Sorbent Materials for Rapid Remediation of Wash Water during Radiological Event Relief

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Abstract

Procedures for removing harmful radiation from interior and exterior surfaces of homes and businesses after a nuclear or radiological disaster may generate large volumes of radiologically contaminated waste water. Rather than releasing this waste water to potentially contaminate surrounding areas, it is preferable to treat it onsite. Retention barrels are a viable option because of their simplicity in preparation and availability of possible sorbent materials. This study investigated the use of aluminosilicate clay minerals as sorbent materials to retain ^{137}Cs , ^{85}Sr , and ^{152}Eu . Vermiculite strongly retained ^{137}Cs , though other radionuclides displayed diminished affinity for the surface. Montmorillonite exhibited increased affinity to sorb ^{85}Sr and ^{152}Eu in the presence of higher concentrations of ^{137}Cs . To simulate flow within retention barrels, the vermiculite was mixed with sand and used in small-scale column experiments. The GoldSim contaminate fate module was used to model breakthrough and assess the feasibility of using clay minerals as sorbent materials in retention barrels. The modelled radionuclide breakthrough

profiles suggest that vermiculite-sand and montmorillonite-sand filled barrels could be used for treatment of contaminated water generated from field operations.

Keywords: radionuclides, retention, breakthrough, vermiculite, cesium, montmorillonite

1.0 Introduction

Atmospherically-deposited radionuclides, resulting from a nuclear or radiological disaster (i.e. nuclear reactor meltdown, dirty bomb), should be rapidly removed from interior and exterior surfaces of homes and businesses to reduce exposure.[1-6] Radionuclides can be disseminated long distances in contamination plumes from the disaster site.[7,8] Of the long lived radionuclides, ^{137}Cs is generally the most abundant, making it a primary concern in mitigation procedures.[8-11] In addition, ^{90}Sr and low levels of transuranic radionuclides (i.e. ^{241}Am) have been detected in nuclear fallout and should be considered when developing practices.[11,12] Initially, the removal of dust and debris is prescribed as an early course of action to remove radioactive particulate matter from surfaces.[13-15] However, wet deposited radionuclides, especially those that are positively charged (^{137}Cs , ^{90}Sr , ^{241}Am), are subject to ion exchange reactions with building materials.[9,16,17] Exchanged radionuclides can be removed by washing building surfaces with water or concentrated salt solutions.[9,16,17] Washing procedures can result in a large quantity of contaminated wastewater, which, if left untreated, can spread radiological contamination to surrounding areas.[1,6,18] A potential technique to manage this wash water is the treatment of dissolved radionuclides using sorbent materials located inside retention barrels. These barrels would contain sorbent materials that retain dissolved radionuclides while allowing wash water to flow through. The barrels with contaminated solids

can then be efficiently transported due to their compact nature and properly disposed. The sorbents utilized within the barrels must be widely available, economical, and have a high selectivity to sorb dissolved radionuclides from backgrounds containing other inorganic cations.

Aluminosilicate clay minerals are naturally abundant, widely available minerals that often have high, non-pH dependent, cation exchange capacity (CEC) and a high selectivity for cationic radionuclides.[19,20] For example, illite has high specificity to sorb ^{137}Cs from aqueous solutions due to a collapsed interlayer and a higher amount of isomorphic substitutions in the silicon oxide layer.[21,22] The silicon oxide layer substitutions are located closer to the surface for 2:1 clays; which decreases the area over which the charge is spread, focusing the charge over only three adjacent surface oxygen atoms.[20,23,24] The interaction energy is far greater between focused charge sites and ions that can shed hydration shells, creating a natural selectivity for ^{137}Cs or similar ions.[20,23,24] However, this process occurs within the collapsed interlayer, making it kinetically slow compared to electrostatic interactions between dissolved cationic radionuclides and other clays.[21,22,25] Therefore clay minerals without a collapsed interlayer may be preferable as sorbents deployed in retention barrels, since contact time is limited in flow through applications.

The fully hydrated interlayers of vermiculite and montmorillonite clay minerals may result in fewer limitations due to kinetic effects during cationic radionuclide uptake.[26,27] The main differences between vermiculite and montmorillonite are the abundance and placement of isomorphic substitutions.[20,23,24] Montmorillonite has more aluminum oxide substitutions, resulting in less focused charge sites and CECs ranging from 75 to 90 meq/100 grams.[20,23,24] Sorption coefficients to montmorillonite can vary drastically for cationic radionuclides depending on the identity and abundance of background cations.[19,28,29] For instance, sorption

coefficients of ^{137}Cs onto montmorillonite with calcium as the dominant ion are 10 times lower than those with potassium or sodium as the dominant exchange ion at background concentrations lower than 10 mM.[19] Vermiculite, on the other hand, displays less of these effects as most of the substitutions occur in the silicon oxide layer near the surface similar to illite.[20,23,24,30,31] The high energy of interaction between focused charge groups of vermiculite and ^{137}Cs increases the selectivity of the clay.[30] However this selectivity decreases the sorption coefficient for other radionuclides on vermiculite, including ^{90}Sr and ^{241}Am , especially in the presence of ^{137}Cs . [32,33] Lower sorption coefficients indicate decreased retention of these radionuclides if vermiculite is the clay mineral deployed in the retention barrels. Additionally, the swelling nature of montmorillonite and vermiculite decreases their hydraulic conductivity, restricting the flow in the retention barrel.[34] A possible, readily available, solution to this problem is mixing the clay minerals with sand (which has high hydraulic conductivity but low CEC) to allow both flow and radionuclide retention. The presence of such a mixture, however, greatly complicates retention barrel design. Predictive models must be used to initially assess operational parameters, such as the relative amount of aluminosilicate minerals and sand needed in a retention barrel.

This study aims to evaluate vermiculite and montmorillonite as possible sorbent materials for use in retention barrels prior to large-scale testing. Removal of ^{137}Cs was the primary goal, however, ^{85}Sr , and ^{152}Eu were also studied. ^{85}Sr and ^{152}Eu were served as radioactive surrogates for ^{90}Sr and ^{241}Am , respectively, because of detection and waste classification issues. ^{152}Eu is documented as an adequate surrogate for ^{241}Am in regards to sorption to geologic minerals.[35] Radiochemicals were exclusively utilized to enable low contaminant concentrations without detection limit issues and to fully account for competition effects with other salts present in

retention barrel water. The Goldsim contaminant fate module was employed to predict field-scale operational parameters.

2.0 Experimental

2.1 Materials

^{137}Cs , ^{85}Sr , and ^{152}Eu were obtained from Perkin Elmer (MA, USA). Vermiculite was from Specialty Vermiculite (Grace vermiculite: SC, USA) and the Strong Company (Strong vermiculite: AR, USA). Montmorillonite was from the American Colloid Company (Volclay 205x: IL, USA), Across Organics (K10 montmorillonite: MA, USA) and the Clay Minerals Society (Wyoming montmorillonite: Wyoming, USA). Sand was obtained from New Plant Life (IA, USA). All solids were used as received. Tap water (pH 7.5 ± 0.3) is supplied and routinely analyzed at the DuPage County Department of Public Works. At the time of the experiments a sample was analyzed for metals by ICP-MS (Table 1).

Table 1. Concentrations of metals in tap water detected by ICP-MS ($\mu\text{mol/L}$)

Metal	Na	Mg	Al	K	Ca	Fe	Sr	Cs	Ba
Concentration	342	473	1.4	37	833	0.76	1.4	< 0.01	0.15
($\mu\text{mol/L}$)	± 34	± 47	± 0.2	± 4	± 83	± 0.7	± 0.1		± 0.02

2.2 Batch Experimental Methods

Sorption experiments to all clays were performed for ^{137}Cs with a solid-to-water ratio of 1 mg/mL. 1.5 mL reactors were set up in duplicate with initial ^{137}Cs radioactivities of 824 $\mu\text{Ci/L}$ (0.07 μM). Initial ^{137}Cs concentrations were designed to keep sorbed concentrations well below 1% surface coverage of the clay with the lowest CEC (Wyoming montmorillonite: 0.76 meq/ 100

g) while keeping aqueous concentrations above the limit of detection (30 $\mu\text{Ci/L}$). Sorbed concentrations below 1% of the CEC have previously shown not to be influenced by isotherm non-linearity, thus keeping point sorption coefficients within the linear range.[36,37] Further, wash waters generated from mitigation procedures are expected to have low concentrations due to dilution;[18] therefore, the low surface coverage maintained is assumed to reflect field scale applications. Clay minerals were suspended for the duration of the experiment using an end over end rotator. To keep solid-to-water ratios constant throughout the experiment, 350 μL aliquots of the clay-solution mixtures were taken at time intervals of approximately 1, 10, 30, and 60 min. These aliquots were centrifuged at 3500 rpm for 3 min with 200 μL of supernatant removed for analysis of aqueous concentration (C_w) by gamma-counting (WIZARD² Automatic Gamma Counter, Perkin Elmer). The “contact time” was defined as the time when the 200 μL aliquot was removed. Non-equilibrium sorption coefficients (K_d') were calculated at each contact time:

$$K_d' = \frac{C_s'}{C_w'} \quad (1)$$

where C_w' refers to the aqueous concentration and C_s' is the sorbed concentration at contact time.

Additional batch experiments were performed to understand competition effects on sorption of ^{137}Cs , ^{85}Sr , and ^{152}Eu to Grace vermiculite, Volclay 205x, and sand. Sorption experiments to clay minerals were performed with solid loadings of 1 mg/mL, while sorption to sand was performed at 100 mg/mL. Experiments included each radionuclide sorption independently, ^{137}Cs and ^{85}Sr together, and equal radioactivities of all present, each in tap water background. Radionuclide stock solutions and tap water were added to achieve desired radioactivities (300 $\mu\text{Ci/L}$) in triplicate and were designed to keep total sorbed concentrations

below 1% of the CEC. Samples were mixed for 2 hours then centrifuged at 3500 rpm for 3 minutes. Duplicate 100 μ L aliquots were taken from the supernatant for analysis of equilibrium aqueous concentration (C_w) by gamma counting. Detection windows were 580-750 keV, 445-580 keV and 300-388 keV for ^{137}Cs , ^{85}Sr , and ^{152}Eu , respectively. The sorbed concentration, C_s (mol/kg), was calculated by difference and the sorption coefficient (K_d) was determined:

$$K_d = \frac{C_s}{C_w} \quad (2)$$

A control set with no sorbent addition verified there was no sorption onto tubes. All experiments were performed at room temperature.

2.3 Column Experiments

Masses of vermiculite (250 mg) and sand (100 g) were combined in a vial and vortexed for 3 minutes to create a homogeneous mixture. This mixture was dry packed into a polypropylene column with a 2.54 cm (1 in) inner diameter and a 25.4 cm (10 inch) length. The column contained two outlets, one on the center line (middle 1.27 cm of the inner diameter) and one on the outer edge, which were separated by a 1.27 cm tall divider. Two outlets were used to ensure that flow was not channeled on the outside of the column. Column experimental flow rates were determined as the sum of the flowrates for both outlets over a period of time. For pulse experiments, spikes of 0.5mL containing 25 or 10 μCi of either ^{137}Cs or ^{85}Sr , respectively, were injected into a pre-wet column. A solution containing 0.14 $\mu\text{Ci/L}$ of both ^{137}Cs and ^{85}Sr in tap water was used for the continuous input experiments. Flow was kept constant using a

Mariotte bottle, and samples were taken every 20-30 minutes from the outer and inner outlet in duplicate for 9 hrs. Concentrations were determined by gamma counting 1 mL of each sample.

2.4 Modeling Methods

GoldSim contaminant fate module (version 11.1 [38]), designed for the transport of radionuclides in an aquifer, was used to model radionuclide breakthrough using only available or easily obtainable parameters. Darcy's law using the hydraulic conductivity of sand and the clay minerals was the basis of predicting flow through the column, and radionuclide retention in the column was predicted using the sorption coefficients derived in the batch sorption tests. Only three solid parameters (porosity, hydraulic conductivity, bulk density) were used (Table 2). Dispersivity was assumed to match that of a sandy aquifer (0.073 m).[39] The GoldSim contaminant fate module is detailed elsewhere.[40,41]

Table 2. Bulk densities, porosities and hydraulic conductivities for the solids used to model breakthrough curves (from ref. [42])

Solid	Bulk Density (g/cm ³)	Porosity	Hydraulic Conductivity (cm/sec)
Vermiculite	1.1	0.58	1×10^{-10}
Sand	1.8	0.6	0.03
Montmorillonite	1.1	0.58	1×10^{-10}

3.0 Results and Discussion

3.1 Clay selection for cesium removal from tap water

At low contact times K10 montmorillonite had higher sorption coefficients than the other clays studied, likely arising from the difference in exchange ions on K10 montmorillonite (Figure 1). K10 montmorillonite is an acid treated reaction catalyst, and therefore some of the natural exchange ions are replaced with H^+ ions.[43] Protons are seemingly less subject to kinetic effect when desorbing from the clay surface, increasing sorption coefficients at low contact times. However, the presence of exchangeable protons causes concern for the consistency of sorption coefficients as more protons are exchanged with other inorganic cations in the tap water. Additionally, K10 montmorillonite displayed lower sorption coefficients at longer contact times; therefore K10 montmorillonite was eliminated as a possible sorbent for use in retention barrels.

Vermiculite demonstrated a higher affinity to sorb ^{137}Cs than montmorillonite. Sorption coefficients (K_d) of ^{137}Cs to the two vermiculites (Grace and Strong) were higher than those of the montmorillonite studied (Figure 1). Vermiculite has more isomorphous substitutions in the tetrahedral layer increasing the selectivity for ions that have the ability to shed their hydration shells, such as ^{137}Cs . The increased selectivity results in increased sorption coefficients compared to montmorillonite, which has more isomorphous substitutions in the octahedral layer. Therefore vermiculite is a promising sorbent material when ^{137}C was the only radionuclide of interest. However, how the selectivity of vermiculite influenced sorption of other radionuclides, especially in the presence of ^{137}Cs , still needed investigation.

Figure 1. ^{137}Cs non-equilibrium sorption coefficients (K_d') as a function of contact time to Grace vermiculite (black circles), Strong vermiculite (white circles), K10 montmorillonite (black triangles), Wyoming montmorillonite (black squares), and Volclay montmorillonite (white squares). Error bars represent standard deviation of duplicate measurements. Where not visible, error bars are smaller than the symbol size.

3.2 Competition between radionuclides

Each radionuclide sorbed differently to vermiculite, where ^{137}Cs sorbed strongest, followed by ^{152}Eu and ^{85}Sr (Table 3). This order deviates from the cation selectivity series for clay minerals,[44,45] where multivalent cations $^{85}\text{Sr}^{2+}$ and $^{152}\text{Eu}^{3+}$ (at neutral pH) are expected to have higher affinities for vermiculite than $^{137}\text{Cs}^{+}$. The lower affinity of ^{85}Sr is likely caused by the large decrease in concentration (7 orders of magnitude) at the same radioactivity for ^{85}Sr . The increased disintegrations per time period lead to lower concentrations of ^{85}Sr , that result in the same radioactivity as the other radionuclides studied. The lower concentration causes a reduction in sorption coefficients in the presence of higher relative concentrations of the other inorganic cations in tap water. ^{152}Eu , however, has at a higher concentration compared to ^{137}Cs , indicating

a variation for the selectivity series between these two radionuclides. The smaller ionic radius of ^{152}Eu increases the hydration energy of the ion, inhibiting the removal of its hydration shell, and prevents the formation of inner sphere interactions with the focus charge sites of vermiculite. [44,46] Both ^{85}Sr and ^{152}Eu display decreased sorption to vermiculite compared to ^{137}Cs due to their inability to shed hydration shells causing the charge to be spread over the entire hydrated radius.[47,48]

Focused surface charge sites also limit the ability of vermiculite to sorb ^{85}Sr in the presence of ^{137}Cs and ^{152}Eu . Decreased concentrations and less favorable sorption sites cause the affinity of ^{85}Sr for the surface to be drastically reduced in the presence of ^{137}Cs . Sorption of ^{85}Sr decreases by a factor of 10 in the presence of ^{137}Cs and sorbs even more weakly in the presence of both ^{137}Cs and ^{152}Eu (Table 3). ^{152}Eu also shows a distinct decrease in sorption coefficient when in the presence of ^{137}Cs and ^{85}Sr . ^{137}Cs shows little difference in sorption in the presence of ^{85}Sr and a slight decrease in the presence of both ^{85}Sr and ^{152}Eu (Table 3). One positive aspect of this phenomenon is that ^{137}Cs contamination may be the most widespread of the long-lived radionuclides from radiological releases, making vermiculite a convincing option for the sorbent employed in retention barrels. However, the reduced ability for vermiculite to sorb ^{85}Sr in the presence of ^{137}Cs is troubling. Therefore, montmorillonite was investigated as a possible sorbent to increase retention ^{85}Sr .

Table 3. Sorption coefficients (mL/g) for ^{137}Cs , ^{85}Sr , and ^{152}Eu onto vermiculite, montmorillonite, and sand either alone in solution or in the presence of other radionuclides.

Vermiculite			
	Radionuclide Only	^{137}Cs and ^{85}Sr	All Present
^{137}Cs	4000 ± 340	3600 ± 280	1170 ± 40
^{85}Sr	600 ± 70	62 ± 6	31 ± 2
^{152}Eu	1550 ± 10	N/A	390 ± 10
Montmorillonite			
^{137}Cs	NP	670 ± 10	640 ± 10
^{85}Sr	250 ± 60	230 ± 20	230 ± 10
^{152}Eu	NP	N/A	730 ± 10
Sand			
^{137}Cs	1.9 ± 0.1	0.4 ± 0.1	0.3 ± 0.1
^{85}Sr	0.4 ± 0.1	ND	ND
^{152}Eu	ND	N/A	1 ± 0.1

NP = Not performed; ND = No sorption detected N/A = Not applicable

^{85}Sr had an increased affinity for montmorillonite in the presence of ^{137}Cs in comparison to vermiculite (Table 3). ^{85}Sr displayed lower sorption coefficients to montmorillonite in comparison to vermiculite, which is expected because of the lower CEC of montmorillonite. However in the presence of ^{137}Cs , ^{85}Sr had a larger sorption coefficient to montmorillonite than vermiculite (Table 3). The defocused nature of the charge sites on montmorillonite, arising from substitutions in the aluminum oxide layer, decreased its preference for inner sphere interactions, allowing the multivalent, outer sphere sorbing ions to compete with ^{137}Cs . [24,49] ^{152}Eu also showed increased affinity to montmorillonite in the presence of ^{137}Cs , while the addition of ^{152}Eu did not decrease ^{85}Sr sorption. The ability of montmorillonite ability to sorb ^{85}Sr , especially

when it is at vastly lower concentrations than other radionuclides, suggests it may be a viable option for retention barrel sorbent material at locations where ^{137}Cs and ^{85}Sr are both present.

3.3 Column experiments

Column experiments enabled validation of breakthrough modeling. Vermiculite was chosen as the sorbent material for small-scale model experiments due to the potential prevalence of ^{137}Cs in nuclear and radiological releases. The difference in sorption between ^{137}Cs and ^{85}Sr on vermiculite permitted us to assess the ability of the model to predict large differences in retention. In fact, for the purposes of the scope of this study – to investigate the model for its application to retention barrels – this made vermiculite the preferred material to utilize. Namely, once the important model parameters are confirmed to accurately predict breakthrough for the more challenging case of vermiculite, they can be applied to montmorillonite, which has similar properties (Table 2) and sorption kinetics (Figure 1). Separate montmorillonite-only or montmorillonite-vermiculite mix columns were beyond the scope of this study

Breakthrough was well modeled for both pulse and continuous inputs (Figure 2). Batch experiments to sand showed little sorption ($K_d \leq 2$, Table 3); therefore, vermiculite was the dominant sorbent in the column. No differences in concentrations were observed between the inner and outer flow paths suggesting a homogenous mixture with minimal channeling. Flow rates matched (within 10%) those predicted by Darcy's Law using the physical characteristics of the vermiculite and sand (Table 2). Pulse breakthrough curves for both ^{137}Cs and ^{85}Sr showed considerable tailing attributed to local hydrodynamic dispersion, which always increases in the direction of fluid velocity in a forced gradient system.[50-52] As expected, ^{137}Cs was better retained on vermiculite with ^{85}Sr showing little retention (Figure 2A). Pulse experiments were

well modeled (average absolute error = 0.007 $\mu\text{Ci/L}$) using the individual batch K_d values of vermiculite and sand for ^{137}Cs and ^{85}Sr , and a dispersivity value in sandy aquifers from the literature (0.073 m).[39] Column experiments seemingly reached equilibrium. Isotherm non-linearity was assumed not present because modeling captured the breakthrough without incorporating these effects. Continuous input of both ^{137}Cs and ^{85}Sr followed the same trend. Retention was modeled well (average absolute error = 0.009 $\mu\text{Ci/L}$) using K_d values from the corresponding batch experiments (Figure 2B). The slight difference in breakthrough volume between pulse and continuous input experiments was attributed to the increased concentration gradient in pulse input experiments causing increased diffusion, which was captured in predictive models. The ability of the model to capture the different breakthrough curves with no parameters, besides K_d , which were experimentally determined, demonstrates its robustness and suggests its use in field scale projections.

Figure 2. Breakthrough curves for individual pulse inputs (A) and combined continuous input (B) of ^{137}Cs (black circles) and ^{85}Sr (white circles) on a vermiculite/sand column with corresponding model output (^{137}Cs : black line, ^{85}Sr : dashed line)

3.4 Field Scale Projections

Modeling provided a baseline estimate for full-scale application of a retention barrel using vermiculite or montmorillonite to treat wash water containing dissolved radionuclides. Pulse inputs of contaminants were modeled because it demonstrated a faster breakthrough time in the small-scale testing. In GoldSim, we constructed a 55-gallon (208 L) barrel filled 75% with the solids mixture. The top 25% was used to keep a constant head of water flowing in the barrel. The concentrations of the pulse inputs were kept below 1% of the total CEC in the barrel. However, outputs are presented qualitatively to represent breakthrough if radionuclides are only subject to linear sorption coefficients. The general objective in determining proposed mixtures of clay mineral and sand was to retain radionuclides while allowing the highest flow rates. A higher flow rate would allow for faster washing procedures and possible wash water reuse. The proposed vermiculite to sand dry mass ratio was 1:3 as ^{137}Cs is strongly retained by vermiculite. Lower amounts of vermiculite were shown to treat wash water while allowing for a higher flowrate. Darcy's law predicted the flowrate to be 2.6 L/min with breakthrough occurring after 112,000 L were treated (Figure 3A). This volume treated before breakthrough would greatly reduce the amount of contaminated material that needs disposal, resulting lower remediation costs.

The presence of ^{85}Sr further complicated retention barrel design. A higher amount of montmorillonite is needed to prevent breakthrough, in turn limiting the possible flowrate. The three montmorillonite to sand ratios investigated were 1:3, 1:2 and 1:1. Flow rates predicted by Darcy's Law were 2.5, 2.2, and 1.6 L/min in order of increasing montmorillonite mass. At these flow rates, ^{85}Sr would break through after 5,400, 6,300 and 9,200 L were treated. Flow rates

decreased sharply for barrels with montmorillonite to sand ratios greater than 1:1. Therefore, to treat wash water while allowing flow, a ratio of 1:1 montmorillonite to sand is seemingly the best option. In this case, ^{137}Cs would break through after 26,800 L treating followed by ^{152}Eu at 30,500 L treated (Figure 3B). Overall, these predicted treated water volumes suggest retention barrels as a viable method to treat wash water contaminated with these radionuclides.

Figure 3. (A) Predicted breakthrough for ^{137}Cs through barrel containing 1:3 mixture vermiculite to sand if concentrations are kept below 1% of the clay CEC. Flow rate was predicted to be 2.6 L/min. (B) Breakthrough curve for ^{137}Cs (solid line), ^{85}Sr (dashed line), and ^{152}Eu (dotted line) through barrel containing 1:1 mixture montmorillonite to sand. Flow rate was predicted to be 1.6 L/min.

4. Conclusions

Vermiculite and montmorillonite are seemingly viable options for the use in retention barrels for the treatment of radiologically contaminated wash water. These clay minerals, when mixed with sand, allowed for flow while retaining the radionuclides ^{137}Cs , ^{85}Sr and ^{152}Eu . The high affinity of ^{137}Cs for vermiculite was caused by the presence of focused charge sites arising

from isomorphic substitutions within the tetrahedral layer of the clay. Vermiculite was therefore concluded as a possible sorbent material if ^{137}Cs is the dominant radionuclide of concern. However, other radionuclides, such as ^{85}Sr and ^{152}Eu , may be better treated by montmorillonite, as they displayed increased affinity for montmorillonite especially in the presence of ^{137}Cs . Therefore, montmorillonite may be a viable sorbent material for areas of mixed radiological contamination.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors declare no competing financial interest.

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Graphical Abstract

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