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S. V. S. Rao^a; K. B. Lal^a; S. V. Narasimhan^b; Jaleel Ahmed^{ac}

^a CENTRALIZED WASTE MANAGEMENT FACILITY, FUEL REPROCESSING & NUCLEAR WASTE MANAGEMENT GROUP, ^b WATER AND STEAM CHEMISTRY LABORATORY, ^c BHABHA ATOMIC RESEARCH CENTRE, INDIRA GHANDI CENTRE FOR ATOMIC RESEARCH CAMPUS, KALKAPPAM, INDIA

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S. V. S. RAO and K. B. LAL

CENTRALIZED WASTE MANAGEMENT FACILITY
FUEL REPROCESSING & NUCLEAR WASTE MANAGEMENT GROUP

S. V. NARASIMHAN

WATER AND STEAM CHEMISTRY LABORATORY

JALEEL AHMED

CENTRALIZED WASTE MANAGEMENT FACILITY
FUEL REPROCESSING & NUCLEAR WASTE MANAGEMENT GROUP

BHABHA ATOMIC RESEARCH CENTRE

INDIRA GHANDI CENTRE FOR ATOMIC RESEARCH CAMPUS
KALKAPPAM, INDIA

ABSTRACT

Studies have been carried out on the removal of radioactive cobalt (^{60}Co) from synthetic intermediate level waste (ILW) and decontamination waste using neat polyurethane (PU) foam as well as *n*-tributyl phosphate–polyurethane (TBP–PU) foam. The radioactive cobalt has been extracted on the PU foam as cobalt thiocyanate from the ILW. Maximum removal of cobalt has been observed when the concentration of thiocyanate in the solution is about 0.4 M. Cobalt can be separated from decontamination waste containing ethylenediaminetetraacetic acid (EDTA) and iron(II). The extent of extraction of cobalt is slow and the separation of iron and cobalt is better with the neat PU foam compared to the TBP–PU foam. The presence of iron in the decontamination waste facilitates the extraction of cobalt thiocyanate on the PU foam. Column studies have been carried out in order to extend these studies to the plant scale. The capacities of the PU foams for cobalt have been determined. The effect of density and the surface area of PU foam have been investigated. Fourier Transform Infrared (FT-IR) spectral studies have been conducted to find out the interaction between PU foam and cobalt thiocyanate species.

1. INTRODUCTION

A variety of structural materials such as stainless steel, carbon steel, and stellite are employed in the primary heat transport system of nuclear reactors. During reactor operation the materials corrode by interaction with the coolant and get neutron activated during their transit through the core. The activated corrosion products (ACP) subsequently deposit on out of core surfaces, as a result of which the radiation field in the surroundings increases. In order to remove the ACP and reduce the man-sievert exposure, chemical decontamination is carried out periodically.

The principal gamma-emitting nuclides of ACP present in the decontamination waste are ^{51}Cr , ^{59}Fe , ^{58}Co , ^{65}Zn , ^{54}Mn , and ^{60}Co . Among these radionuclides, ^{60}Co is important with respect to treatment of waste because of its longer half-life and high gamma energy. However, the chemical concentration of radioactive cobalt is of negligible magnitude in comparison with the other inactive ions present in the decontamination waste, namely Fe^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Cr^{3+} , and Co^{2+} . In pressurized heavy water reactors (PHWRs) specifically, the Fe concentration during the decontamination ranges between 100 and 250 mg/L and most of it remains as Fe(II) due to the reductive nature of the formulations. The details of the decontamination operation and the chemicals employed are given elsewhere (1–3). Generally the decontamination formulations are acidic in nature (pH 3–5) and involve complexing agents like ethylenediaminetetraacetic acid (EDTA) to dissolve the iron oxides. The composition of the decontamination waste is given in Table 1. After the decontamination operation, the ACP such as ^{60}Co are absorbed on the strongly cationic resin. As the ion-exchange resin is equally selective to cobalt(II) and iron(II), a large amount of inactive iron, say 99% of 1.8 meq/mL, is absorbed on the resin, and therefore the volume of waste in the form of ion-exchange resin increases. Therefore, a method which could separate iron(II) and cobalt(II) in the presence of EDTA would yield a reduction in the volume of radioactive waste because the waste could be segregated into two groups depending on the radioactive content.

In addition to the decontamination waste, the normal radioactive liquid wastes of a nuclear power plant, which are categorized as low level wastes (LLW) and intermediate level wastes depending on their specific activity level, contain radioactive cobalt. If the activity of the wastes is more than 3.7 MBq/kg, then such wastes are considered to be intermediate level wastes (4). The aqueous intermediate level wastes are mostly produced in nuclear fuel reprocessing plants. About 4 M HNO_3 is used during the reprocessing operations. Finally, the acidic wastes are neutralized with alkali washings of TBP (5). The chemical composition of the synthetic

TABLE 1
Composition of Decontaminated Waste^a

Chemical	Quantity (g/m ³)
Ethylenediaminetetraacetic acid (EDTA)	~300
Ascorbic acid	~300
Citric acid	~300
Iron(II)	~200
Cobalt-60	3.7×10^6 Bq/L

^a Other metal ions like Fe³⁺, Ni²⁺, Cu²⁺, and Cr³⁺ are present to an extent of <10 g/m³.

intermediate level waste (ILW) is given in Table 2. The concentration of sodium nitrate may vary between 3 and 4 M in the final waste.

In order to remove the cobalt from radioactive liquid wastes, various techniques, viz., chemical precipitation and sorption methods, are used (6, 7). Generally, the chemical precipitation methods offer low decontamination factors, i.e., 10–100. The decontamination factor (DF) is the ratio of initial specific activity to the final specific activity of the waste solution. The volume of the sludges generated after chemical precipitation are quite high because the water content in the sludge is 99%. Even after filtration of the sludge, the water content will remain around 85%. The volume reduction factor (VRF), which is the ratio of the initial volume of the waste to the final volume of the waste, will be around 30 in this method. When the salt concentration increases in the waste, the amount of chemicals needed for precipitation also increases, which results in a larger volume of sludges. The use of ion-exchange resins is limited by the presence of a dissolved salt concentration in the ILW. The method reported (6)

TABLE 2
Composition of Synthetic Intermediate Level Waste

Chemical	Quantity (kg/m ³)
Sodium nitrate	340
Sodium carbonate	159
Sodium sulfate	5
Sodium phosphate	17.8
Sodium chloride	5

for cobalt removal by chemical precipitation requires the oxidation of cobalt(II) to cobalt(III). The cobalt(III) is then precipitated as cobalt hydroxide. Oxygen gas has been used for the oxidation of cobalt(II). The solution has to be stirred vigorously. The presence of carbonate, phosphate, and borate ions is reported to interfere in the removal even when their concentration is in the millimolar range. Due to the presence of these ions, the removal of cobalt has been reduced to 80%, which means the DF attained is 5. Since the ILW has large amounts of salts such as phosphates, application of this method may not yield good decontamination factors. Also, this method involves the precipitation of hydroxides and in such a case both the iron and cobalt may be precipitated. Therefore, separation of iron and cobalt from the decontamination waste is difficult.

Another method (7) has been reported which makes use of mineral mixtures in the separation of cobalt. About 80% removal of cobalt has been reported for a contact time of 2 minutes. The mineral mixture has been reported to perform better in the 2–9 pH range. However, when foreign cations are present in the solution, the performance of the mineral mixture is affected because of their occupation of the sites available for cobalt. Since the decontamination wastes contain a large amount of iron compared to radioactive cobalt, this method may not be suitable. The stability and the performance of mineral mixtures has to be verified because many of the synthetic and natural inorganic exchangers are only moderately stable in solutions of very low salt content (8).

PU foams have been used in the extraction and separation of various inorganic and organic species. Much literature (9–12) is available on this subject. Palágyi and Braun recently reviewed work on the separation and preconcentration of trace elements and inorganic species on solid polyurethane foam sorbents (9). The extraction of trace levels of cobalt on neat PU foams or PU foams loaded with different chelating agents such as 1-nitroso-2-naphthol, diethyldithiocarbamate, and 1-(2-pyridylazo)-2-naphthol has been described in the literature (10). Braun and Farag investigated the extraction of thiocyanate complexes of cobalt(II) and iron(III) from solutions containing 0.5 M thiocyanate and 0.1 M HCl or H₂SO₄ (13). It has been reported that cobalt and iron can be removed on PU foam of the polyether type from thiocyanate solution. The high efficiency of extraction with the polyether-type foam has been ascribed mainly to the presence of polyether in the foam, which dissolves the thiocyanate complex.

Hamon et al. extensively investigated the extraction of cobalt thiocyanate complex on PU foam (14, 15). They demonstrated that PU foam acts predominantly as a long noncyclic polyether, and the metal ions are extracted in the form of anionic metal complexes which are solvated by ether groups present in the PU foam. High thiocyanate concentration,

high ionic strength, and a pH between 1 and 9 have been reported to increase the efficiency of the extraction. Separation of iron(III), cobalt(II), and cadmium in aqueous halide solutions using methyl tricaprylyl ammonium chloride has been reported (16).

From the literature cited above it is inferred that PU foams have good potential for the removal of cobalt, particularly when the ionic strength of the medium is high. Since the ILW has a high dissolved salt concentration, the application of PU foam may be advantageous. Further, no method has been described in the literature on the separation of cobalt(II) and iron(II), especially in the presence of EDTA. An attempt has been made to separate iron(II) and cobalt(II) from waste-containing complexing agents such as EDTA using PU foams.

The aim of this paper is to study the extraction efficiency and extent of cobalt(II) extraction with time from synthetic intermediate and decontamination radioactive wastes and to estimate the efficiency of cobalt extraction on PU foams with different densities and surface areas. Column studies have been carried out in order to extend laboratory studies to plant scale. Infrared spectroscopy data have been used to understand the bonding between the PU foam and the cobalt thiocyanate.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Chemicals and Their Grade

Polyether-type PU foam with an open pore content of 95–97% was obtained from DP foam Ltd., Pondichery, India. Ammonium thiocyanate and sodium nitrate were LR reagents from Ranbaxy, India. EDTA; ferrous ammonium sulfate; and cobaltous nitrate were of AR grade obtained from B.D.H., Glaxo, India; Fischer, India; and Chemico Fine Chemicals, India, respectively. *n*-TBP was procured from B.D.H., England. Ascorbic acid; citric acid, sodium chloride; and NaH_2PO_4 were of LR quality and were obtained from Loba Chemie; Fischer; SD Fine chemicals; and Sarabhai and Merck, India, respectively. The reagents were used without any further purification.

2.2. Methodology

2.2.1. Preparation of TBP–PU Foam

Polyurethane foam was cut into cubical pieces with side lengths of 5 mm. The PU foam pieces were washed with 1 M HCl followed by deionized water and acetone, and were then dried in air at room temperature.

To prepare the TBP-PU foam, about 0.1 g of PU foam and 3 mL of TBP were stirred together for 10 minutes and left overnight. The TBP-PU foam was then dried between two sheets of filter paper as reported in the literature (17). The weight of the TBP was found to vary with the density of the foam. The weight of the TBP absorbed on 20, 26, 32, and 50 kg/m³ foams was observed to be 6, 5.7, 5.2, and 7 times the weight of the foam respectively, and the coefficient of error in the estimation of TBP weight was 11%.

2.2.2. Determination of the Degree of Extraction and the Distribution Coefficients

In all the experiments about 0.1 g of PU foam was kept in contact with 100 mL of 10⁻⁵ M cobalt solution containing radioactive cobalt tracer. The activity (⁶⁰Co) of the tracer in the solution was 11 kBq/L. The contents were stirred for 2 minutes. To determine the extent of extraction, an aliquot of 4 mL was taken in a test tube and the radioactive cobalt was estimated. The sample was transferred back into the original flask after the measurement. A single channel analyzer supplied by M/S Electronics Corporation of India Limited, India was used for ⁶⁰Co estimation. The percentage of extraction (%E) was calculated using

$$\%E = \frac{({}^{60}\text{Co}_{\text{initial}} - {}^{60}\text{Co}_{\text{final}})}{{}^{60}\text{Co}_{\text{initial}}} \times 100 \quad (1)$$

2.2.3. Removal of Cobalt from the Synthetic Intermediate Level Waste

Sodium nitrate is a major constituent in the intermediate level waste and its concentration is in the 2.5–4 M range. Unless otherwise stated, the studies were carried out with solutions containing 3 M sodium nitrate. The bulk density of the foam used in these experiments was 20 kg/m³. Cobalt-60 has been chosen as a representative element of the transition metals present in the ILW. The pH of the solution was maintained between 6 and 7 during the course of the experiments.

2.2.4. Removal of Cobalt from the Waste Solution at a Contact Time of 2 Minutes

The synthetic ILW was neutralized and the pH was maintained between 6 and 7. Ammonium thiocyanate salt was added to both the synthetic ILW and the decontamination wastes to make its concentration about 0.4 M. Sodium nitrate equal to 3 M was added to increase the ionic strength of the decontamination waste. The effect of iron was also studied by carrying

out experiments with different concentrations of iron. The inactive cobalt concentration in the solution was 10^{-5} M and the activity of ^{60}Co tracer was 49 kBq/L. About 100 mL of waste solution and 0.1 g foam were stirred for 2 minutes. Then the sample was taken and analyzed to determine the percentage of cobalt removed.

2.2.5. Column Studies

2.2.5.1. Synthetic ILW. About 2.75 g of PU foam (20 kg/m³) in the form of 5 mm cubes was loaded in a column. The diameter of the column was 15 mm and the volume of the packed foam was 28 mL. The synthetic ILW was neutralized to a pH between 6 and 7. About 7.5 L of a solution containing ammonium thiocyanate (0.4 M) and ^{60}Co (42 kBq/L) was prepared. Around 1.5 mL of 10^{-5} M inactive cobalt was also added to this solution. The solution was passed through the column at a flow rate of $6.6 \text{ mL}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$.

2.2.5.2. Decontamination Waste. Ammonium thiocyanate (0.4 M) and sodium nitrate (3 M) were added to the decontamination waste. About 1.5 mL of 10^{-5} M inactive cobalt and ^{60}Co (42 kBq/L) tracer were also added to the decontamination waste to give a final volume of 7.5 L. The concentration of iron in the waste was generally about 200 mg/L, therefore the column experiments were carried out with a solution containing the same iron concentration. The pH of the final solution was around 3. The diameter of the column and the weight, density, and volume of the PU foam are given in Section 2.2.5.1. The flow rate of the solution was $9 \text{ mL}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$.

2.2.6. Determination of the Capacities of the PU Foams for Cobalt(II)

The capacities of PU foams having different densities were determined in the synthetic ILW as well as in the decontamination waste. After adjusting the thiocyanate concentration, the inactive cobalt and the cobalt-60 were added. The concentration of the inactive cobalt was 10^{-3} M and the activity of the ^{60}Co tracer was 0.1 MBq/L. In addition to the ammonium thiocyanate, sodium nitrate was added to the decontamination waste to keep its concentration about 3 M. About 0.1 g of foam was kept in contact with 100 mL of solution, stirred for 2 minutes, and then left. After a contact time of 24 hours, the samples were analyzed and the capacities were determined. In order to determine the effects of the constituents present in the synthetic ILW and the decontamination waste, the capacities of the foams were determined in a solution containing only 3 M sodium nitrate and 0.4 M ammonium thiocyanate.

2.2.7. Surface Area Determination

The BET surface areas of the PU foams with different bulk densities were estimated using a Quantasorb Junior instrument. In this method the nitrogen adsorbed on the foam at different partial pressures of nitrogen and helium was estimated and the surface area of the PU foam was calculated using the BET equation.

2.2.8. Infrared (IR) Spectra

Infrared spectral studies were carried out using a BOMEM Fourier Transform Infrared Spectrophotometer. A thin sheet of PU foam was used for recording the IR spectra.

3. RESULTS AND DISCUSSIONS

3.1. Studies on the Removal of Cobalt from the Synthetic ILW

3.1.1. Optimization of Thiocyanate Concentration

In order to optimize the thiocyanate concentration, various amounts of ammonium thiocyanate were added to a solution containing only 3 M

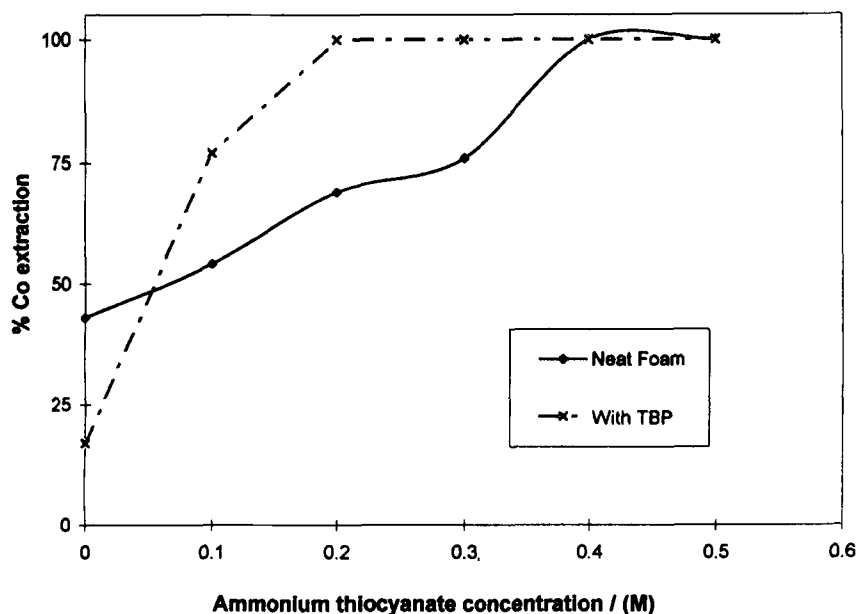


FIG. 1 Effect of ammonium thiocyanate concentration on extraction of Co by PU foam.

sodium nitrate. The percentage extraction of cobalt on the neat PU foam was compared with that of the TBP-PU foam. Figure 1 shows the percentage extraction of cobalt versus the thiocyanate concentration. It is inferred from the figure that the neat PU foam removes cobalt completely when the thiocyanate concentration is around 0.4 M in the solution. In the case of TBP-PU foam, complete extraction of cobalt was obtained at 0.2 M thiocyanate concentration because the TBP present on the foam removed ammonium cobalt thiocyanate by a solvent extraction mechanism. Therefore, the TBP-PU foam extracted cobalt completely even at a lesser thiocyanate concentration. The role of the TBP present on the foam in the removal of cobalt has been described separately.

3.1.2. Extent of Cobalt Removal with Time

The percentage extraction of cobalt on the neat PU foam as well as on the TBP-PU foam was determined at different time intervals from a solution containing cobalt(II) and ammonium thiocyanate. Figure 2 shows the percentage extraction of cobalt versus time. The extent of extraction of cobalt was higher in the case of TBP-PU foam. At the end of 1 hour the percentage extraction of cobalt on the TBP-PU foam was about 88%,

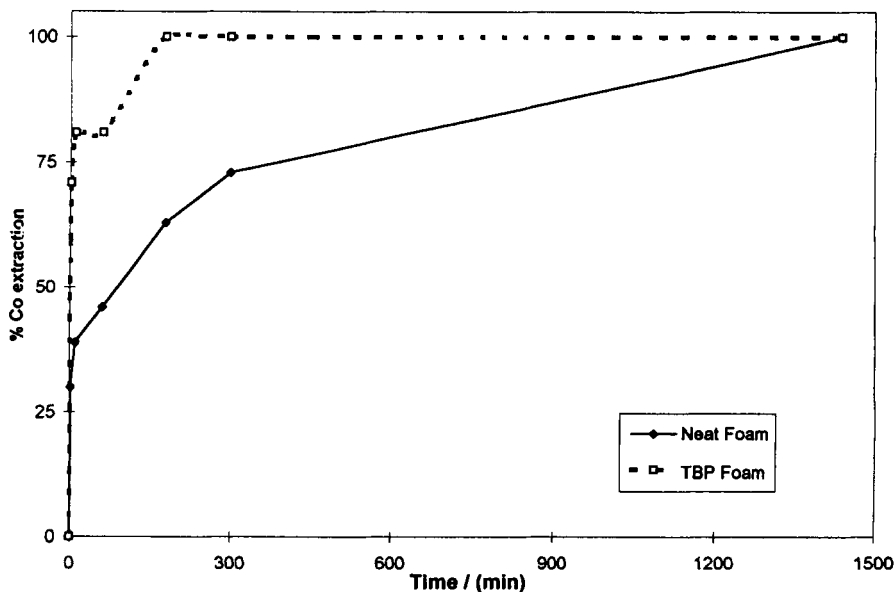


FIG. 2 Rate of Co extraction by PU foam.

whereas that on the neat PU foam was only 50%. This difference is attributed to the combined extraction effect of TBP and PU foam.

3.1.3. Effect of the Density of the PU Foam on the Extent of Cobalt Extraction

PU foam with different densities (such as 20, 26, 32, and 50 kg/m³) was employed to remove cobalt from a solution containing cobalt, sodium nitrate, and ammonium thiocyanate. The percentage of cobalt extraction on the PU foam was determined at different time intervals. Figures 3 and 4 show the extraction of cobalt by neat PU foam and TBP-PU foam respectively. The time axis is shown in log scale because it facilitates distinguishing the data points obtained in the initial period, i.e., 2 to 60 minutes. From these figures it is apparent that the extent of extraction of cobalt at a given time is related to the PU foam density. The higher extraction of cobalt in low density foam is attributed to the faster diffusion of cobalt in the foam matrix. The higher rate of spreading of ammonium cobalt thiocyanate [(NH₄)₂Co(SCN)₄] in the foam matrix was further confirmed by visual observation.

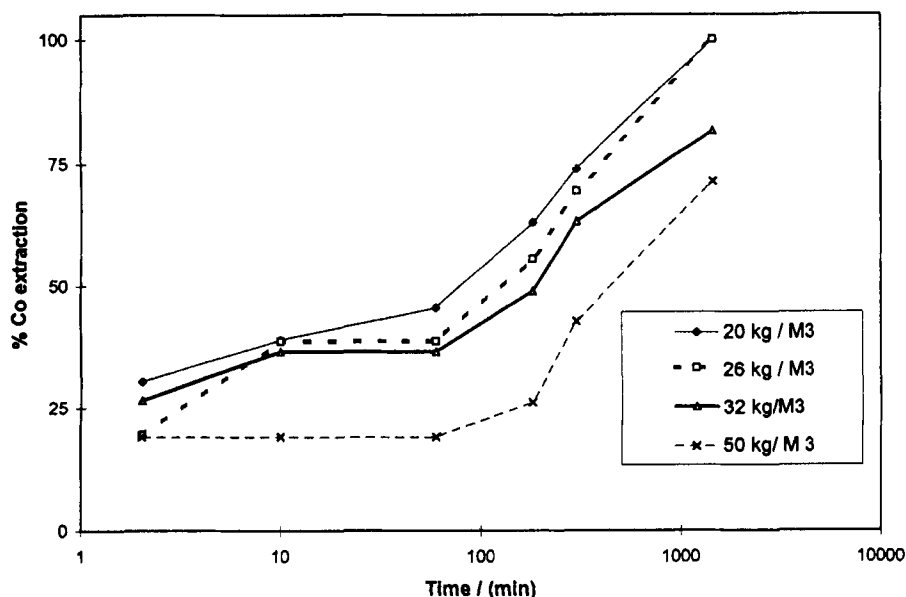


FIG. 3 Effect of foam density on extent of removal of Co by neat PU foam.

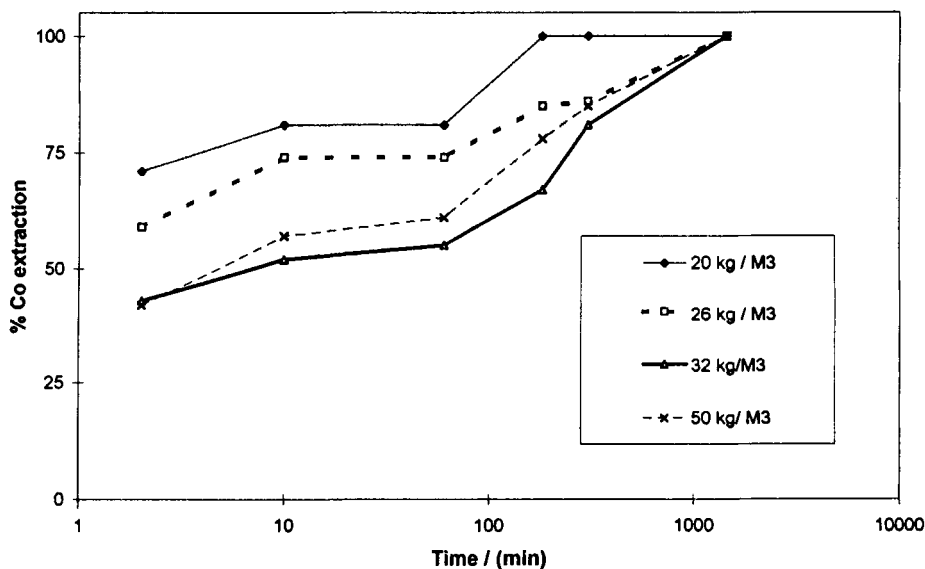


FIG. 4 Effect of PU foam density on extent of removal of Co by TBP-PU foam.

3.1.4. Role of the TBP Present on the TBP-PU Foam in the Removal of Cobalt

TBP, which was present on the PU foam, removed ammonium cobalt thiocyanate by a solvent extraction mechanism. This process reached equilibrium in about 10 minutes. In this time interval the PU foam also contributed to the removal of cobalt. Subsequently, the TBP did not extract cobalt on its own but facilitated the transfer of ammonium cobalt thiocyanate from the solution to the foam. On comparison of Figs. 3 and 4, it is inferred that the percentage of cobalt removal obtained with TBP-PU foam at 60, 180, 300, and 1440 minutes is equal to the sum of the percentage increase caused by TBP-PU foam at 10 minutes and the percentage of cobalt removal on the neat foam at that particular time interval. Therefore, it was concluded that after a time period of 10 minutes the TBP present on the PU foam was not contributing much to the removal of cobalt. The curves converge in Fig. 4 because of the above-mentioned phenomena.

3.1.5. Interference of the Other Ions Present in the ILW

In order to investigate the interference of other ions such as phosphate, chloride, and sulfate present in synthetic ILW, experiments were carried

out in accordance with the procedure given in Section 2.2.4. The cobalt removal was observed to be 40%. The percentage of cobalt removal obtained at 2 minutes for the same foam, i.e., the foam having the same bulk density (20 kg/m^3) when the above ions were absent, was about 30 (Fig. 3). Therefore, from these results it was deduced that the phosphate, chloride, and sulfate ions present in the ILW did not interfere in cobalt removal. Further, the increase in extraction from 30 to 40% was due to the increase in sodium nitrate concentration from 3 to 4 M.

3.1.6. Column Studies with the Synthetic ILW

Column studies were conducted with synthetic ILW, and the details are given in Section 2.2.5.1. More than 200 bed volumes of the solution were passed, and the decontamination factor (DF) was better than 100. After the column studies the radioactive foam pieces were collected and their activity was estimated. It was observed that most of the activity (more than 99%) was retained in the first 12 mL of the column.

3.2. Studies on the Removal of Cobalt from the Decontamination Waste

3.2.1. Removal of Cobalt on the Neat Foam and TBP-PU Foam

The solution used for the decontamination contained EDTA, ascorbic acid/oxalic acid, and acetic acid/citric acid. After the decontamination, in addition to the above compounds, the waste contained iron(II) in amounts ranging from 50 to 200 mg/L. Therefore, a synthetic decontamination waste was prepared with varying amounts of iron(II) (50 to 200 mg/L), EDTA (300 mg/L), and cobalt (10^{-5} M). The pH of the solution was maintained between 4 and 6, where the absorption of cobalt on the PU foam was reported to be maximum (15). The contents were kept in contact with the neat foam which had a density of 20 kg/m^3 . After 24 hours the solutions were analyzed for iron(II) and radioactive cobalt. The iron(II) was estimated by spectrophotometry after the iron was converted into the iron-*O*-phenanthroline complex which has its maximum absorbance at 515 nm (18). When the samples were prepared for the estimation of iron, the concentration of iron in the solution was maintained between 1 and 5 mg/L. In this range the EDTA did not interfere in the analysis. The percentage of extraction of cobalt on the PU foam was around 50–60%, and most of the iron(II) remained in solution. The low degree of extraction of cobalt was attributed to the low ionic strength of the solution. To improve the extent of extraction with time, sodium nitrate was added in later experi-

ments to increase the ionic strength of the solution. The concentration of sodium nitrate in the solution was 3 M. The percentage of iron(II) that remained in the solution and the percentage of cobalt extracted on the foam are given in Table 3. When the concentration of the iron(II) in the solution was near zero, the percentage extraction of cobalt on the neat PU foam and TBP-PU foam was very low. This may be due to complexation of EDTA with cobalt(II). After the addition of iron(II), the percentage extraction of cobalt(II) had increased. The larger concentration of iron(II) compared to that of cobalt facilitated the release of cobalt from the cobalt-EDTA complex. In the case of neat PU foam, the percentage extraction of cobalt increased with an increase in the concentration of iron(II). However, a concentration of iron beyond 150 mg/L decreased the percentage extraction of cobalt due to the pick up of iron on the foam. From the analysis of iron(II), it was observed that most of the iron (90–100%) remained in solution when the concentration of iron in solution was in the 50–150 mg/L range. In the case of TBP-PU foam, the percentage of cobalt extraction increased with an increase in the concentration of iron. From the estimation of the iron present in the solution, it is evident that a significant amount of iron along with cobalt was extracted on the TBP-PU foam. These results also show that there was preferential extraction of cobalt on the neat PU foam. Therefore, the separation of cobalt from iron can be done effectively by using neat PU foam provided the ratio of EDTA to iron concentration is suitably adjusted. The ratio of iron to EDTA concentration should fall in the 1 : 1 to 1 : 3 range, which it usually does.

3.2.2. Interference of Other Chemicals Present in the Decontamination Waste

In addition to the EDTA, the decontamination waste contains citric acid and ascorbic acid. To determine the interference of these ions when

TABLE 3
Removal of Cobalt from the Synthetic Decontamination Waste

Concentration of iron (mg/L)	Cobalt on the foam (%)		Iron in the solution (%)	
	Neat foam	TBP foam	Neat foam	TBP foam
0	4	9	0	0
50	84	25	100	26
100	83	91	100	63
150	89	100	92	75
200	65	100	61	54

the iron concentration was varied between 50 and 300 mg/L, experiments were conducted as per the procedure given in Section 2.2.4. The percentage of cobalt removed from solutions containing 50, 100, 150, 200, and 300 mg/L iron(II) was observed to be about 30, 35, 35, 25, and 20, respectively. The percentage removal of cobalt on neat PU foam (20 kg/m³) from a solution which did not contain EDTA, citric acid, and ascorbic acid was 30% (Fig. 3). The percentage removal of cobalt was comparable except when the iron concentration was more than 200 mg/L. It was confirmed that citric acid, ascorbic acid, and EDTA do not interfere in the removal of cobalt.

3.2.3. Column Studies with the Decontamination Waste

Details of the experiment are given in Section 2.2.5.2. About 150 bed volumes were passed and the DF was around 50. From an estimation of the iron in the treated waste solution, it was observed that most of the iron (nearly 100%) remained in the sixth and subsequent bed volume eluates.

3.3. Extrapolation of the Column Studies to the Plant Scale

The height and the diameter of a probable packed bed column will be 1.2 and 0.7 m, respectively. The required weight of the foam will be 45 kg. From the column studies described in Section 2.2.5.1, the calculated flow rate will be 25 L·min⁻¹. The contact time in this case will be 18 minutes, which is much higher than the contact time of 2.4 minutes employed in our laboratory studies. Hence, the DF is expected to be higher than the laboratory results.

3.4. Disposal of the Treated Waste and Radioactive Foam

The treated waste solution will be in the range of low level waste, and it will be treated in the normal low level waste treatment facilities prior to discharge to the environment.

The radioactive PU foams can be either incinerated or subjected to acid digestion. In the case of incineration, a volume reduction factor (VRF) of 50 can be obtained. Then the total VRF would be in the range of 10³ to 10⁴. The volumes of the resulting wastes will be very small, and they can be fixed in a cement or glass matrix and disposed of in an intermediate or deep geological repository as per regulation.

3.5. Capacities of the PU foams for Cobalt(II)

The capacities of the PU foams were determined in accordance with the procedure given in Section 2.2.6. The capacity of the foam is reported

TABLE 4
Determination of the Capacities of PU Foam for Cobalt

Density of the PU foam (kg/m^3)	Synthetic ILW (mole/kg)	Decontamination waste (mole/kg)	3 M NaNO_3 (mole/kg)
20	0.80	0.34	0.50
26	0.76	0.31	0.43
32	0.70	0.25	0.36
50	0.65	0.22	0.30

in terms of number of moles of cobalt per kilogram of PU foam, and the results are given in Table 4. It is evident from these results that the capacity of the foam decreased with an increase in the density. Further, the capacities of the PU foams which were in contact with the synthetic ILW were high, while those of the PU foams which were in contact with the decontamination waste were low. The reduction in the capacities was attributed to the presence of iron (200 mg/L). However, these capacities are so high in terms of radioactivity that it may never be possible to ex-

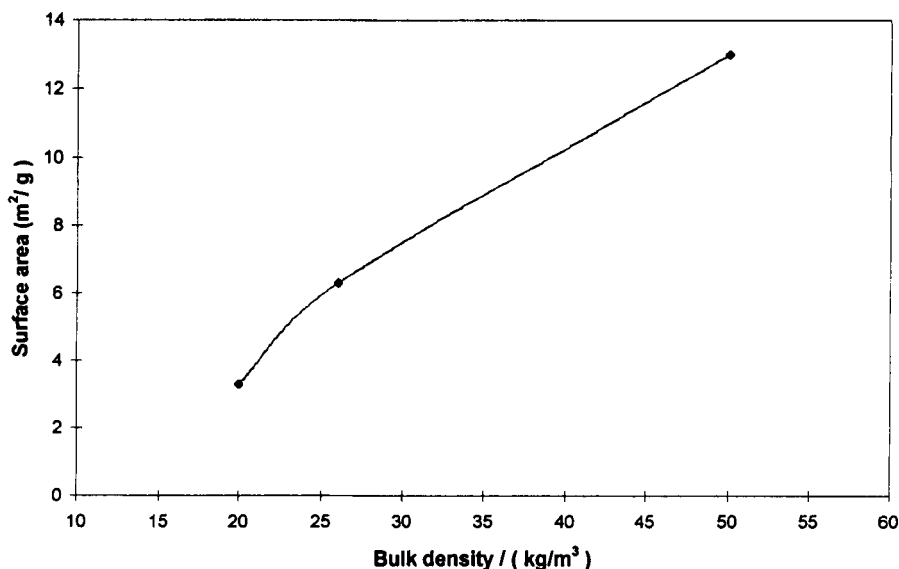


FIG. 5 Variation of surface area as a function of bulk density.

haust the PU foam in the column operation. It is quite likely that the radioactive field around the column may determine the time of disposal of the foam present in the column.

3.6. Studies on the Surface Area of PU Foam

The surface areas of polyurethane foams having different densities were estimated. Figure 5 shows the surface area versus the bulk density. The surface area of the foam increased with an increase in density. The results confirmed that the surface area of the foam plays no significant role in the extraction of cobalt. Hamon et al. (15), observed that the sorption of cobalt thiocyanate by foam involves the entire bulk of the polyurethane polymer rather than only the surface area of the PU foam.

3.7. Infrared Spectral Studies

The IR spectra of *N*-methyl formamide, *N,N*-dimethylurea, which might mimic *N*-containing groups in the PU foam, have been studied to verify the role of —NH group in the extraction of cobalt thiocyanate (15). The authors observed that there was no participation of the —NH group of PU foam in the extraction of cobalt thiocyanate. In our studies the neat PU foam and ammonium cobalt thiocyanate-loaded PU foam were taken directly, and the FT-IR spectra were recorded. Figure 6 shows the infrared spectra of PU foam and $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$ -loaded PU foam. The IR spectra of PU foam shown in Fig. 6 is comparable with the reported spectra (19, 20). The band at 3270 cm^{-1} has been assigned to the pure $\nu(\text{N—H})$ stretching frequency. The peaks appeared at 1530, 1293, and 1221 cm^{-1} have been assigned to the combination peaks of $\delta(\text{N—H}) + \nu(\text{C=N})$ of PU foam. In the case of $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$ -loaded PU foam, these four bands appeared at 3258, 1527, 1291, and 1217 cm^{-1} . Since there is no significant shift in the frequencies of these bands, it is concluded that the —NH group of PU foam is not involved in bonding during the extraction of $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$.

To determine the nature of bonding of cobalt thiocyanate and PU foam, the IR spectrum of pure $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$ was recorded and it is given in Fig. 7. This spectrum was compared with that of $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$ -loaded PU foam. The bands appearing at 2042 and 820 cm^{-1} in the case of pure ammonium thiocyanate have been attributed to $\nu(\text{C=N})$ and $\nu(\text{C=S})$ respectively (21). In the IR spectrum of $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$ -loaded foam, these bands appear at 2042 and 804 cm^{-1} . Since there is no change in $\nu(\text{C=N})$ stretching, the nitrogen of NCS^- in $[\text{Co}(\text{NCS})_4]^{2-}$ does not participate in bonding with the PU foam skeleton. However, the negative shift observed in $\nu(\text{C=S})$ has been attributed to a weak interaction between the

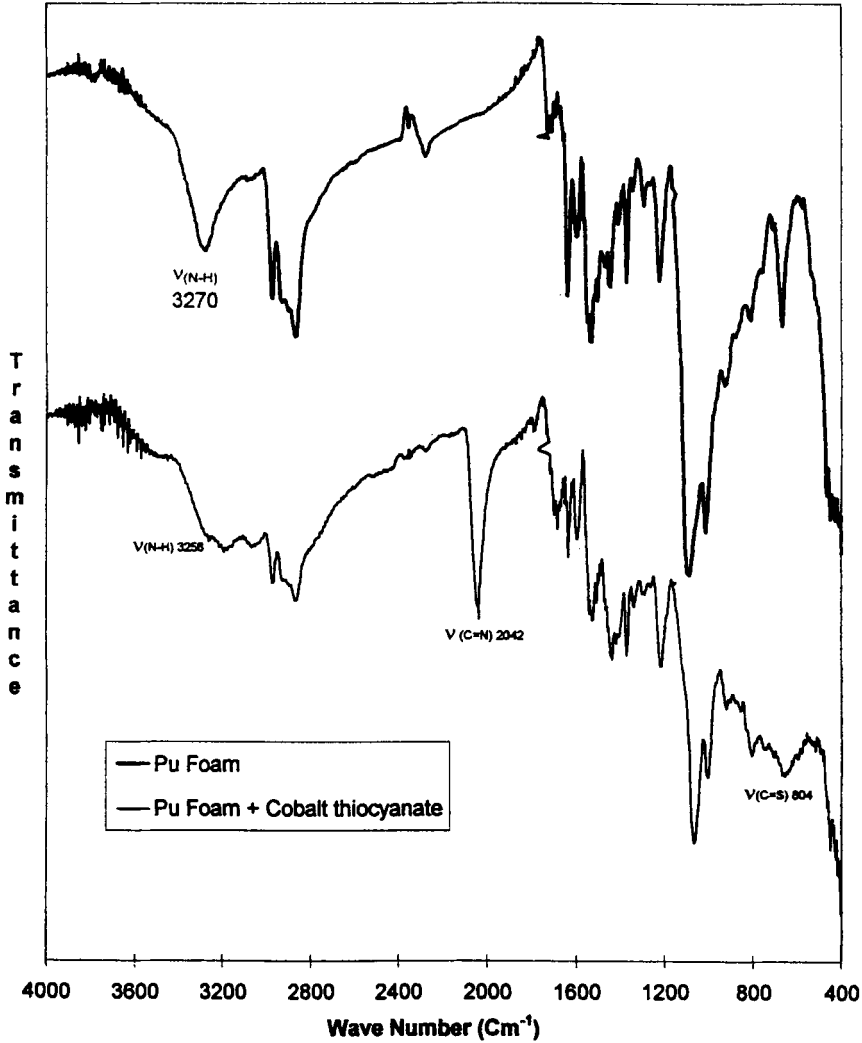


FIG. 6 IR Spectra of polyurethane foams.

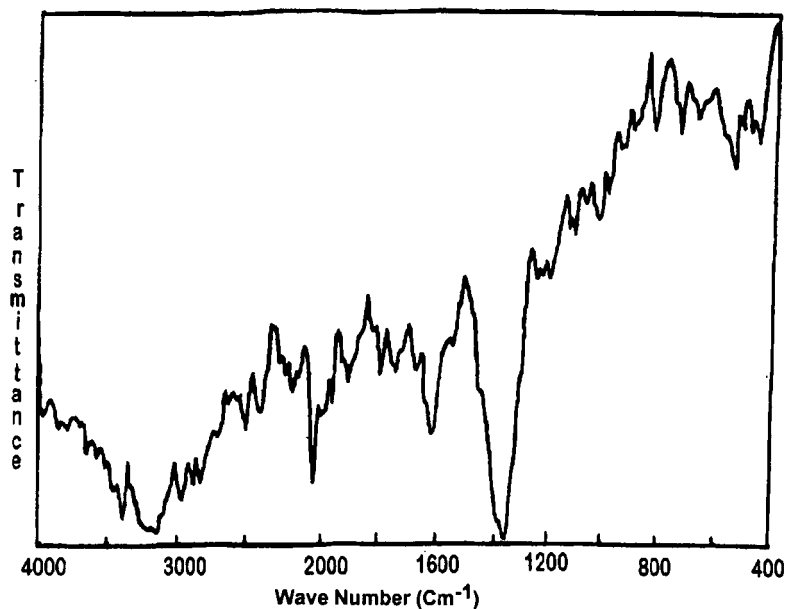


FIG. 7 IR spectrum of ammonium cobalt thiocyanate.

sulfur atom of thiocyanate and the hydrogen atoms present in the PU foam.

4. CONCLUSION

Efficient extraction of cobalt from the synthetic intermediate level as well as from decontamination wastes is possible by using PU foams. Low density PU foam (20 kg/m^3) facilitated better extraction of cobalt. From column studies of ILW a decontamination factor (DF) of 100 for ^{60}Co could be attained, and the results were consistent throughout the column operation. By using neat PU foam, separation of cobalt(II) from a solution containing iron(II) and EDTA is possible. The DF obtained in the case of decontamination waste was about 50, and almost all the iron(II) (nearly 100%) remained in the eluate. The surface area of the foam has no significant role in the removal of cobalt. These studies can be extended to the removal of cobalt from the decontamination wastes arising from boiling water and pressurized heavy water reactors (PHWRs). During the full system decontamination of PHWRs with in-situ regeneration, the foam-

based methodology may not be practicable because it involves the addition of thiocyanate. However, this methodology can very well be employed to provide off-line treatment for decontamination effluent.

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