

# Uptake of cesium and strontium by crystalline silicotitanates from radioactive wastes

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Received: 14 September 2010/Published online: 17 October 2010  
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**Abstract** Crystalline silicotitanate inorganic ion exchanger, with a sitinakite structure is candidate material for remediation of aqueous nuclear waste streams. The syntheses of crystalline silicotitanate (CST) and Nb-substituted crystalline silicotitanate (Nb-CST) were carried out under hydrothermal conditions and the products were characterized using techniques viz., XRD, SEM/EDS, DTA/TGA, surface area respectively. Batch experiments were carried out to study the kinetics of uptake of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ , to estimate the decontamination factor (DF) values and distribution coefficients ( $K_d$ ) for the above synthesized CST and Nb-CST samples from actual radioactive waste solutions. The DF values for uptake of Cs and Sr by Nb-CST after 24 h of equilibration was 355 and 136 whereas for CST it was found to be 40 and 176 respectively. The  $K_d$  values for uptake of Cs and Sr for Nb-CST after 24 h of equilibration was found to be 35,490 and 13,500 mL/g respectively whereas the  $K_d$  values for uptake of Cs and Sr for CST was found to be 4,025 and 17,525 mL/g respectively. The ion exchange capacity of Nb-CST towards  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  was estimated to be 11.8 and 3.2 meq/g respectively whereas the ion exchange capacity of CST towards  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  was estimated to be 14.6 and 4.4 meq/g respectively.

**Keywords** Crystalline silicotitanate · Distribution coefficient · Decontamination factor · Cesium · Strontium

## Introduction

The need for efficient and selective ion exchangers exists in the treatment of radioactive waste effluents. The inorganic ion-exchangers serve as useful materials compared to organic resins because of their high radiation, chemical and thermal stability as well as compatibility with immobilization matrices. Also the more uniform ion exchange sites achievable in crystalline inorganic materials can lead to remarkable selectivity [1]. The benefits from using highly selective inorganic exchangers are not only the significant reductions in the liquid waste volumes and radioactive discharges into the environment, but also considerable reductions in the costs of waste management and processes for disposal. The presence of  $^{137}\text{Cs}$  ( $t_{1/2} = 30.1$  years) and  $^{90}\text{Sr}$  ( $t_{1/2} = 28.5$  years) in the waste solution poses a lot of problem due to long half lives and high fission yields. Extensive literature is available on the treatment of radioactive wastes using inorganic ion-exchangers for the removal of the above radionuclides and a comparison of the inorganic ion exchangers for the removal of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  has been reported [2–6]. However the pH of the waste solution and the presence of high dissolved solids often is a limiting factor in the use of ion exchangers available today.

The titanosilicates are a new class of inorganic ion exchangers which have shown promise in the fine tuning of ion exchange properties. A large number of titanium silicates are known to exist among the minerals in nature. The pure crystalline silicotitanates (CST) and niobium substituted crystalline silicotitanates (Nb-CST) with a sitinakite topology have frame work structures that enclose tunnels or cavities which are highly selective to  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  respectively over a broad pH range and in the presence of  $\text{Na}^+$  [7]. The frame work of CST is made up of  $(\text{TiO}_4)$  cubane like clusters that are linked by  $\text{SiO}_4$  units which

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results in a 3D structure with tunnels along *c*-axis which are of an ideal size for selective exchange of Cs<sup>+</sup> and Sr<sup>2+</sup> thus making these exchangers one of the most promising materials for their removal. The origin of selectivity appears to arise from the higher coordination number of cesium and strontium due to various hydration sites in the tunnel. In addition to the above characteristics the radioactive ions trapped inorganic material can be directly immobilized to a ceramic waste form for final disposal [8–10].

We report here the synthesis, characterization and comparative ion-exchange behaviour of CST and Nb-CST for uptake of <sup>137</sup>Cs and <sup>90</sup>Sr from an actual radioactive waste solution from pretreatment tank (PTT) at Centralised Waste Management Facility (CWMF), Kalpakkam. The distribution coefficients (*K<sub>d</sub>*) which indicate the selectivity towards the uptake of Cs and Sr and the decontamination factors (DF) after 24 h of equilibration for the above-said ion exchangers were determined. Kinetics of the uptake of the above-said radionuclides from PTT sample was also investigated. The ion exchange capacity of both CST and Nb-CST towards the uptake <sup>137</sup>Cs and <sup>90</sup>Sr was also estimated.

## Experimental

### Synthesis of CST and Nb-CST

The hydrothermal synthesis of CST with composition (58.5 mmol Ti, 6 mmol Si, and 620 mmol Na) was carried out by addition of chemicals in the order as mentioned below [11]. A total of 6.66 mL of TiCl<sub>4</sub> was mixed with 25 mL of ultra pure water and 40 mL of 30% hydrogen peroxide and stirred vigorously. To the stirring mixture 40 mL of 10 M NaOH was added followed by 150 mL of ultra pure water and a solution of 6 mmol of SiO<sub>2</sub> in 1 M NaOH. Finally to the clear solution 0.12 mol of NaOH was added. The mixture was sealed in an autoclave and kept at 200 °C for 10 days. After cooling to room temperature the solid product was separated by filtration, washed with 1 M NaOH and ethanol and dried for 24 h at 60 °C at air.

In the case of hydrothermal synthesis of Nb-CST with composition (12 mmol Ti, 16 mmol Si, 4 mmol Nb and 165 mmol Na) 3.43 g of titanium isopropoxide, 3.33 g of tetraethylorthosilicate and 0.54 g Nb<sub>2</sub>O<sub>5</sub> were added to 50 mL aqueous NaOH (6.6 g) solution in an autoclave, stirred for half an hour and then placed in an oven for 200 °C for 3 days. The resulting product was collected by filtration. Since there is possibility of formation of a crystalline by-product with the major Nb-CST product formed the former was removed by a two-step process: first the filtered product was exposed to 1 M aqueous HCl wash for 3 h at room temperature to amorphize the by product

and secondly the resulting solid was then exposed to 1 M NaOH wash for 3 h at 40 °C to dissolve the resulting amorphous material. The chemicals and the reagents used were of analytical grade.

### Characterisation of CST and Nb-CST

Powder X-ray diffraction (XRD) pattern was collected on a STOE diffractometer using Cu K<sub>α</sub> radiation between 2θ = 5 and 90° at a step size of 0.1° and a step time of 5 s. Scanning electron microscope (SEM)/energy dispersive spectroscopy (EDS) data was collected on a Philips XL-30 system. Surface area of the ion exchangers were determined using Smartsorb 90/91 using single point measurement technique. The DTA/TGA experiments were performed on Rheometric STA 1500 DTA/TGA instrument. Samples 10–20 mg were heated in air.

### Ion exchange properties

All ion exchange experiments were performed using the actual radioactive waste solution from pretreatment tank at CWMF by the batch method. The characteristics of the waste are given in Table 1. The major cations in the waste solution were calcium, sodium and the anions were chloride and nitrate contributing to the total dissolved solids.

### Kinetic studies and determination of decontamination factor (DF)/distribution coefficients (*K<sub>d</sub>*)

About 1 g of the as-synthesised sample of CST/Nb-CST was equilibrated with 100 mL of the actual radioactive waste solution (initial activity of <sup>137</sup>Cs –204 Bq/mL and <sup>90</sup>Sr –37 Bq/mL) from pretreatment tank at CWMF at ambient temperature. Aliquots of the solution were taken at regular time intervals till 24 h viz., instantaneous, 0.5, 1, 1.5, 2, 2.5 and 24 h for estimation of radioactivity. The samples were centrifuged at 6,000 rpm and filtered. The radioactive cesium and strontium in the supernatant were estimated using gamma counter and Cerenkov radiation technique respectively.

The distribution coefficient (*K<sub>d</sub>*) was calculated using Eq. 1

$$K_d \text{ (mL/g)} = \frac{\text{Initial activity} - \text{Final activity}}{\text{Final activity}} \times \frac{V}{m} \quad (1)$$

**Table 1** Characteristics of pretreatment tank (PTT) waste

pH	9.0
TDS	1450 mg/L
<sup>137</sup> Cs	204 Bq/mL
<sup>90</sup> Sr	37 Bq/mL

Where  $V$  (in mL) is the volume of the solution and  $m$  (in g) is the mass of the ion exchanger respectively.

The percentage removal (%) was calculated using Eq. 2

$$\% \text{ Removal} = \frac{\text{Initial activity} - \text{Final activity}}{\text{Initial activity}} \times 100 \quad (2)$$

$$\text{Decontamination factor (DF)} = \frac{\text{Initial activity}}{\text{Final activity}} \quad (3)$$

#### Estimation of ion-exchange capacity

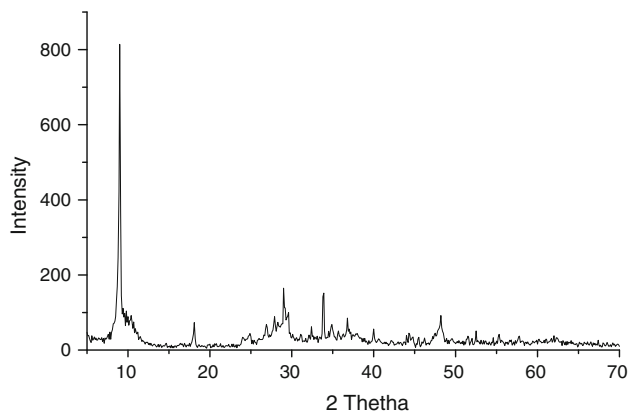
The ion exchange capacity of CST and Nb-CST towards the uptake of both cesium and strontium by each of them was determined by the method described below. In this experiment 1 g of the exchanger was equilibrated at ambient temperature with 100 mL of solution containing  $10^{-1}$  M of Cs and Sr ion spiked by  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  tracer. After 24 h of equilibration the radioactivity of the supernatant was measured as described above. From the initial and final activity the amount of cesium and strontium exchanged was calculated.

## Results and discussion

### Synthesis and characterisation

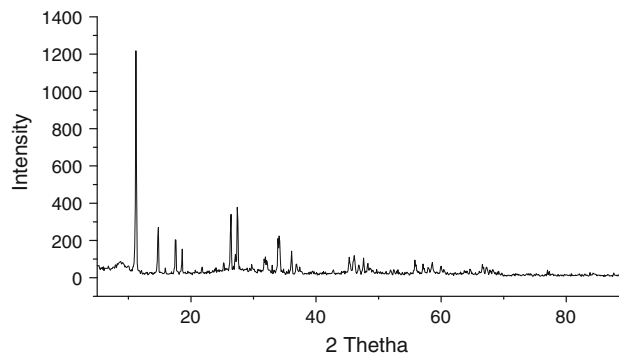
The CST synthesized was light brown in colour and the yield was around 6–8 g in each run. The Nb-CST was a white microcrystalline powder of yield around 2.0–2.3 g. The powder patterns in Figs. 1 and 2 depict primary X-ray diffraction line of CST and Nb-CST at  $2\theta = 9^\circ$  and at  $11.2^\circ$  respectively [12]. The typical surface area for the samples was in the range of 65–70  $\text{m}^2/\text{g}$  which is in conformity with the literature [9].

The SEM image of CST depicted in Fig. 3 exhibit large quantities of crystallites with cubic morphology of size 2.4–42  $\mu\text{m}^2$  comprised primarily of Ti, Na, O and with

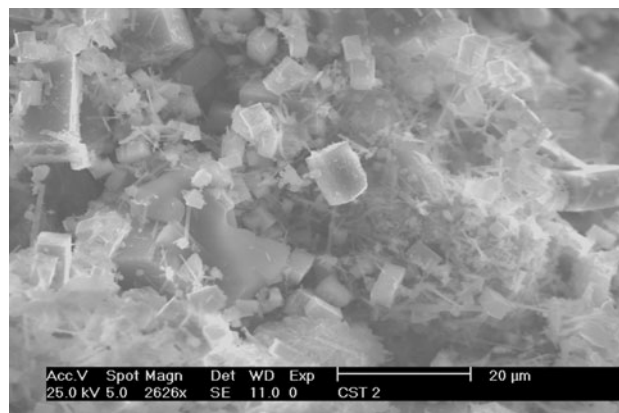


**Fig. 1** X-ray powder pattern of CST

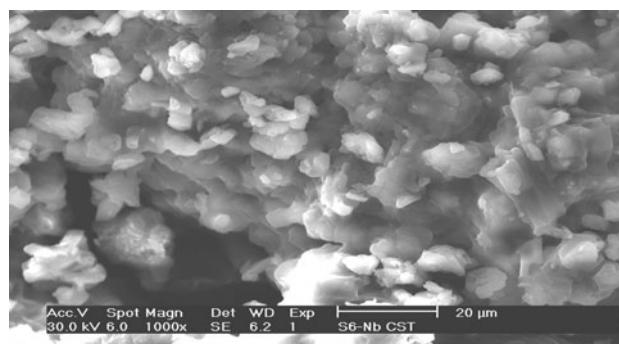
small amount of Si as revealed by an EDS analysis and rod shaped morphology of size 0.3–0.9  $\mu\text{m}^2$  comprised of primarily Ti, small amounts of Na, O and traces of Si as revealed by EDS analysis. The SEM image of Nb-CST depicted in Fig. 4 exhibit large quantities of crystallites with cubic morphology of size 2.9–18.1  $\mu\text{m}^2$  comprising of primarily Na and O and equal amounts of Ti and Nb and small amount of Si as revealed by an EDS analysis and small quantities of rod shaped crystallites of size 2.9–17  $\mu\text{m}^2$  comprising of primarily Na and O with small



**Fig. 2** X-ray powder pattern of Nb-CST



**Fig. 3** SEM image of CST



**Fig. 4** SEM image of Nb-CST

amounts of Ti and Nb with traces of Si as revealed by EDS analysis [9, 12].

From Fig. 5 which depicts the DTA/TGA curve for CST it can be observed that there is majority weight loss (~18wt%) by 150 °C with ~10% up to 1,000 °C. The endotherm centered 100 °C is accompanied by a weight loss in TGA and can be attributed to loss of water. The endotherm centered at 950 °C indicates a phase change as there is no weight loss in TGA. From Fig. 6 which depicts the DTA/TGA curve for Nb-CST there is majority weight loss (~17%) by 150 °C and ~11% up to 1000 °C. The

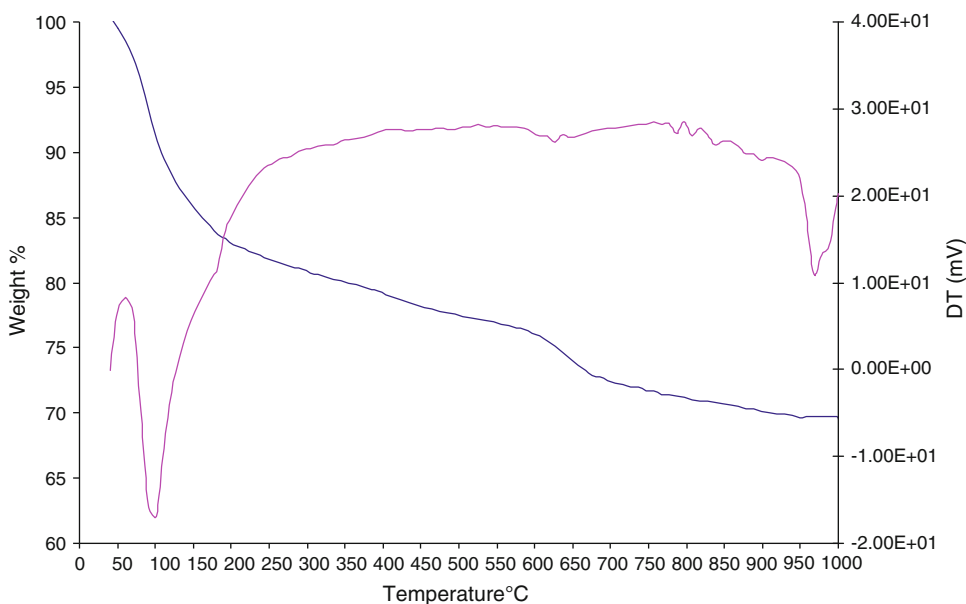
endotherm centered around 100 °C is accompanied by a weight loss in TGA and can be attributed to loss of water.

Ion exchange properties

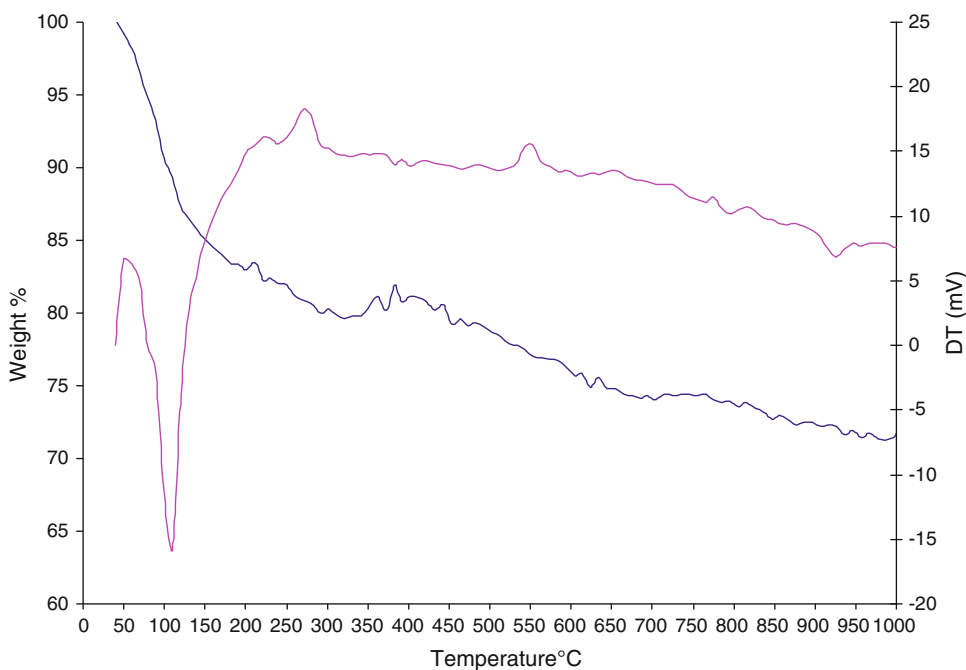
*Kinetic studies and determination of decontamination factor (DF)/distribution coefficients ( $K_d$ )*

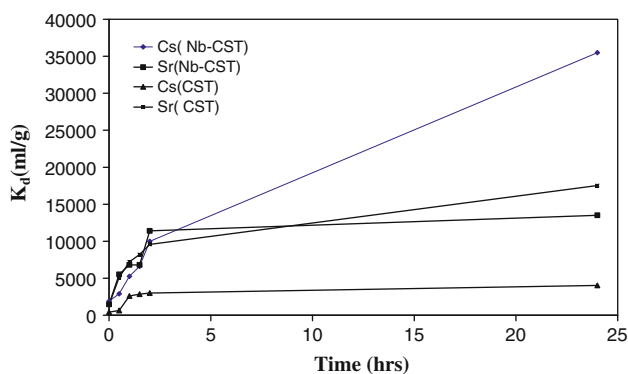
The kinetics of uptake of cesium and strontium by CST and Nb-CST is given in Fig. 7. It is evident from the figure that the kinetics of removal of  $^{90}\text{Sr}$  from actual waste solution is

**Fig. 5** DTA/TGA analysis of CST



**Fig. 6** DTA/TGA analysis of Nb-CST





**Fig. 7** Uptake of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  by CST and Nb-CST

**Table 2** Ion exchange properties of CST and Nb-CST after 24 h of equilibration

Ion exchange property	CST		Nb-CST	
	$^{90}\text{Sr}$	$^{137}\text{Cs}$	$^{90}\text{Sr}$	$^{137}\text{Cs}$
DF	176	40	136	355
$K_d$ (mL/g)	17,525	4,025	13,500	35,490

the same for both CST and Nb-CST. There was 94% uptake of  $^{90}\text{Sr}$  by both CST and Nb-CST instantaneously. The ion exchange properties viz., DF and  $K_d$  values of both CST and Nb-CST after 24 h of equilibration are depicted in Table 2. A DF value of 176 and 136 was obtained after 24 h of equilibration for uptake of  $^{90}\text{Sr}$  by CST and Nb-CST respectively. The  $K_d$  value for  $^{90}\text{Sr}$  after 24 h of equilibration was 17,525 mL/g for CST whereas it was found to be 13,500 mL/g for Nb-CST. The similarities in the shape of the curves suggest that although  $\text{Nb}^{5+} \leftrightarrow \text{Ti}^{4+}$  substitutions increased the tunnel capacity it did not affect the Sr diffusion rates [11]. Similar results were obtained by Oji et al., which depicted significant affinity and uptake (greater than 96%) for both cesium and strontium from high caustic nuclear waste simulants by CST loaded membranes [13].

The uptake of  $^{137}\text{Cs}$  by Nb-CST is low till 2 h of equilibration unlike  $^{90}\text{Sr}$  but after 24 h of equilibration there was an increase in the  $K_d$  from 9,982 to 35,490 mL/g which resulted in 99% uptake implying kinetics of  $^{137}\text{Cs}$  uptake by Nb-CST is slower than that of  $^{90}\text{Sr}$ . This is due to the larger size of  $\text{Cs}^+$  than  $\text{Sr}^{2+}$  its diffusion rate is expected to be lower than that of  $\text{Sr}^{2+}$  [11]. A DF of 40 and 355 was obtained for uptake of  $^{137}\text{Cs}$  by CST and Nb-CST after 24 h of equilibration. The uptake of  $^{137}\text{Cs}$  by pure CST is less than that of Nb-CST. From the above studies it can be concluded CST is selective to uptake of Sr and Nb-CST is selective to uptake of  $^{137}\text{Cs}$ . The selectivity of the above mentioned silicotitanate exchange materials may be

due to chemistry and geometry of the tunnels and pores [14]. The selectivity is a result of physico-chemical and stereochemical factors such as the hydrated radii, hydration energy, valence of cations and space requirement in tita-nosilicate [15].

The cesium  $K_d$  values varied from 15,000 to 1,24,000 mL/g and Sr  $K_d$  values varied from 610 to 33,000 mL/g during the performance evaluation of 17 inorganic ion exchange materials (pharmacosiderite, sodium zirconium silicate, different forms of crystalline silicotitanate materials developed by Sandia National Laboratory, zeolite exchangers etc.) for removal of Cs and Sr from actual N-reactor storage basin water [16]. The  $K_d$  values for the uptake of Cs and Sr by the crystalline silicotitanates synthesized at CWMF are in conformity with the values obtained in the literature.

#### Estimation of ion-exchange capacity

The ion exchange capacity of Nb-CST towards  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  was estimated to be 11.8 and 3.2 meq/g respectively whereas the ion exchange capacity of CST towards  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  was estimated to be 14.6 and 4.4 meq/g respectively.

The ion exchange capacity towards cesium for some of the commercial inorganic ion exchangers viz., zeolite (modernite), silicotitanate (CST UOP), hexacyanoferrate (Cs Treat) and laboratory synthesized sodium form of CST are  $\sim 2$ ,  $\sim 2$ , 0.36, and 1.06 meq/g respectively whereas for Sr it is found to be in the range of 2–5 meq/g [15–20]. The ion exchange capacities for the CST and Nb-CST synthesized at CWMF have higher exchange capacities towards Cs and Sr thus proving to be potential ion exchangers for their application in column studies.

Based on the above results further studies are underway for the development of microspheres encapsulating both the ion exchangers, their characterization and also to explore their feasibility in continuous column operations for treatment of radioactive wastes.

#### Conclusion

A complete study on the synthesis, characterization and uptake of Cs and Sr from actual radioactive waste solution at CWMF by CST and Nb-CST has been carried out. The CST and Nb-CST ion exchangers are highly crystalline with bright cubic and rod like morphology with varying amounts of Ti, Si, Na, Nb and O. The kinetics of removal of  $^{90}\text{Sr}$  from actual waste solution is same for both CST and Nb-CST whereas the kinetics of  $^{137}\text{Cs}$  uptake by Nb-CST is slower than that of  $^{90}\text{Sr}$  which is due to the larger size of  $\text{Cs}^+$  than  $\text{Sr}^{2+}$  and hence its diffusion rate is expected to be

lower than that of  $\text{Sr}^{2+}$ . The ion exchange capacity of both the ion exchangers towards the uptake of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  also enhances the evidence towards their selectivity. Hence CST and Nb-CST are promising ion exchangers for the selective removal of Sr and Cs respectively from radioactive waste solutions.

**Acknowledgments** The authors acknowledge Ms. S. Kalavathy, MSD, IGCAR for the XRD analysis, Ms. R. Sudha, MCG, RCD, IGCAR for SEM analysis, Sh P.T. Hariharan, CWMF for surface area analysis, Sh AGS Mani, CWMF, for DTA/TGA and Sh T.S.S. Raghavan, CWMF for technical assistance.

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