Recovery and purification of 4.66 TBq (126 Ci) of ^{137}Cs from a 20-year-old spent sealed source

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ABSTRACT

An attempt to recover and purify 4.66 TBq (126 Ci) of ^{137}Cs as solution from a 20-year-old doubly encapsulated sealed source containing ^{137}CsCl was made successfully. The primary capsule was first cut open to retrieve the secondary capsule. The top end of the secondary SS capsule was then cut to render it as an open cylinder and the ^{137}CsCl pellet inside was dissolved in small aliquots of water. Each aliquot of the ^{137}CsCl solution was dispensed into glass vials, sealed, assayed and stored. Barium formed during the radioactive decay of ^{137}Cs was removed by carbonate precipitation. Chloride was removed by heating with HNO_3 and evaporation. About 91.8% of the total activity could be recovered and used subsequently for making brachytherapy sources.

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1. Introduction

Sealed radioactive sources of radioisotopes such as ^{241}Am, ^{137}Cs, ^{210}Po, ^{60}Co, and ^{192}Ir are extensively used for varied applications in medicine, industry, agriculture and diverse research fields [1–7] throughout the world. Each source is indispensable for enabling unique applications, where other means are not available. The sources vary widely in physical size, properties and their radioactivity level. Once their certified useful life is over, the sealed sources containing radioisotopes pose an inherent risk from liability, safety and security angles owing to the possibility of inadvertent or deliberate misuse of the radioactive materials. Hence, the security of such unused sealed sources is of concern, particularly due to the potential of using such sources for malevolent purposes such as radioactive dispersal device (RDD) or "dirty bomb" [8–10]. Post 11 September 2001, the concern about the deliberate dispersion of radioactive material to cause panic and chaos has further grown. It can be assumed that all radioactive sealed sources with nuclides such as ^{241}Am, ^{137}Cs, ^{210}Po, ^{60}Co, and ^{192}Ir can be used as a dirty bomb. But, ^{60}Co, ^{192}Ir, ^{241}Am and ^{210}Po generally exist as solid metals and would not be readily dispersible. Of the isotopes used in sealed sources, ^{137}Cs is probably the largest threat as it is often used primarily as a fine ^{137}CsCl powder which is easily dispersible

in aerosol form and is soluble in water. It is a hard gamma emitter, has a half-life of 30 years, with high radiological threat and once contaminated, its cleaning is extremely difficult. All other types of RDD pale in comparison to the ^{137}CsCl RDD. The safety of the disused ^{137}Cs sources is also a subject of concern as the accidental release of radioactivity from the sources could also result in widespread contamination and significant health concerns. Perhaps the best known case is the Goiania accident [11], in which the ^{137}Cs source was stolen from an abandoned hospital in the Brazilian city of Goiania and subsequently handled by several people. They suffered serious contamination, resulting in several deaths and injuries. The probability of such events is more with unused sources stored.

Sealed radiation sources are of concern from two angles. The safety aspect is addressed to minimize the probability of radiation exposure to personnel. On the other hand, the security of a source aims at preventing any unauthorized possession and malevolent actions with the source. The measures to render a sealed radioactive source safe as well as secure are generally taken by the manufacturers, laying stress on safety as the primary concern. In this context, unused ^{137}CsCl sources if tampered open could be a cause for security concern.

In view of the vulnerabilities and security risks of ^{137}CsCl sources, alternate chemical forms of ^{137}Cs or radioisotope or technologies for similar application have been considered. ^{60}Co source is replacing ^{137}Cs for many applications, despite the major disadvantages that twice the shielding thickness may be required for a source for achieving the same dose rate, and the half-life of ^{60}Co

being shorter, the useful lifetime of the source is significantly curtailed. But, owing to various logistical, operational and financial obstacles, an immediate or complete conversion to the use of ^{60}Co is still far away. As per the recent survey, most of the cesium units have been reliable and hence most of the users have no immediate plans to replace them. All sealed ^{137}Cs sources currently in use will eventually become disused but will be returned back to the source manufacturer. While future technologies may diminish the need for ^{137}Cs sources, the inventory of disused ^{137}Cs is likely to be increased in future at source manufacturer's end.

Our laboratory routinely fabricates and supplies ^{137}Cs sources in MBq (mCi) level for industrial gauging and brachytherapy applications [12]. To cater to the demands for such low activity ^{137}Cs sources, there is a constant requirement of ^{137}Cs activity in solution form. In the past, most of the sealed ^{137}Cs sources used in our country for various applications were procured from overseas suppliers and these contained ^{137}Cs in the form of ^{137}CsCl. Once their certified life is over, these unused radioactive sources were directly sent to our center for surveillance and management purpose. Owing to the liabilities involved in the storage of disused ^{137}CsCl source as a possible source for "dirty bombs" or "radiological dispersal device (RDD)", efforts are being made to transfer them to an engineered storage facility where it can be safely allowed to decay [13] with significant economic burden. Alternatively, they could be recycled and used in the preparation of industrial and medical sources of lower activities [14]. Taking into account the cost of storage (capital cost and annual operational cost) as well as the cost of fresh ^{137}CsCl, recycling of ^{137}CsCl was considered economically a better option for our institution where there is an active ^{137}Cs source preparation programme. The inherent value of these materials and the need to avoid storage make recycling economically attractive. Thus we opted to recycle ^{137}CsCl from the disused source rather than disposing it, as recycling reduces the security liabilities as well as financial burden of procuring fresh ^{137}CsCl. The decision of recycling disused ^{137}CsCl source has been taken by considering the risks and costs of the proposed intervention.

The practice of recycling ^{137}Cs from high activity sealed sources post-expiration is known to be followed by some manufactures [15]. However, no technical information is available in the literature or in the internet about the detailed method used by them because of the attached commercial interest. In view of this, it was felt necessary to develop an indigenous technology to recover ^{137}Cs from a disused source which could be used as a universal strategy. In the present work, an attempt was made to recover 4.66 TBq (126 Ci) of ^{137}Cs in the solution from a 20-year-old disused sealed source, having no further information regarding its composition or history. Our interest was to develop a technically feasible simple process to leach out ^{137}Cs from the source container. The overall extraction capability of the process depends on the solubility of the ^{137}CsCl, accessibility of the solvent to the ^{137}CsCl in the capsule and the efficiency of removing the solution. Barium arising from the decay ^{137}Cs was separated from the solution by chemical precipitation methods. Since some loss of the ^{137}Cs is expected due to its adhering to the capsule and recovery losses, recovering to the extent of >90% is considered a successful campaign.

In this report, we have demonstrated a simple, facile, fast, and effective method to recover and purify the ^{137}CsCl from a sealed source. The primary purpose of this communication is to describe an experience of recovering and purifying ^{137}CsCl from an unused sealed radiation source.

2. Materials and methods

Radioactivity was measured by gamma spectrometry using a HPGe Multichannel analyzer, Eurysis Measure coaxial photon detector system, France, with 0.5 KeV resolution and range from 1.8 KeV to 2 MeV. A 0.6 cc Farmer 2517 precalibrated ion chamber coupled to 2670 Farmer electrometer was used to measure the ^{137}Cs activity. A UV-1601 UV–vis spectrophotometer (Rigaku, Japan) was used for measuring the optical density. The ion chamber was placed inside the hot cell and was controlled from outside the cell. A clamping device was used to hold the capsule firmly. A tube cutter was used to cut the capsule with the help of the manipulator. A remote handling glass vial sealing machine developed indigenously in our division was used for sealing the vials. A digital area monitoring system was installed in the working area to facilitate monitoring of radiation level of surroundings. Inductively coupled plasma/mass spectrometer Model VG-PQ Excel (VG Elemental, Winsford, UK) with TJA solutions software was used for the determination of concentration of Cs and Ba. Chloride concentrations in the recovered product was spectrophotometrically estimated using the mercury thiocyanate–iron method [16]. The concentrations of ammonia was determined by colorimetric method from the purple color formed with a pyridine pyrazolone reagent [17].

2.1. Clamping device

The clamping tool consists of a chuck which can have two positions, namely gripping position and release position. A spindle attached to the chuck enables positioning the chuck either in gripping or in release position. During gripping position, the jaws of the chuck contract and hold the capsule firmly. In release position, the jaws open and the capsule is released. The spindle can be manipulated with the help of MSM (master slave manipulator Model-8 of CRL, USA). This unit enables one to remotely remove and place the radioactive capsule.

2.2. Recovery and dissolution of the ^{137}Cs pellet

Fig. 1 represents the schematic view of the stainless steel (SS) capsule. Total activity inside the capsule was measured remotely inside the hot cell prior to cutting. The SS capsule admeasuring approximately 7.5 cm (l) × 1.8 cm (ϕ) containing 4.66 TBq (126 Ci) of ^{137}Cs was fixed firmly on a chuck of the clamping device. The capsule was cut by placing the cutting tool near the top end of the radioactive capsule and rotating the tool with the arm of the manipulator until no resistance was felt. With the application of pressure to either side of the cut, it snapped apart. The secondary container was also subsequently cut employing the same procedure. The top lid of the secondary container along with the spacer
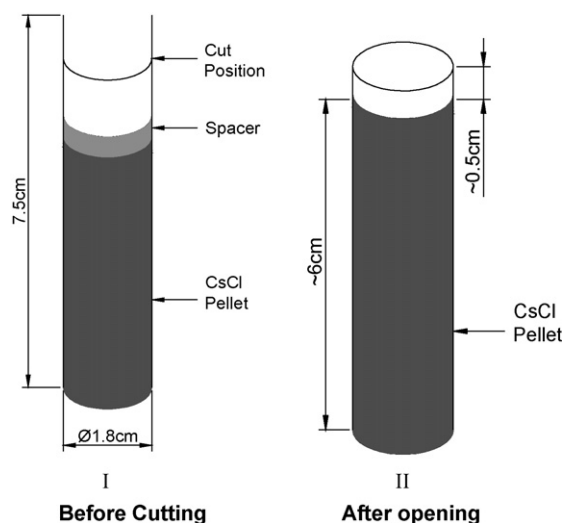

Fig. 1. Schematic view of the SS Capsule.

was removed carefully and kept separately for disposal as waste. The inner open capsule was placed inside a 50-mL beaker enclosed in another 100-mL beaker for safety purpose. The whole assembly was fixed on a laboratory clamping device. Approximately 20 mL of deionised water was added in 1 mL lots using a semi-automatic micro pipette with the help of the manipulator arms. At the end of each addition of deionised water, the resulting ^{137}Cs solution was dispensed in 1 mL aliquots into 10-mL capacity annealed USP glass vials using the semi-automatic micro pipette. The glass vials were then covered with rubber bungs followed by an aluminum cap and an automatic aluminum seal crimping machine. The activity in the vials was assayed and the vials were stored individually in 75-mm thick lead pots. The total ^{137}Cs activity recovered was estimated.

2.3. Experimental set-up for the removal of Ba^{2+} and Cl^-

Fig. 2 represents the schematic view of the experimental arrangement set-up carried out inside a containment box of 100 mm thick lead shielded facility for the removal of Ba^{2+} and Cl^- ions and recovery of ^{137}Cs. A 500-mL capacity three necked round bottom flask was kept in a heating mantle. $^{137}CsCl$ solution recovered from the sealed source was transferred from the glass vial to the separating funnel containing a sintered disc at the bottom keeping the stop cock at closed position. An additional funnel fitted with a stop cock at the bottom was connected to the round bottom flask for transferring the reagents into the reaction mixture. The top of this flask was connected to a series of traps containing solid as well as liquid trap materials via glass tubes to absorb ^{137}Cs vapors liberated during the recovery process. In order to absorb the liberated gas along with ^{137}Cs vapor in the trap solution, the whole set-up was maintained under negative pressure using a vacuum line available inside the processing facility

2.3.1. Effect of pH on the precipitation of $BaCO_3$

Since the disused ^{137}Cs source is very old, it was estimated that appreciable quantities of ^{137}Ba would have accumulated due to the decay of ^{137}Cs. This barium has to be removed, as otherwise it would interfere with the vitrification of ^{137}Cs. It was decided to precipitate Ba^{2+} as $BaCO_3$ using non radioactive carrier. Before handling the active ^{137}Cs solution, preliminary experiments to optimize the precipitation step were carried out as follows:

216 mg of barium chloride (115 mg of Ba^{2+}) and 508 mg of CsCl (400 mg of Cs^+ equivalent to 10 Ci of ^{137}Cs) were boiled with 20 mL

of distilled water in a 50-mL capacity beaker and spiked with ~370 kBq (10 μCi) each of ^{134}Cs and ^{133}Ba. 1 mL of solution was pipetted out and kept as reference. 10 mL of saturated solution $(NH_4)_2CO_3$ was added to the reaction beaker and the pH of the resulting solution was adjusted to desired value by drop wise addition of concentrated NH_4OH. The chemical yield of $BaCO_3$ was studied at pH 8–11. All the experiments were carried out in duplicate. The insoluble solid was filtered off using a Whatman 542 filter paper. After the reaction, the resulting ^{137}Cs solution was separated as the filtrate from the insoluble barium carbonate precipitate, by filtration. 1 mL of filtrate was pipetted out. Radioactivity content in small aliquots (100 μL) of both the reference and filtrate were measured in an HPGe detector coupled to a multichannel analyzer, to determine the amount of ^{133}Ba from its principal photo peak. The total activity of ^{133}Ba in the initial solution and in the filtrate was estimated by correcting for the total volumes, which were 20 mL in the case of initial solution and 30 mL in the filtrate. The activity in the precipitate was calculated as the difference in the total ^{133}Ba activity in reference solution and the ^{133}Ba activity in the filtrate. The ratio of the count rates in the precipitate to that of reference solution was calculated as the recovery of Ba^{2+} as precipitate. The optimal pH for maximum recovery was estimated.

2.3.2. Separation of barium and removal of chloride ions

The aged ^{137}Cs source contains significant amount of barium arising from radioactive decay. About 370 GBq (10 Ci) of $^{137}CsCl$ containing about ~115 mg of barium was warmed to 50 °C to get a clear solution. A few drops of 2 M HCl was added to dissolve $Ba(OH)_2$ formed. The radioactive solution was transferred to the separating funnel containing sintered disc at the bottom. The stop cock was closed to retain the solution in the funnel. The radioactive solution was treated with 10 mL of saturated solution $(NH_4)_2CO_3$. Concentrated NH_4OH solution was added drop wise till the pH of the solution reached 11–12. Under this condition, Ba^{2+} precipitates and settles at the bottom of the funnel over the sintered glass disc. The $BaCO_3$ precipitate was filtered by opening the stop cock and applying vacuum to the round bottom flask. To the filtrate collected in the round bottom flask, 5 mL of concentrated HNO_3 was added through the side funnel and heated to remove excess of NH_4^+ and CO_3^{-2}. Following the acid treatment period of 1–2 h, the solution was taken to incipient dryness until complete evaporation of nitric acid was achieved. The reaction was carried out under controlled heating conditions to minimize ^{137}Cs vapor loss. Addition of concentrated HNO_3 was repeated twice to expel Cl^- ions completely
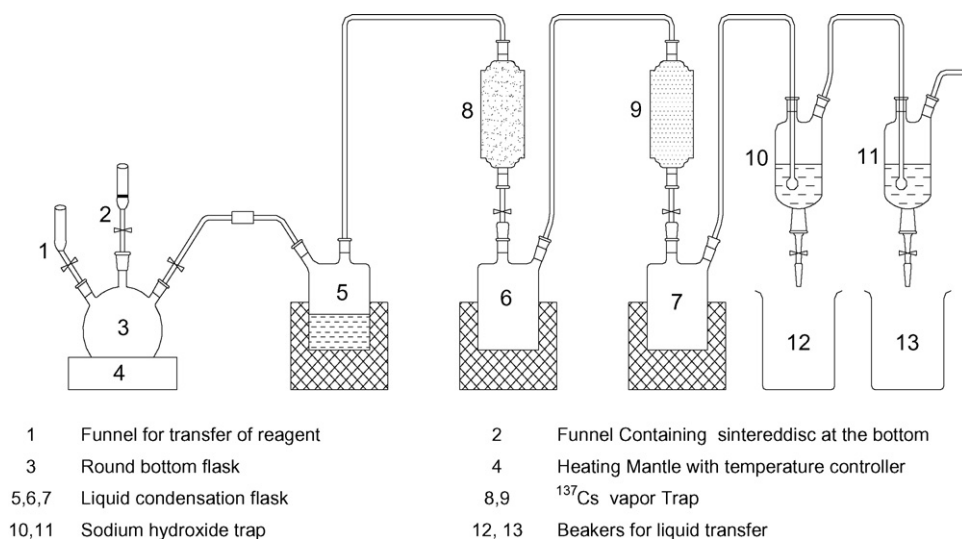

1	Funnel for transfer of reagent	2	Funnel Containing sintereddisc at the bottom
3	Round bottom flask	4	Heating Mantle with temperature controller
5,6,7	Liquid condensation flask	8,9	^{137}Cs vapor Trap
10,11	Sodium hydroxide trap	12, 13	Beakers for liquid transfer

Fig. 2. Experimental set-up for the removal of Ba^{2+} and Cl^-.

and also to convert $^{137}CsCl$ to $^{137}CsNO_3$. Finally the radioactive concentration of the product was adjusted to $\approx 37\,GBq(1\,Ci)/mL$ with $2\,M\,HNO_3$.

2.4. Radiological safety

The immediate vicinity of the hot cell area was lined with polyethylene sheets to contain possible contamination. A check list of all possible materials and supplies anticipated were prepared and made available prior to the actual operation. A designated and labeled foot operated waste bin was kept near the hot cell area to contain all ^{137}Cs contaminated materials. Radioactive waste materials were segregated, collected and properly labeled for waste management. After the completion of the job, the entire hot cell area as well as the master slave manipulator was decontaminated by washing manually with the help of cotton to minimize the contamination spreading during subsequent operations.

Proper radioactive procedures were adopted during the whole process. The entire process of ^{137}Cs recovery starting from the transfer of radioactive source from the lead storage container to the clamping device and then transformation of $^{137}CsCl$ into solution form were carried out inside a 1 m thick high density concrete shielded hot cell equipped with master slave manipulators. Removal of Ba^{2+} from the aged ^{137}Cs solution and subsequent conversion into nitrate was carried out in 370 GBq(10 Ci) batches in a 100 mm thick lead shielded facility.

During the entire operation, no work which was not anticipated and planned, involving radioactive materials was conducted. The ALARA principle was observed with regard to the radiation exposure of the operating staff. Continuous and systematic monitoring and control of radioactive contamination were carried out.

3. Results and discussion

The goal of the present study was to recover and purify ^{137}Cs from a sealed disused source. Retrieval of ^{137}Cs from the sealed sources beyond their certified life is one of the options to minimize waste disposal problem. The $^{137}CsCl$ pellet was doubly encapsulated in stainless steel (SS) capsules. Although $^{137}CsCl$ pellet remains intact, the integrity of the welded SS capsule deteriorates because of normal wear and tear. In order to avoid accidents that can arise from improper storage, it was felt necessary to recover the ^{137}Cs and reuse them.

The work was planned to achieve our goal with maximum safety. The dose rates on the surface and at 1 m away from source were determined and recorded to select the shielded facility to be used. In addition to the dose rates, the activity content of the source was also determined using a precalibrated ion chamber. Then, the possibility of removable contamination on the surface of source container was checked to avoid the contamination of hot cell and associated gadgets. Physical properties (weight, dimensions) of the source were assessed remotely.

An action plan identifying all operations to be carried out was drawn. Cold runs were carried out twice, involving all aspects of the cutting process using ordinary SS capsules containing ∼4 g of CsCl to simulate the proposed cesium recovery system. Remote handling tools were used as far as practicable to reduce the dose expenditure. In particular, attention was given to the operation of all the equipment involved. All the procedures were documented as a GMP measure and for retrospective analysis of the safety measures. On gaining confidence, actual sample was handled.

Since ^{137}Cs source fabrication and encapsulation data are of proprietary nature, no information was available regarding the internal morphology of the source. In the absence of actual data, it was assumed that cesium would be doubly encapsulated with config-

uration of a capsule placed inside another. The standard loading sequence of the inner source capsule consists of a $^{137}CsCl$ pellet and a spacer vertically along the length. The top and bottom end of the source were ascertained by visual inspection of the capsule. The end where welding marks were observed was considered as the top portion of the capsule. The bottom end of the radioactive capsule was placed into the clamping device designed to hold the capsule firmly.

It was decided to open only the top end of the capsule so as to make an open cylinder, and it was also planned to carry out the dissolution of $^{137}CsCl$ in situ at room temperature to avoid spreading of contamination. Such an approach was possible owing to the convenient amenable design of the capsule. The mechanical stability and chemical compatibility characteristics of SS capsule were particularly attractive features for implementation of this methodology. It was not only possible to prevent unwanted interaction of in cell gadgets with the $^{137}CsCl$ pellet, but also to confine the activity.

We have used a tube cutter which is an inexpensive unit and allows clean, smooth, quick, and precise cut without the need of a lubricant or cutting fluid. In all, two cuts were required to expose $^{137}CsCl$ pellet for its recovery. After the cutting of inner capsule, the $^{137}CsCl$ pellet was visually inspected and was found to be grayish instead of white in color. The free space inside the capsule above $^{137}CsCl$ pellet was about 1 mL. A schematic diagram of the capsule is shown in Fig. 1.

Since the source was 20-years-old, considerable amount of stable ^{137}Ba would be present, produced from the decay of ^{137}Cs. Solubility of CsCl and $BaCl_2$ in water are 162 g/100 mL and 36 g/100 mL respectively. Therefore deionised water for the dissolution of pellet seemed to be a practicable and feasible approach for the dissolution of radioactive cesium. Boiling water was not necessary because the solutes were not bound strongly to the SS capsule. The use of acid in this process was precluded as it is likely to corrode the equipment and associated gadgets. Any heating procedure was avoided to prevent the contamination of the hot cell.

We chose to leach $^{137}CsCl$ along with other soluble constituents in the capsule by percolating deionised water. In order to achieve good recovery, multistage recovery was adapted with aliquots of deionised water.

Leaching out ^{137}Cs activity in small aliquots was considered to be more effective when compared with complete dissolution of CsCl pellet. After transferring the capsule inside the beaker, deionised water was added in 1 mL lots to dissolve the $^{137}CsCl$. After the addition of each aliquot, $^{137}Cs^+$ along with its decay products dissolved to form a saturated solution governed by the solubility of $^{137}CsCl$. The aliquot containing saturated solution of $^{137}CsCl$ was removed from the mixture each time followed by addition of fresh aliquot of deionised water. Complete dissolution of the solid $^{137}CsCl$ and hence complete retrieval of ^{137}Cs from the capsule could be achieved by the repeated procedure of dissolution and removal of the saturate solution of $^{137}CsCl$.

After each addition of water, small amount of white solid crept out due to brisk effervescence despite the fact that the dissolution of CsCl is an endothermic process. Some white turbidity was observed in the final solution which might be due to the presence of $Ba(OH)_2$ which has very low solubility in water. The fractional recovery in this process was estimated to be 97.84% as detailed below. During the entire process, no air-born activity inside the cell was observed. This method involves no acidic solvent, no separation funnels, no boiling and no filtration procedures.

Fig. 3 is a graphical representation of the recovered ^{137}Cs in different fractions. Recovery of ^{137}Cs in the initial steps was less. This was perhaps because of the limited solubility of $^{137}CsCl$ pellet in water and also due to limited contact surface between the water and the dry pellet. As dissolution progressed, water percolated deeper
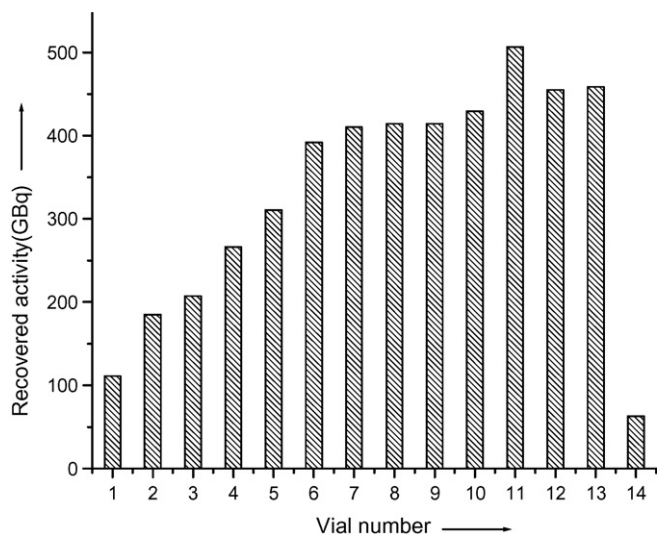
Fig. 3. Recoveries of ^{137}Cs in different fraction.

into the sample, facilitating dissolution of ^{137}CsCl from areas that could not be reached initially.

It was observed that more than 97% of activity could be recovered. Table 1 depicts the distribution of recovered and unrecovered ^{137}Cs activity. It was seen that the inner capsule along with its lid retained a substantial proportion of activity. As the inner capsule contains a spacer which was in intimate contact with the ^{137}CsCl capsule, some amount of activity was irreversibly transferred to the spacer that was difficult to leach as the chemical history of the spacer was unknown.

The process adapted has several advantages. For instance, it works at room temperature, uses non corrosive leaching solution (deionised water), avoids the use of complicated and expensive equipment, and the amount of ^{137}Cs extracted per step can be easily controlled. Further, this process could be carried out within a day and was feasible using remote accessories.

Decontamination of the hot cell after this operation was necessary as the hot cell was to be used for the fabrication/preparation of radiation sources of other isotopes such as ^{192}Ir and ^{60}Co. In order to prevent the cross contamination of ^{137}Cs and to reduce the man rem expenditure, decontamination of the hot cell after this operation was necessary. However, if the hot cell was to be used for the recovery of ^{137}Cs in a continuous basis, such labor intensive decontamination operation after each batch is not required.

^{137}Cs undergoes β^- decay to form stable ^{137}Ba (directly-6.5% and indirectly via ^{137m}Ba-93.5%). The ^{137m}Ba changes into stable ^{137}Ba with a half-life of 2.55 min. Considering radioactive transmutation of ^{137}Cs, in the absence of oxygen, ^{137}CsCl would become BaCl$_2$ and Ba metal over long time [22]. Assuming the specific activity of ^{137}Cs to be 3202.72 GBq/g (86.56 Ci/g), a 7.4 TBq (200 Ci) ^{137}Cs corresponds to 2.31 g of Cs. After 20 years decay, the activity of ^{137}Cs would be 4.662 TBq (126 Ci). A 0.37 TBq (10 Ci) ^{137}Cs batch typically contain 183.3 mg of ^{137}Ba.

Table 1
Distribution of ^{137}Cs activity after leaching.

Material	Activity	Percentage (%)
Outer capsule + lid	0.2 (0.1) GBq (Ci)	0.0042
Inner capsule + lid	69.6 (1.9) GBq (Ci)	1.5
Beaker used for dissolution	10.4 (0.3) GBq (Ci)	0.22
Vial used for pipetting out water	22.2 (0.6) GBq (Ci)	0.47
Cutter used for cutting	0.2 (0.1) GBq (Ci)	0.0042
Total activity recovered as solution	4.55 (122.74) TBq (Ci)	97.8
Total ^{137}Cs activity	4.65 (125.74) TBq (Ci)	99.998

A procedure for vitrification of ^{137}Cs in borosilicate glass matrix developed in our laboratory, has been suitable for the preparation of brachytherapy sources [18]. The products exhibit good chemical durability; low leach rate, uniform distribution of ^{137}Cs and the formation temperatures are amenable for adaptation in laboratory. It was, however, found that the presence of barium in the ^{137}Cs feed, in greater than 4 mg/Ci not only increases the melting temperature of cesium borosilicate glass but also enhances viscosity of the glass, which in turn restricts the flow of the molten glass. Additionally, presence of Ba in the feed at such concentrations also leads to the formation of a separate phase with high leachability of ^{137}Cs, low chemical durability and non homogeneous distribution of ^{137}Cs. Therefore, it was essential to develop a simple, easy-to-operate, singly effective manageable method to separate the ^{137}Ba from ^{137}Cs below the acceptable level.

Thus, the amount of Ba tolerable in 37 GBq (1 Ci) of ^{137}Cs for vitrification into borosilicate glass is 4 mg and correspondingly the radiochemical purity acceptance criterion is >90.0% ^{137}Cs and <10% ^{137}Ba. Among the different techniques such as precipitation, solvent extraction and ion exchange for separation of ^{137}Ba from ^{137}Cs solution to the desired levels, we found precipitation method to be the most attractive. It is rapid, simple, inexpensive and capable of providing ^{137}Cs with acceptable purity and yield for our application. Although ion exchange would yield very pure ^{137}Cs, it is a time-consuming process, besides generating large amounts of liquid waste. Solvent extraction on the other hand, is tedious, less adaptable for remote operation for a small batch size and requires handling of inflammable solvents. Both ion-exchange and solvent extraction could have resulted in an undesirable increase in the total volume of ^{137}Cs solution after the separation of barium. This would necessitate an additional step of concentration. Owing to such disadvantages, these methods were not considered. The major advantage of precipitation method is its simplicity, being a single step operation and compatibility for remote operation.

The success of any precipitation process depends chiefly on the solubility of the products. Clearly, if high decontamination factors (DF), are sought, the formation of compounds with very low solubility must be favored. In aqueous media containing only a few ionic species, it is often possible to predict from solubility tables, which combination of ions will result in the formation of a stable insoluble compound.

Table 2 summarizes the solubility product of the various insoluble precipitates of barium in water [19] along with the solubility of the analogous Cs compounds in water [20–21]. It was observed that all the analogous compounds of Cs except iodate are soluble in water having high solubility. Separation of Ba^{2+} from Cs$^+$ can be possible using chromate, sulfate, carbonate, fluoride and hydroxide ions. Thus, any one of the precipitate could be selected for separating Ba ions from Cs$^+$.

Although the solubility of barium sulphate and barium chromate are less compare to others, they require an additional tedious manipulation step for the removal of the excess precipitating agent (CrO$_4^{2-}$, SO$_4^{2-}$) as they are likely to interfere in the subsequent vitrification process for making brachytherapy source. Hydroxide and carbonate precipitation are best suited for our purpose. Although metal hydroxide precipitation methods has the potential to remove Ba(OH)$_2$ from the alkaline solution to provide ^{137}Cs product, the efficiency of this method is less compared to carbonate precipitation method because of the higher solubility product of Ba(OH)$_2$ as compared to BaCO$_3$. Owing to the extremely low solubility of BaCO$_3$, high decontamination factors could be achieved. It is important that precipitate is easily formed and readily filterable. Barium hydroxide precipitation is slow, inefficient and hence not adapted in this case. Additionally, barium hydroxide precipitate is gelatinous and difficult to filter, making the process tedious. BaCO$_3$ is a dense precipitate permitting easy separation by simple filtration. Thus, the

Table 2
Solubility of various salts of cesium and barium.

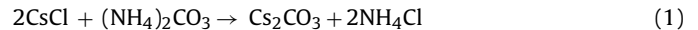| S.No	Chemical compound	Formula of Ba compound	Solubility product K_{sp}	Formula Cs compound	Solubility in water (g/100 g of water)
1	Chromate	$BaCrO_4$	1.17×10^{-10}	Cs_2CrO_4	71.4
2	Sulfate	$BaSO_4$	1.08×10^{-10}	Cs_2SO_4	179
3	Carbonate	$BaCO_3$	2.5×10^{-9}	Cs_2CO_3	260
4	Iodate	$Ba(IO_3)_2$	4.1×10^{-9}	$CsIO_3$	2.6
5	Fluoride	BaF_2	1.84×10^{-7}	CsF	322
6	Hydroxide	$Ba(OH)_2 8H_2O$	2.55×10^{-4}	$CsOH$	860
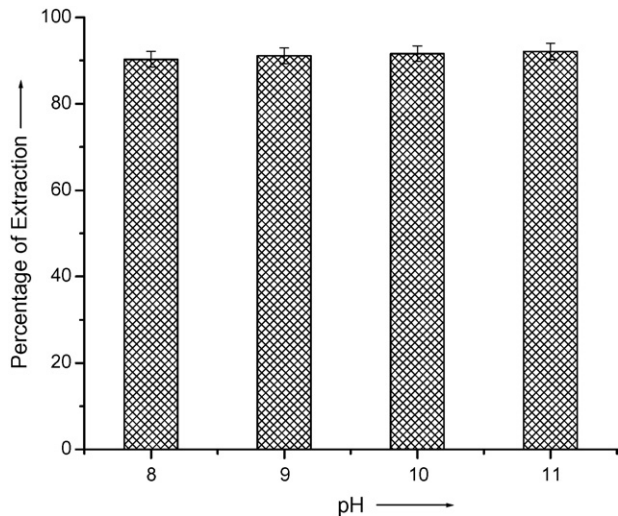
Fig. 4. Effect of pH on the $BaCO_3$ precipitation.

reason for preferential precipitation of $BaCO_3$ are based on the high degree of Ba^{2+} removal efficiency, the insoluble nature of carbonate precipitates, favorable filtering characteristics and the stability of the $BaCO_3$ formed.

Use of Na_2CO_3 was to be avoided as the presence of Na^+ ion in the ^{137}Cs feed will interfere in the glass formation. Precipitation of barium was preferentially carried out using $(NH_4)_2CO_3$ because excess of this reagent can be decomposed merely by heating with acid into ammonia and carbon dioxide which escape without leaving any residue. However, since its solubility in water is limited, a saturated solution of $(NH_4)_2CO_3$ was used. But, at saturation, it is of sufficiently high molarity that it causes the precipitation of most Ba^{2+}. Further, the other advantages are that (1) it does not have a large heat of solution, allowing heat generated to be easily dissipated; (2) its saturated solution (4.04 M at 20 °C) has a density (1.235 g/cm³) that does not interfere with the sedimentation of precipitated $BaCO_3$ by filtration; (3) the alkaline pH required for the carbonate precipitation is provided by the reagent itself.

The pH dependence of the $BaCO_3$ precipitation over a pH range 8–11 is presented in Fig. 4. It was found that there is marginal increase in percentage of recovery with increasing pH. This could be ascribed as due to the decrease in solubility of $BaCO_3$ with concomi-

tant increasing of pH. The optimum pH for $BaCO_3$ precipitation was in the range of 10–11. Therefore carbonate precipitation was carried out at pH range 10–11 to remove barium as per the equation shown below:

$$2CsCl + (NH_4)_2CO_3 \rightarrow Cs_2CO_3 + 2NH_4Cl \tag{1}$$

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow BaCO_3\downarrow + 2NH_4Cl \tag{2}$$
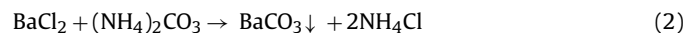
Owing to the very high solubility of Cs_2CO_3, the possibility of ^{137}Cs Coprecipitation as carbonate is remote. Experimentally it was observed that 97–98% of ^{137}Cs could be filtered out from the $BaCO_3$ precipitate as seen from Table 3. The precipitate consists of barium carbonate with a little ^{137}Cs adsorbed on it. The loss of ^{137}Cs at this stage may be due to the adsorption of Cs^+ ions in solution onto the freshly prepared precipitates and onto the wall of the sintered filter disc. These losses have been indicated in Table 4.

The next stage involves the chemical treatment of the filtrate with HNO_3 to convert the Cs_2CO_3 to $CsNO_3$ and subsequent evaporation to remove the other reaction products formed during precipitation reaction as well as the excess of HNO_3.

The ^{137}Cs remains dissolved in the solution from which the barium was removed. For the removal of chloride, the filtrate was treated with concentrated nitric acid at near boiling temperature. Conversion of Cs_2CO_3 to $CsNO_3$ takes place as per the reaction shown below:

$$Cs_2CO_3 + 2HNO_3 \rightarrow 2CsNO_3 + CO_2\uparrow + H_2O \tag{3}$$
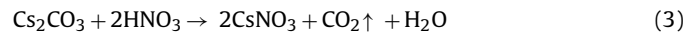
Ammonium chloride formed during the precipitation reaction decomposes to ammonia (NH_3) and HCl. Ammonia (NH_3) gas escapes from the reaction mixture and gets collected in the trap.

$$NH_4Cl \rightarrow NH_3\uparrow + HCl\uparrow \tag{4}$$

Part of the HCl gets liberated as gas, while some parts remains in the solution. The HCl that remains in the reaction mixture gets destroyed on reaction with HNO_3 as shown below.

$$HNO_3 + 3HCl \xrightarrow{\Delta} NOCl\uparrow + Cl_2\uparrow + 2H_2O \tag{5}$$
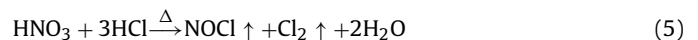
The liberated NOCl and Cl_2 gas escape and get collected in the trap. The excess of ammonium carbonate used in the precipitation reaction reacts with nitric acid to generate carbon dioxide with formation of ammonium nitrate.

$$2HNO_3 + (NH_4)_2CO_3 \rightarrow 2NH_4NO_3 + CO_2\uparrow + H_2O \tag{6}$$
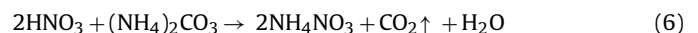
Table 3
Chemical recoveries of ^{137}Cs after Ba^{2+} and Cl^- removal step.

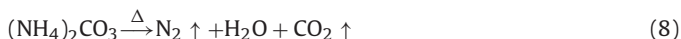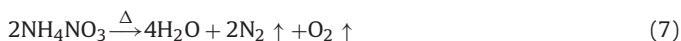| S.No	Amount of ^{137}Cs activity used GBq(Ci)	Amount of ^{137}Cs activity recovered GBq(Ci) after filtration	Amount of ^{137}Cs activity recovered GBq(Ci) after conversion	Amount of unrecovered ^{137}Cs activity GBq(Ci)	% Recovery
1	414.4 (11.2)	410.4 (11.08)	390.7 (10.6)	19.7 (0.5)	94.3
2	414.4 (11.2)	406.12 (10.97)	400.3 (10.8)	5.82 (0.2)	96.6
3	466.2 (12.6)	447.56 (12.09)	438.8 (11.9)	8.76 (0.2)	94.4
4	414.4 (11.2)	406.12 (10.97)	393.3 (10.7)	12.82 (0.3)	94.9
5	510.6 (13.8)	505.5 (13.66)	477.7 (13.0)	27.8 (0.7)	93.5
6	495.8 (13.4)	485.9 (13.13)	465.5 (12.6)	20.4 (0.5)	93.9
7	414.4 (11.2)	406.2 (10.97)	395.2 (10.7)	11 (0.3)	95.4

Table 4
Chemical purity needed versus the chemical purity obtained for 37GBq(1 Ci) of ^{137}Cs.

	Element	Acceptable amount for making borosilicate glass	Amount present in the separated product
1	Cesium (Cs^+)	≥ 36 mg	39–38 mg
2	Barium (Ba^{2+})	≤ 4000 μg	25–30 μg
3	Ammonium (NH_4^+)	≤ 300 ppm	10–15 ppm
5	Chloride (Cl^-)	≤ 100 ppm	8–10 ppm

Table 5
Accounting of ^{137}Cs activity during recovery process.

	Material	Activity TBq(Ci)	Percentage (%)
1.	Total amount of ^{137}Cs available in the disused source.	4.65 (125.74)	100
2.	Total amount of ^{137}Cs recovered after leaching	4.55 (122.74)	97.84
3.	Total amount of ^{137}Cs recovered after precipitation.	4.44 (119.91)	95.48
4.	Total amount of ^{137}Cs recovered after chemical conversion	4.27 (115.4)	91.82

The ^{137}CsNO$_3$ solution containing ammonium nitrate when heated gently, results in the decomposition of ammonium nitrate into water, nitrogen and oxygen while CsNO$_3$ remains in solution. Any excess $(NH_4)_2CO_3$ remaining also gets decomposed on heating, thus leaving only CsNO$_3$ in solution.

$$2NH_4NO_3 \xrightarrow{\Delta} 4H_2O + 2N_2 \uparrow + O_2 \uparrow \qquad (7)$$

$$(NH_4)_2CO_3 \xrightarrow{\Delta} N_2 \uparrow + H_2O + CO_2 \uparrow \qquad (8)$$

In order to expel the gases liberated during the nitric acid treatment, the reaction vessel was kept marginally at a negative pressure. These liberated vapors were capable of corroding the containment box of the hot cell and therefore trapped using suitable solutions as shown in Fig. 2.

The process of removal of barium and chloride ions in two separate steps using two different equipment increases processing time and reduces process yield. Hence an apparatus was designed (Fig. 2) to couple both the processes in the same set-up. Performing different processes like barium precipitation, its filtration, thermal decomposition followed by expulsion of excess precipitating agent and final conversion of the cesium to nitrate form in the same apparatus increased the yield and decreased processing time. This process did not generate any additional radioactive waste.

In order to carry out the purification of ^{137}Cs solution in a technically simple and most economical manner, we resorted to using glass apparatus. However, we do realize that a glass set-up could have limited useful life. We have carried out 10 batches of purification operation using the same apparatus and the equipment is still intact. After 20 operations, we plan to change the apparatus. We also expect that the glass apparatus would turn brown due to radiation damage. Chemical recoveries of ^{137}Cs after precipitation step and chemical conversion step in seven batches are shown in Table 3.

Although the carbonate precipitation method adapted is ideal for removing Ba from ^{137}Cs, a small fraction of Ba can readily go back into solution, despite BaCO$_3$ being sparingly soluble. But, since the recovered ^{137}CsCl was to be used for the preparation of ^{137}Cs sources by vitrification as borosilicate glass [12], presence of trace amounts of Ba, chloride or nitrate in the product does not affect the product quality.

The chemical purity of the recovered products is an important quality that we were interested in evaluating, before preparation of brachytherapy sources. Measurement of chemical impurities in the recovered ^{137}Cs is possible by using ICP-AES or ICP-MS; but this could not be performed owing to the difficulty in handling radioactive solution and non availability of dedicated equipment for testing radioactive samples in our institute. Consequently, the chemical purity of the radioactive product could not be ascertained. How-

ever, a few simulated studies under real conditions were carried out to evaluate the purity of the recovered product and to assess the usefulness of the process for practical purposes. The purity of the samples was evaluated by analytical techniques. Spectrophotometric methods were employed to evaluate the concentration of ammonium (NH_4^+) and chloride (Cl^-) ions in the samples. Inductively coupled mass spectrometry (ICP-MS) was used to the determine the concentration of cesium (Cs^+) and barium (Ba^{2+}) after appropriate dilution. The results are presented in the Table 4.

It can be seen that the recovery method employed here is able to give a product with no significant impurities of ammonium (NH_4^+) and chloride (Cl^-) ions. It is further observed that levels of Ba^{2+} present are far less than the acceptable limit. This allows us to speculate that the impurity level in the radioactive samples might be of similar range and would not pose any problem in the vitrification process for making the sources in the form of borosilicate glass, of the chosen composition.

The advantages of the precipitation and purification process we have followed are its technical simplicity, process robustness, use of simple and inexpensive process equipment, feasibility for small-scale production, possibility to carry out at moderate temperature, quick and easy filtration of the coarse BaCO$_3$ precipitates, and adaptability for remote handling operation. The mild experimental conditions of this process facilitate safe handling of large amount of radioactivity.

Table 5 depicts the accounting of ^{137}Cs activity during the entire recovery process. The over all efficiency of the process after purification was observed to be more than 91%. Based on this data, we conclude that the dissolution of ^{137}CsCl with cold water and purification using precipitation and chemical treatment, such as described above, was feasible and effective.

Following the procedure described above, 4.27 TBq(115.4 Ci) of ^{137}Cs were recovered for making brachytherapy sources. Using the above ^{137}Cs solution, about 1200 numbers of brachytherapy sources were fabricated and supplied for use in low dose rate (LDR) treatment of cervical cancers.

4. Conclusion

Recycling of disused ^{137}CsCl source is important. But this technology must be carried out using proper radioactive procedures. Experience is therefore invaluable to perform such a process. We have demonstrated a simple facile, fast and effective method to recover the ^{137}CsCl from a sealed source. The major advantages in our method are the use of simple technology, inexpensive materials and readily available equipment. Thus the present investigation shows the prospect to recover and purify radiocesium from disused sealed sources as a resource material. This technique may also be used to recover ^{137}Cs from other types of disused sources. This

practice would reduce the costs of disposing radioactive materials (sources), while at the same time minimize the radioactive waste.

Acknowledgements

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