Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Ahmad, S. and Qureshi, I. H.(1989) 'Separation of Radionuclides from Liquid Waste Using a Mineral Mixture', Separation Science and Technology, 24: 7, 569 — 579

To link to this Article: DOI: 10.1080/01496398908049792

URL: http://dx.doi.org/10.1080/01496398908049792

SEPARATION SCIENCE AND TECHNOLOGY, 24(7 & 8), pp. 569-579, 1989

Separation of Radionuclides from Liquid Waste Using a Mineral Mixture

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Abstract

The use of a naturally available mineral mixture (MM) for decontamination of low-level radioactive liquid waste has been investigated. Adsorption of ^{137}Cs and ^{90}Sr radionuclides on MM from aqueous solutions is reported by describing the effect of equilibration time, hydrogen ions, and adsorbent and adsorbate concentrations. Optimum physicochemical conditions have been identified. The data suggest the effective use of MM for on-line isolation of the radionuclides from the effluent of a nuclear industry/laboratory and subsequent storing for a long time in reduced solid form.

INTRODUCTION

Natural sorption materials have the potential to be utilized as important components of liquid radioactive waste management resulting from nuclear industries and laboratories (*1–9*). In addition to their good sorption properties and higher radiochemical and thermal resistance compared to organic exchangers, they have a considerable economic importance because of their low cost and availability in abundant quantities (*10–12*). The utilization of locally available inexpensive minerals for retaining radioactive ions from bulk solutions and for storing solid radioactive waste of small volume has proved to be technically reliable and economically justified (*10*, *24*). It has been established that mixed hydrous oxides have better utility as ion-exchangers than individual ones (*12–14*).

Therefore, our investigations studied the sorption behavior of ^{137}Cs, ^{134}Cs, and ^{90}Sr radionuclides (which contribute 80% of the activity of fission products) on a natural mineral mixture (MM). The results obtained were sufficient to define the optimum physicochemical conditions for decontamination of Cs and Sr by MM.

EXPERIMENTAL

Natural Material Used (MM)

The experiments were performed with a locally available natural minerals mixture containing the minerals given in Table 1. The main mineral constituents were determined by optical microscopy and x-ray diffraction techniques (*15*). The chemical composition was established by using INAA and ES techniques (*16*, *17*) and are tabulated in Table 2. The mineral mixture (MM) was ground and sieved to achieve a particle size ranging from 80 to 100 mesh (0.044–0.74 mm fraction) and was used without any pretreatment (e.g., hydrogen saturation) so that natural conditions were simulated as far as possible.

Reagents and Radiotracer

All the reagents used in this study were of AR or equivalent grade. The radiotracers employed were purchased from Amersham Radiochemical

TABLE 1
Mineralogical Contents of Mineral Mixture (MM)

1.	Geothite	$FeOOH$ ($HFeO_2$)
2.	Hematite	Fe_2O_3
3.	Limonite	$2Fe_2O_3 \cdot 3H_2O$, $FeO(OH) \cdot nH_2O$
4.	Magnetite	Fe_3O_4
5.	Quartz	SiO_2
6.	Diaspore	$HAlO_2$
7.	Enstatite, saprolite	$Mg_2(Si_2O_6)$
8.	Ilmenite	$FeTiO_3$
9.	Olivine	$MgFeSiO_4$
10.	Dolomite	$Ca\text{-}MgCO_3$
11.	Bauxite	$Al_2O_3 \cdot 2H_2O$

TABLE 2
Chemical Composition of
Mineral Mixture (MM)
(values in %)

Element	Concentration
Fe	34-41
MgO	6.3-10.5
Al	4.8-9.3
SiO_2	18.5-29.1
Zn	0.014-0.080
Ca	4.23-16.4
Mn	0.51-0.83
Ni	0.31-0.55
Cu	0.07-0.09
Cr	0.35-0.52
Co	0.05-0.08
Ti	0.83-1.89

Centre, Amersham, England, or prepared locally by irradiating the spec-pure metal salts with thermal neutrons in the PARR-I research reactor at our institute with a flux of 2×10^{13} $n \cdot cm^{-2} \cdot s^{-1}$ for appropriate times. After suitable cooling times, the target was dissolved in HNO_3.

Sorption Measurement

The sorption was measured by equilibrating the solid adsorbent MM of known weight with an aqueous solution of a different system containing a known aliquot of a radiotracer of a test element for a specific time. The solution was centrifuged at 5000 rpm for phase separation. The supernatant solution was withdrawn and its activity was compared with the activity of the sorbent (solid) to calculate the adsorption percentage. The activities were measured with a well-type scintillation counter. In the case of mixed radiotracers ^{134}Cs and ^{85}Sr, the gamma activities were measured with a semiplannar 30 cm^3 Ge detector (ORTEC Inc.) with a CANBERA Series MCA hooked to an on-line computer sytem PDP 11/237. The resolution of the system for the 1332.5 keV peak of ^{60}Co is 1.9 keV and a peak to Compton ratio of 40:1. The details of the electronics have been reported (*18*). The pH values of all systems were measured using a glass electrode connected with a Pye model-97 pH meter.

RESULTS AND DISCUSSION

It is essential for decontamination and isolation to have information about the adsorption behavior of the elements in the presence of different concentrations of acid and alkali systems because nuclear waste can be in any pH system or can change during mixing with other effluent channels. Similarly, the pH of the aqueous solution is an important variable which controls the adsorption of the metals by the oxide-water interface (*12*, *24*). Therefore, the effects of pH on the adsorption of cesium and strontium were examined from pH 1 to pH 14 and the yield was also investigated as a function of concentration of nitric, perchloric, and sulfuric acid solutions in the range of 0.01–5 *M*. The results in Figs. 1 and 2 indicate that adsorption decreases with an increase in acid concentration. Both cesium and strontium exhibit maximum adsorption at the very low acid concentration of 0.01 *M*, which corresponds to pH 2. It has been shown that certain elements form hydrolyzed, positively charged colloidal species in an aqueous medium, while iron-III oxide and iron-III hydroxide minerals possess a negative surface charge at pH 2 (*19–24*). It is therefore possible to postulate that fixation may be mainly attributed to the mutual attraction of positively charged elemental species and negatively charged mineral surfaces. Adsorption at higher acidities is relatively less, which may be due to competition between the excess H^+ in the medium and positively charged hydrolyzed species. Second, a higher acid concentration appears to suppress hydrolysis of the elements, resulting in low adsorption. A comparison of the adsorption from different acid solutions shows that there is no significant difference in adsorption behavior of the elements studied. The similar adsorption behaviors indicate that in any acid solution, Cs and Sr species are essentially not influenced by the nature of any anion present. Maximum adsorption was observed from 0.1 *M* HNO_3 solution; therefore, other parameters controlling adsorption have been investigated from this solution.

The pH dependence of the sorption of Cs and Sr on MM is illustrated by Fig. 3 which shows that percent adsorption increases with an increase in the pH of the aqueous solution and attains an almost 100% value around pH 2–3. The small decrease of sorption at pH 12 may be due to the formation of colloidal species which do not undergo complete sedimentation.

The adsorption dependence of Cs and Sr on the amount of mineral mixture was studied in the range of 10 mg to 5 g. The results are shown in Fig. 4. The percent adsorption yield increases with an increasing amount

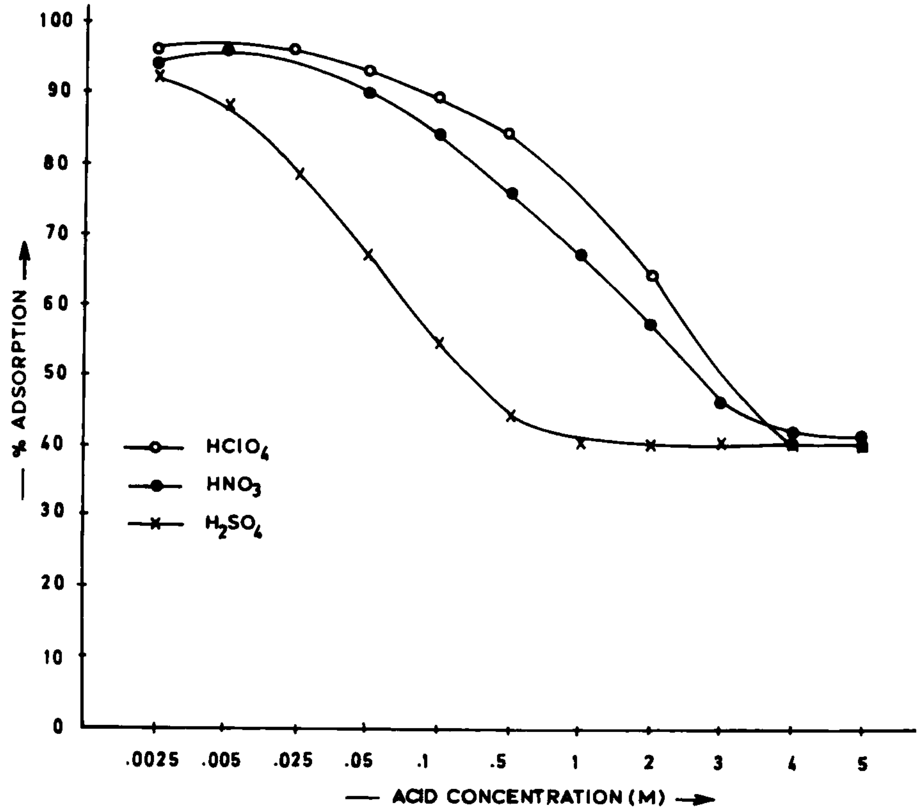

FIG. 1. Percent adsorption of cesium on MM as a function of various acid concentrations.

of adsorbent, reaching a maximum value (~ 100%) around 200 mg. The percentage adsorption remains almost constant above 200 mg. Therefore, all subsequent experiments for other studies were carried out with 200 mg MM.

To determine the optimum contact time required for the adsorption equilibrium of cesium and strontium between solid and liquid phases, a set of experiments was performed as a function of equilibration time between adsorbate and adsorbent in the range of 30 s to 10 min in optimum experimental conditions established previously. Figure 5 indicates that sorption equilibrium between ions and MM can be achieved within 2 min. Therefore, 2 min contact time was employed in all subsequent measurements. A fast contact time also indicates a surface re-

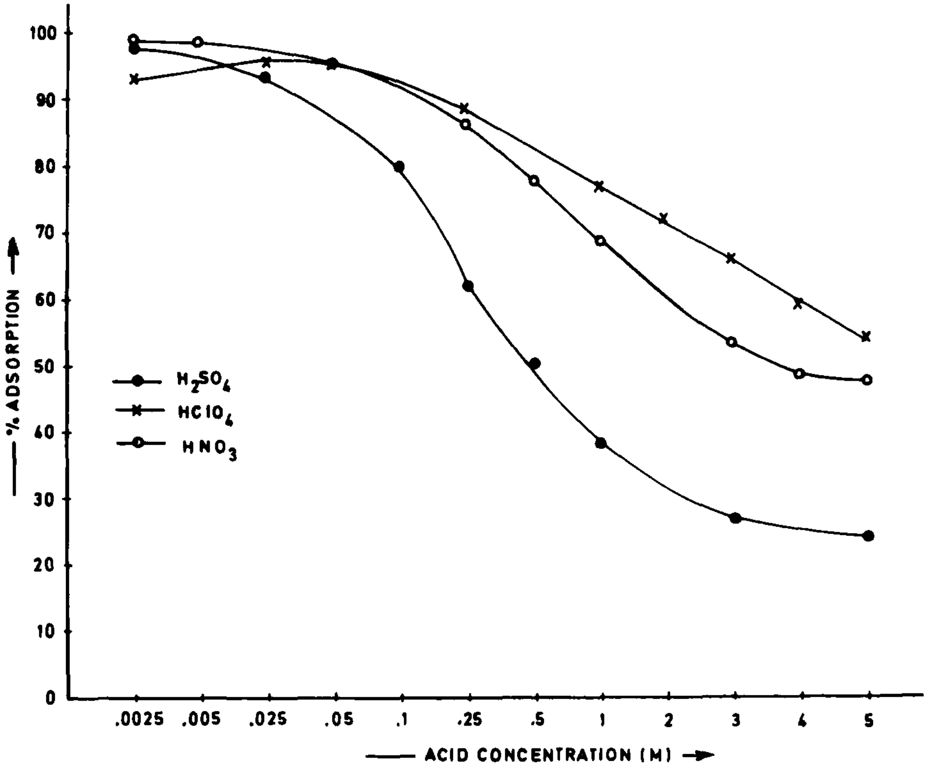

FIG. 2. Percent adsorption of strontium on MM as a function of various acid concentrations.

action, i.e., a hydrolytic adsorption which can be considered to be a simple condensation reaction between the hydrolysis product of the metal ions and the sorbent carrying the OH group, thus forming an oxy-bridge between Fe(III) and the ions (*14*, *20*, *25*).

The adsorption variations of Cs and Sr with different solution concentrations were also studied to calculate the loading capacity of MM. The results, given in Fig. 6, show that loading capacity can be achieved up to 35 g/kg for Cs and 25 g/kg for Sr. Cesium has more loading capacity as compared to Sr because of its greater affinity for iron-containing minerals.

In the light of these observations, it is concluded that fixation of ^{137}Cs and ^{90}Sr can be achieved in less than 2 minutes in a wide range of pH values. Further, no expensive reagents are required.

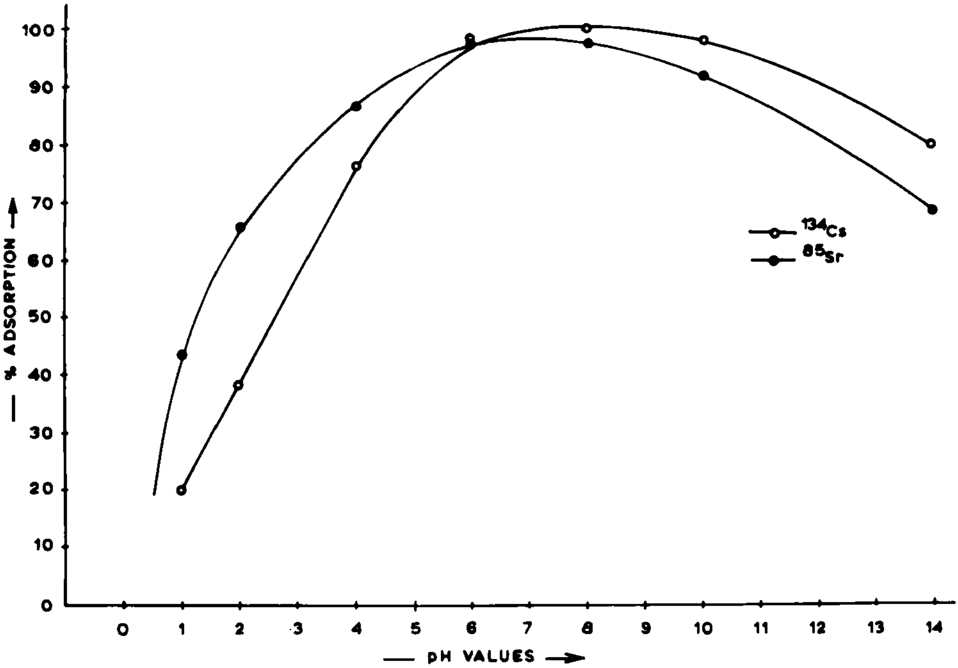

FIG. 3. Percent adsorption of cesium and strontium on MM as a function of pH values.

This study shows that untreated, naturally occurring, inexpensive mineral mixtures can be used effectively for the on-line treatment of radioactive liquid wastes and can also be used for long-term storage in reduced solid form.

Acknowledgments

The authors gratefully acknowledge the technical assistance of Mr. A. K. Rana. We are also grateful to the Reactor Operation Group for arranging the irradiation of the target samples.

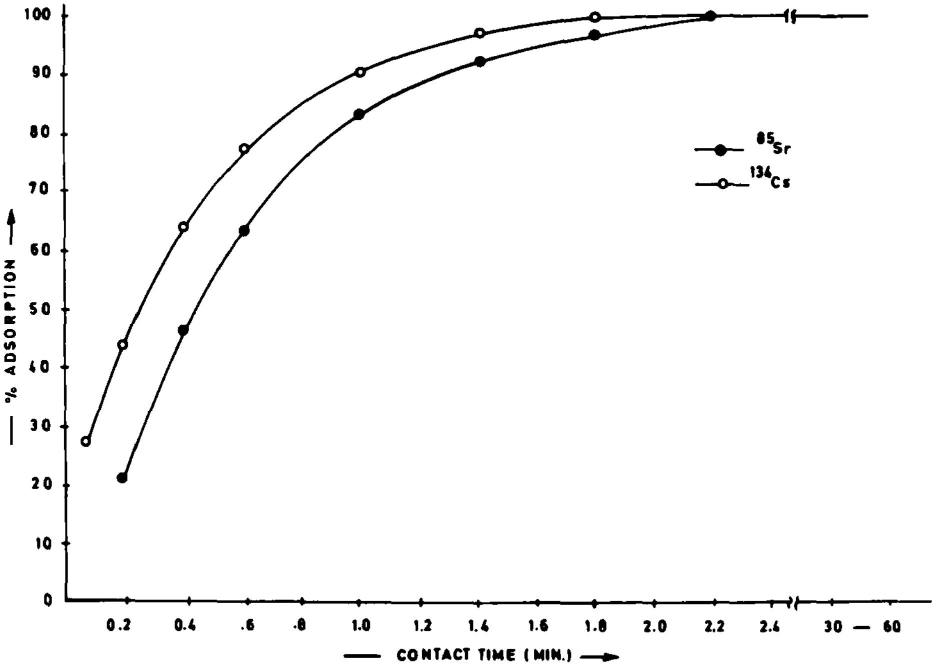

FIG. 4. Percent retention of cesium and strontium on MM as a function of the contact time.

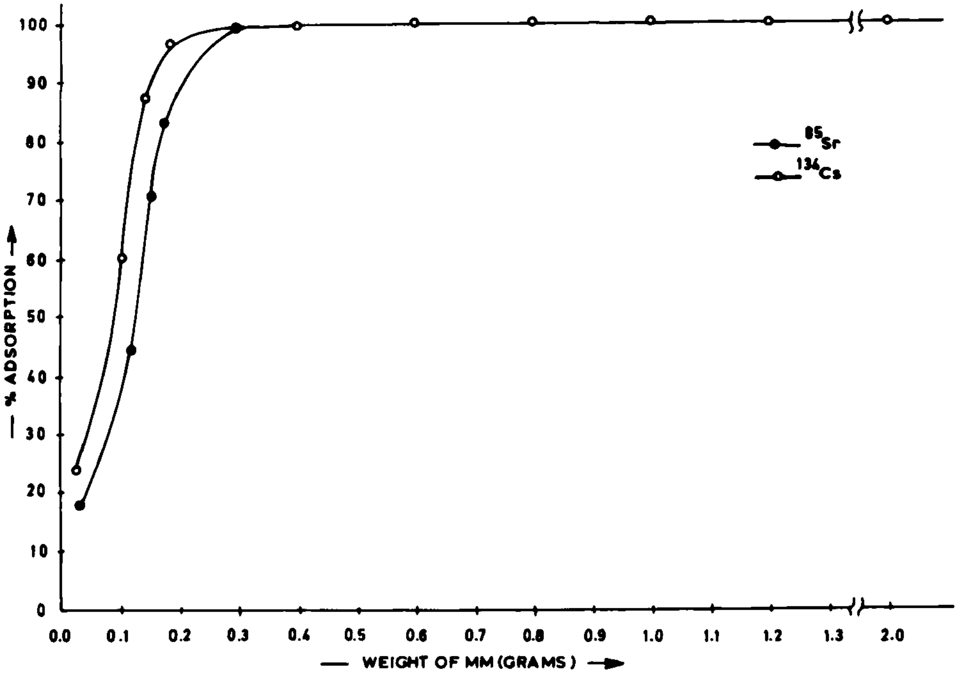

FIG. 5. The dependence of the adsorption of cesium and strontium for different amounts of sorbent.

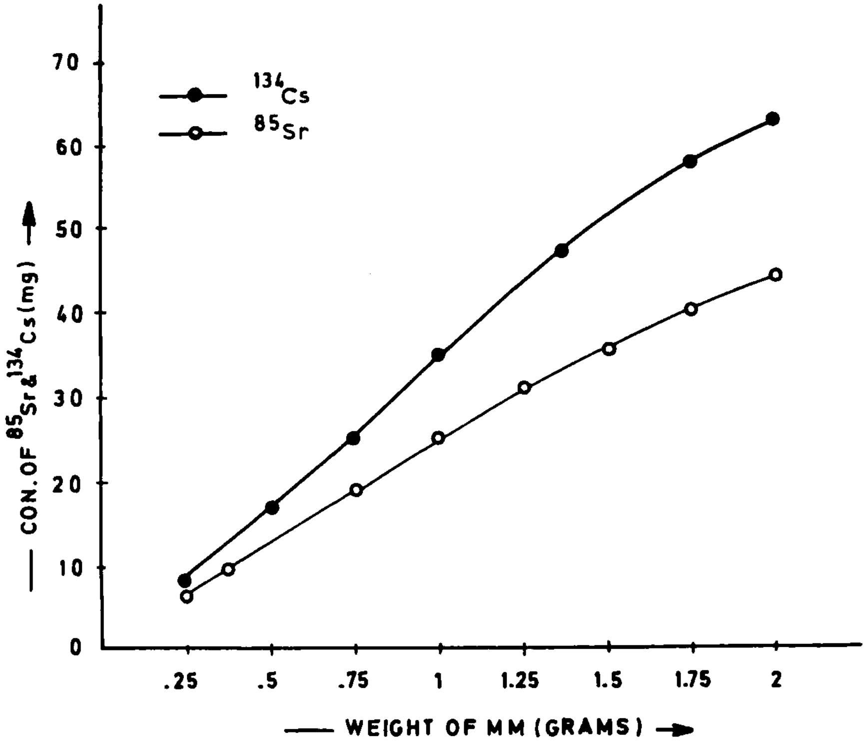

FIG. 6. Loading capacity of cesium and strontium as a function of different weight of MM.

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Received by editor December 7, 1987