with 12 ml (5 g) of cobalt ferrocyanide loaded ion exchange beads. The details of the columns are given in Table 3. Through one of the columns ^{137}Cs spike solution was passed at a flow rate of 120 ml/h. Through the other column clear solution of RLLW waste was passed at the same flow rate. In each case effluent samples were collected periodically and analysed for ^{137}Cs activity.

Breakthrough curve was plotted with fraction of Cs activity loaded (C/C_0) vs bed volumes passed.

2.3.6.2. Pilot plant scale study. A purpex column of 2 l capacity (2.5 inches diameter) was filled with 1.5 l (600 g) of cobalt ferrocyanide loaded ion exchange beads. The details of the column are given in Table 3. The supernatant of the chemically treated waste (ERLLW waste) solution was passed through the column at a flow rate of 15 l/h. Periodic effluent samples were analysed for ^{137}Cs activity. Concentration profile was obtained by plotting the fraction of Cs activity loaded (C/C_0) versus bedvolumes passed.

3. Results and discussion

Modified exchanger was found to have pickup only for Cs ions in the reactor LLW. However the exchanger has some pickup for Pd ions in acidic solutions [21]. Although there are anion exchange site on the modified exchanger, pickup for iodide ions was not observed. During the course of the experiments, neither any wash out of cobalt ferrocyanide from the anion exchanger nor desorption of Co from cobalt ferrocyanide was observed.

The major contribution to the radioactivity of the reactor LLW is due to ^{137}Cs isotope (Table 1) and effective removal of this isotope from the waste solution will qualify it for discharge in to the environment. The dischargeable level of for gross β activity in the liquid waste solution is $<4 \text{ Bq ml}^{-1}$ (BARC safety council is authorized to periodically review this value based on the International Atomic Energy Rule).

3.1. Distribution coefficient (Kd)

To see the effect of the nature of waste solution on the Kd of the exchanger material for Cs uptake, Kd in different waste solutions was determined. From Table 2 it can be seen that the Kd values of the exchanger materials in ^{137}Cs spike solution is more compared to that in actual waste solution. This shows that the presence of inactive salt content affected the Kd of the material. The Kd value of exchanger powder is higher than that of the beads due to the higher specific loading of cobalt ferrocyanide on the exchanger powder.

3.2. Effect of pH

Effect of pH on the Cs uptake of the material was determined to optimize the waste solution pH for the plant scale operations. Fig. 1 shows the DF obtained at different waste solution pH. From the figure it can be seen that the DF values obtained in the pH range of 3–10 are adequate to decontaminate the waste stream to below dischargeable level of activity. Though the DF value at pH 4 is the highest, considering the alkaline nature of the waste solution to be treated the optimum operational pH was selected as 9.

Table 3
Columns details of lab scale and pilot plant scale studies.

	Lab scale study	Pilot plant scale study
Column	30 ml Glass burette column	2 l Purpex column
Column diameter	1.3 cm	6.35 cm
Exchange material	Cobalt ferrocyanide loaded anion exchanger beads	Cobalt ferrocyanide loaded anion exchanger beads
Weight of exchanger material	5 g	600 g
Loading solution	^{137}Cs spike solution and RLLW waste solution	ERLLW waste solution
Bed volume	12 ml	1.5 l
Bed height	9 cm	48 cm
Flow rate	120 ml/h	15 l/h

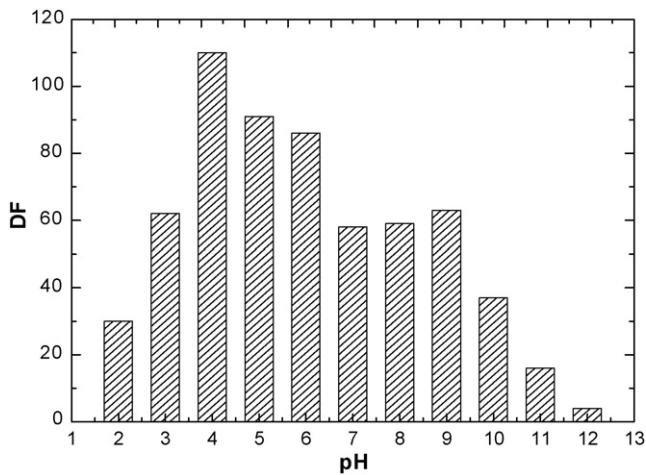


Fig. 1. Effect of pH on Cs removal by cobalt ferrocyanide loaded exchanger powder in reactor LLW.

3.3. Optimum amount of exchanger

The DF obtained with varying amounts of exchanger powder was determined to optimize the minimum amount of exchanger required for batch mode operations. The DF values increased with increasing amount of exchanger in the waste solution and reached almost saturation at about 6 g l^{-1} (Fig. 2). Hence, about 6 g l^{-1} of exchanger powder was considered optimum for batch mode operations to decontaminate the waste solution below dischargeable level of activity.

3.4. Settling characteristics

The true density and bulk density of the exchanger powder were 1.15 and 0.65 g/cm^3 respectively. Fast settling of the exchanger is a parameter necessary to have higher throughputs in the batch operations. From Fig. 3 it can be seen that the settling of cobalt ferrocyanide loaded exchanger powder is very fast. Total settling of the exchanger powder was observed within a time period of 5–6 min. Since the material is having fast settling characteristics it can be effectively used in batch mode operations.

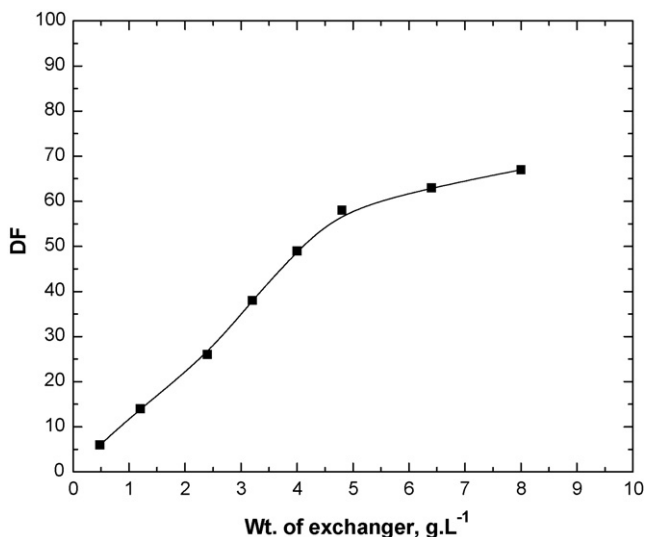


Fig. 2. Cs removal with varying amount of cobalt ferrocyanide loaded exchanger powder in reactor LLW.

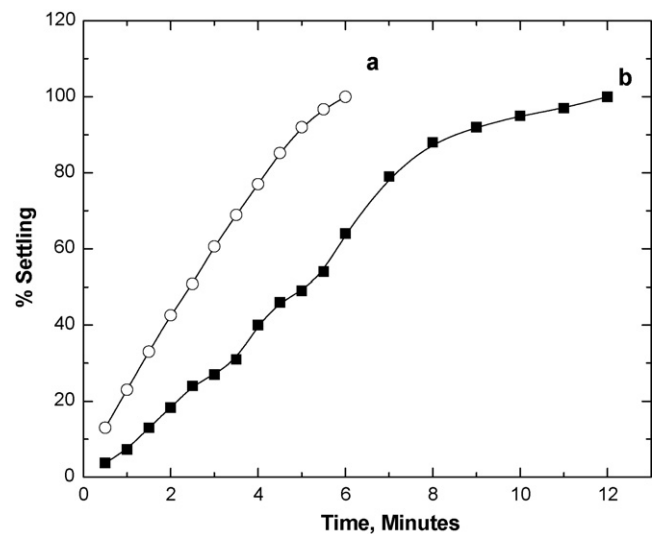


Fig. 3. Settling characteristics of (a) cobalt ferrocyanide loaded exchanger powder and (b) virgin exchanger powder.

3.5. Batch experiments

Use of the exchanger powder in batch mode was studied. It was observed that the exchanger can be used repeatedly in many cycles and can get DF values sufficient to decontaminate the waste. During cascade manner (repeated) use of the exchanger powder in lab scale experiments, it was observed that from 1st batch to 13th batch the DF value decreased from 40 to 13 (Fig. 4). Although the DF got decreased gradually, even the DF (13) obtained in the 13th batch was sufficient to decontaminate the waste stream.

A similar trend of gradual decreasing of DF value was observed during pilot plant scale cascade manner use of exchanger powder too. From 1st batch to 18th batch the DF value decreased from 30 to 5 (Fig. 5). The DFs obtained up to 16th batch were enough to decontaminate the waste solution below dischargeable level of activity. Therefore the exchanger can be reused up to minimum 15 cycles.

In the conventional chemical treatment of the waste stream, the volume of chemical sludge obtained is about 0.2–0.3% of the waste volume treated. Whereas in the case of cascade manner

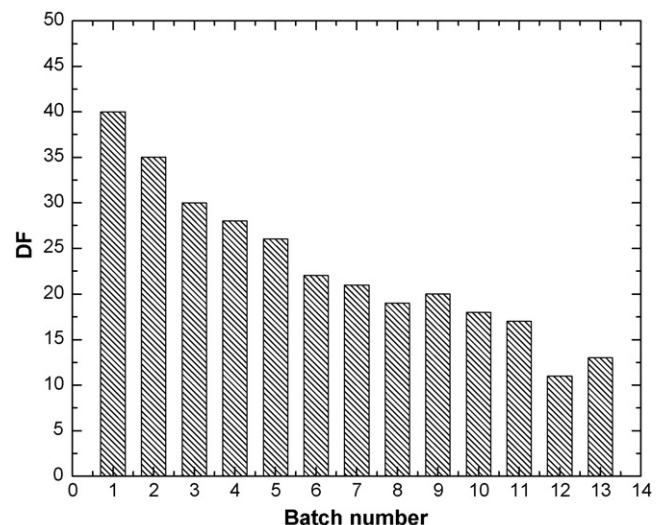


Fig. 4. DF obtained in repeated batch (Cascade) mode experiment—Lab scale study.

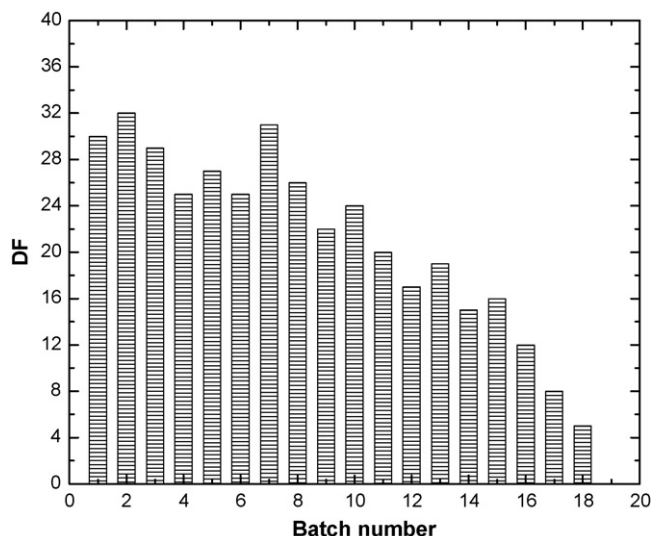


Fig. 5. DF obtained in repeated batch (Cascade) mode experiment—Pilot plant scale study.

use of exchanger powder the sludge volume generated is only 0.025–0.03%. Also the DFs achieved are higher in the case of exchanger powder (25–30) compared to that achieved in the case of chemical treatment (10–15). The time required for settling of cobalt ferrocyanide loaded ion exchange powder is much less (maximum 30–45 min) than that of the chemical treatment sludge (4–5 h). Therefore the cascade manner use of exchanger powder in place of conventional chemical treatment (a) can reduce the generation of sludge volume by 5–10 times without affecting the dischargeable level of activity of the effluent (b) can reduce the activity discharge to the environment due to higher DFs and (c) can increase the through put of the plant due to the fast settling characteristics.

3.6. Column experiments

Use of the cobalt ferrocyanide loaded exchanger beads in column mode operation for removal of Cs from LLW was studied. The breakthrough curves of the cobalt ferrocyanide loaded anion exchanger beads in the ^{137}Cs spike solution and RLLW waste solu-

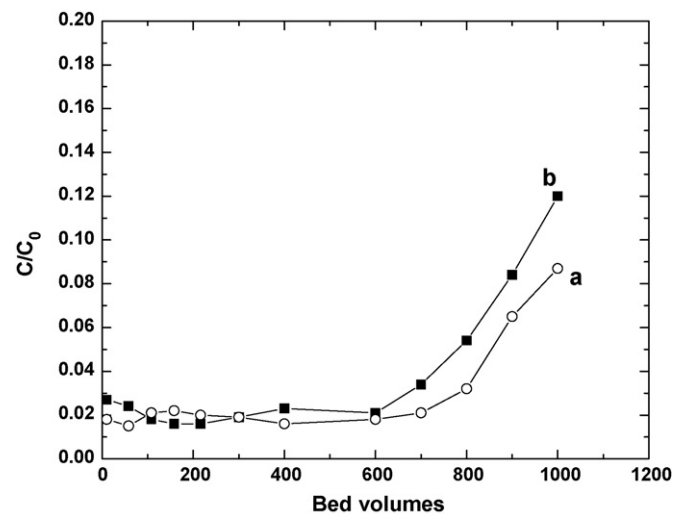


Fig. 6. Breakthrough curves for Cs uptake by cobalt ferrocyanide laded exchanger beads in (a) Cs spike solution and (b) reactor LLW—Lab scale study.

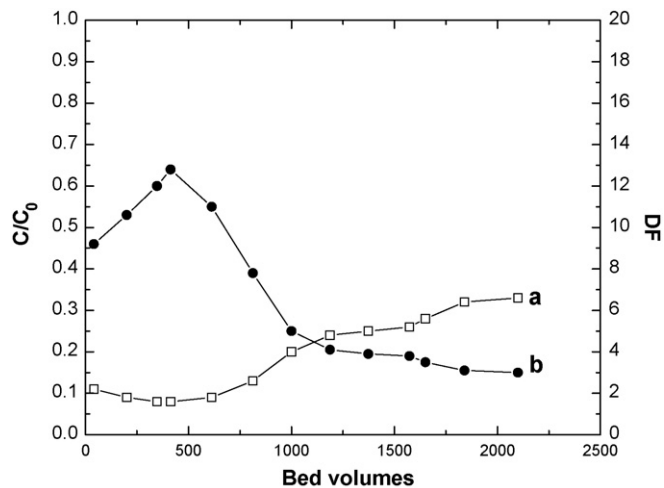


Fig. 7. Graph showing (a) concentration profile and (b) the curve of DF versus effluent volumes for cobalt ferrocyanide loaded exchanger beads in chemically treated waste—Pilot plant scale study.

tion are given in Fig. 6. The 5% breakthrough is at about 775 bed volumes for RLLW waste and 850 bed volumes for ^{137}Cs spike solution. This shows that the presence of inactive salt contents in the waste solution marginally affected the column performance. The DF value obtained at 5% breakthrough is sufficient to bring down the activity well below recommended discharge levels.

Pilot plant scale study of exchanger beads in column mode was carried out with the effluent of chemically treated low level radioactive waste (ERLLW) to polish this effluent before discharging in to the environment. The activity of the stream was in the range of 5–10 Bq ml⁻¹. The pilot plant scale column experiment was stopped before attaining breakthrough due to drastic decrease in flow rate. Fig. 7 shows the concentration profile of the column effluent solution. It also shows the values of DF obtained against effluent volume passed through the column. The DF value was above 10 up to 700 bed volumes (Fig. 7). After that the DF value gradually dropped down to 3 and remained stable till the end of the experiment. Fouling of the column due to the presence of suspended chemical sludge particles in the waste stream caused decrease in DF value. However, even a DF of 2–3 can decrease the activity discharge considerably. The column got completely choked after passing about 2300 bed volumes of waste.

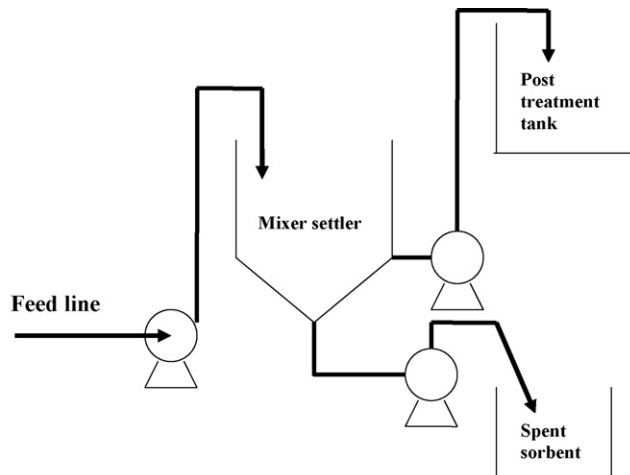


Fig. 8. Schematic diagram for the treatment of LLW by cascade mode batch operation.

Therefore substantial reduction in the radioactivity discharge to sea can be achieved by the introduction of ion exchange polishing as an additional decontamination step for the chemically treated LLW before its discharge to the environment. Cobalt ferrocyanide loaded on anion exchanger beads is a candidate material for the decontamination of chemically treated effluent. Before passing through the column it is required to minimize the suspended solids in the chemically treated effluent in order to avoid fouling and choking of the column.

3.7. Disposal of spent exchanger

Since polymer fixation is a well-established method for conditioning of radioactive spent organic resin [3,22], the spent sorbent can be conditioned by fixing in polymer matrix prior to its disposal.

4. Conclusion

Nanocrystalline cobalt ferrocyanide loaded on powdered anion exchanger exhibits remarkable potential to pick up radioactive Cs from reactor waste and gives decontamination factor of about 25–30. This exchanger has very good exchange kinetics even in the actual waste solutions. The DF values obtained in the pH range of 3 to 10 are adequate to decontaminate the waste stream to below dischargeable level of activity. Batch size of 6 g l^{-1} of the exchanger is good enough to achieve maximum DF in the waste solution in batch experiments.

The exchanger can be used for the removal of radioactive Cs from the LLW in cascade manner up to minimum 15 cycles and can reduce the sludge volume considerably. The cascade manner use of the exchanger has the following advantages. (1) Reduction in the generation of sludge volumes by 5–10 times, (2) reduction in the activity discharge to the environment due to higher DF values and (3) increase in the through put of the plant owing to the fast settling characteristics. Based on the results of the pilot plant scale study, a schematic for treatment of LLW by cascade mode batch operation is presented in Fig. 8.

By introducing an ion exchange polishing column of cobalt ferrocyanide loaded anion exchanger beads, as an additional decontamination step after chemical treatment of the reactor waste solution, considerable reduction in radioactive discharge to sea can be achieved.

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