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

Adsorption Studies of Radioactive Cobalt on a Minerals Mixture

S. Ahmad[a]; A. Mannan[a]; I. H. Qureshi[a]
[a] NUCLEAR CHEMISTRY DIVISION, PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY, ISLAMABAD, PAKISTAN

To cite this Article Ahmad, S. , Mannan, A. and Qureshi, I. H.(1992) 'Adsorption Studies of Radioactive Cobalt on a Minerals Mixture', Separation Science and Technology, 27: 4, 523 — 533
To link to this Article: DOI: 10.1080/01496399208018898
URL: http://dx.doi.org/10.1080/01496399208018898

SEPARATION SCIENCE AND TECHNOLOGY, 27(4), pp. 523–533, 1992

Adsorption Studies of Radioactive Cobalt on a Minerals Mixture

S. AHMAD, A. MANNAN, and I. H. QURESHI
NUCLEAR CHEMISTRY DIVISION
PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY
P.O. NILORE, ISLAMABAD, PAKISTAN

Abstract

Optimum physicochemical conditions have been identified for the removal of ^{60}Co from nuclear industry and reactor effluents by using a naturally available lateritic minerals (LM) mixture. The adsorption behavior of ^{60}Co on an LM from aqueous solution is reported by describing the effect of equilibration time, temperature, shaking time, hydrogen ions, adsorbent quantity, adsorbate concentration, leaching, and irradiation exposure. The data suggest an effective use of LM for isolation of ^{60}Co from the effluent of reactor/radiochemical laboratories and subsequent long-time storage in reduced solid form.

INTRODUCTION

Extensive growth of the nuclear industry and subsequent influx of radioactive waste in the environment has manifested a great deal of interest in the use of natural sorption materials (*1–4*) to monitor and eliminate the radioactive contaminants resulting from nuclear reactors and radiochemistry laboratories. The utilization of 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 (*5–7*). In addition to their good sorption properties and higher radiochemical and thermal resistance compared to organic exchangers, minerals also have considerable economic importance because of their low cost and availability in abundant quantities (*7–10*). It was established in our earlier communications that mixed minerals of a lateritic nature with major component of iron oxides and hydrous oxides have better utility as an absorbent than do individual minerals (*11*, *12*).

^{60}Co is generally one of the major long-lived radionuclides among the low level activities discharged from nuclear establishments. Many procedures for decontamination of ^{60}Co have been reported: sulfide precipitation, solvent extraction, adsorption with chelex resins, etc. (*13–15*). Most of these procedures are expensive and time consuming, i.e., precipitation normally takes 1–2 days to process 50–100 L seawater. In the present study, the sorption behavior of ^{60}Co radiotracer on naturally occurring lateritic minerals (LM) of known composition has been investigated. The objective of this study was to define the optimum physicochemical conditions of sorption and to evaluate the economic worth of its application.

EXPERIMENTAL

Material Used (LM)

A natural lateritic minerals mixture of known composition containing the minerals given in Tables 1 and 2 was used for the experimental studies. The main minerals constituents were determined by optical microscopy and x-ray diffraction techniques (*16*). The chemical composition was established by using INAA and AEA techniques (*17*, *18*). The minerals mixture was ground and sieved to a particle size ranging from 0.0040 to 0.0058″ (100 mesh fraction) and was used without any treatment (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 were purchased from Amersham Radiochemical Centre, Amersham, England, or were prepared locally by irradiating 10 mg spec-

TABLE 1
Minerals in Mineral Mixture (MM)

Geothite	FeOOH ($HFeO_2$)
Hematite	Fe_2O_3
Limonite	$2Fe_2O_3 \cdot 3H_3O$ $FeO(OH) \cdot nH_2O$
Magnetite	Fe_3O_4
Quartz	SiO_2
Diaspore	$HAlO_2$
Enstatite	$Mg_2(Si_2O_6)$
Saprolite	
Ilmenite	$FeTiO_3$
Olivine	$MgFeSiO_4$
Dolomite	$Ca\text{-}MgCO_3$
Bauxite	$Al_2O_3 \cdot 2H_2O$

TABLE 2
Chemical Composition of Mineral Mixture (MM)

Element	%
Fe	34–41
MgO	6.3–10.5
Al	4.8–9.3
SiO_2	18.5–29.1
Zn	0.14–0.080
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

pure metal salts with thermal neutrons in the PARR-1 research reactor at our institute with a flux of 2×10^{13} $n{\cdot}cm^{-2}{\cdot}s^{-1}$ for an appropriate time. After a suitable cooling time, the target was dissolved in HNO_3, placed in an aqueous medium, and then the radiotracer solution obtained was spiked into a 10% cold cobalt solution.

Sorption Measurement

Sorption was measured by equilibrating the solid adsorbent (LM) of known weight with an aqueous solution of different systems containing a known aliquot of radiotracer of a test element for a specific time. The solution was centrifuged at 5000 rpm for phase separation. The supernatant solution was decanted, and its activity was compared with the activity of the sorbent to calculate the adsorption percentage. The activities were measured with a well-type scintillation counter. The purity of the radiotracer was checked with a semiplanner 30 cm^3 Ge detector (ORTEC Inc) with a CANBERA series MCA hooked to an on-line computer system. 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 pH values of all system were measured by using a glass electrode connected with a Pye model-97 pH meter.

RESULTS AND DISCUSSION

The influence of contact time between sorbate and sorbent on adsorption yields was examined for aqueous solutions by varying the duration of con-

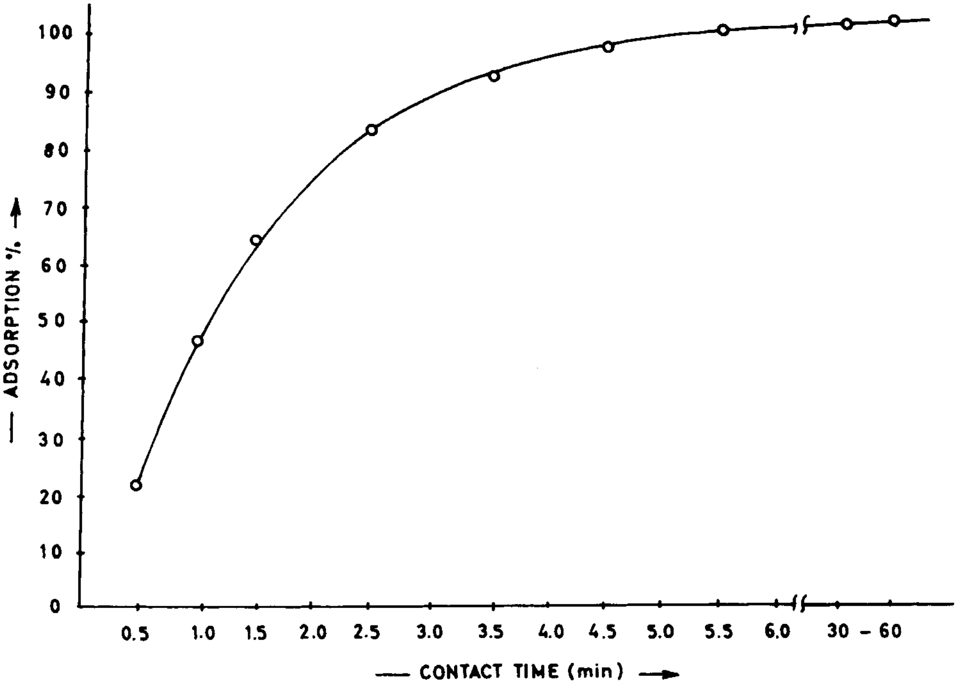

FIG. 1. Percent retention of ^{60}Co on the mineral mixture as a function of contact time.

tact time from 1 to 30 min. Figure 1 shows that the adsorption yield (%) increases sharply from 1–2 min and then attains a constant value of 95%. Therefore, a 2-min contact time of cobalt ion and LM was used for further investigations of the parameters.

The pH of the aqueous solution is an important variable which may control adsorption by the oxide–water interface (*19*). To optimize the adsorption conditions, the behavior was examined in solutions of different pHs (1 to 10). Figure 2 shows the percent adsorption of cobalt as a function of pH. According to the curve, adsorption increases sharply between 2 to 9 pH. A further increase in pH resulted in a decrease of adsorption that could be due to the formation of colloidal species (*20*) which do not undergo complete sedimentation.

The electrolytic concentration has a strong effect on the compact layer and diffuse layer potentiality (*21*), which is why chemical treatment of oxides commonly causes changes in surface properties (*14*, *22*). Studies were conducted to examine the transformation in adsorption behavior of

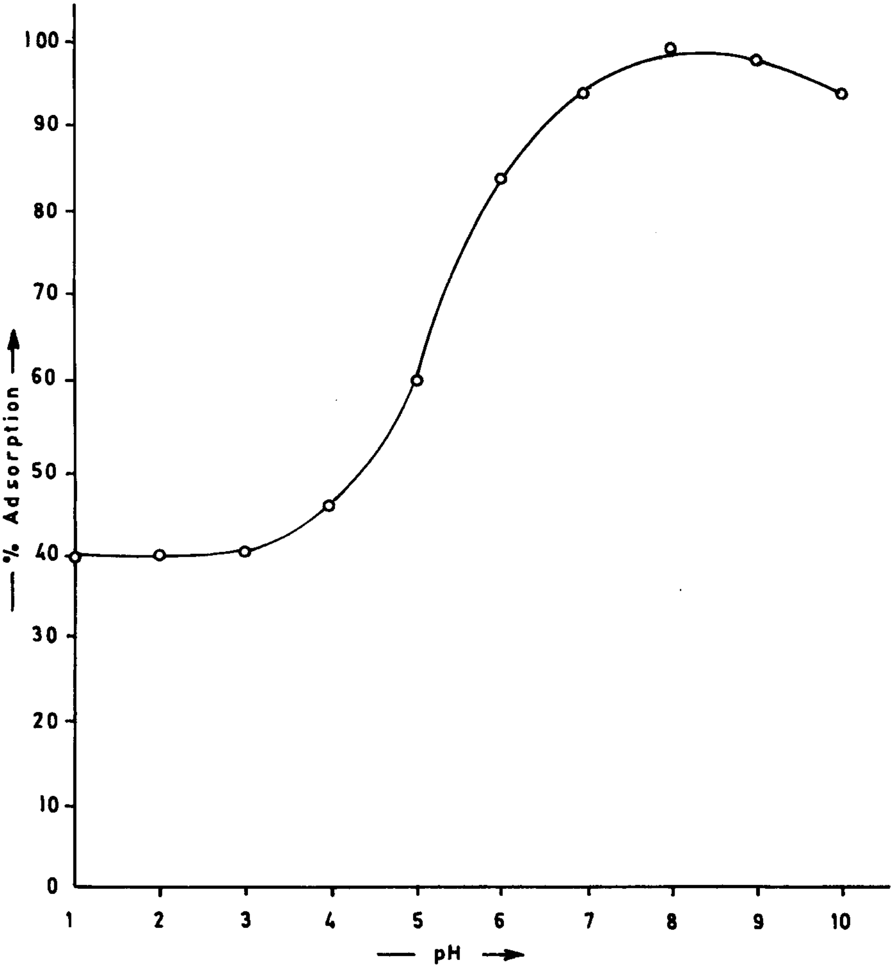

FIG. 2. Percent adsorption of ^{60}Co on the mineral mixture as a function of pH values.

^{60}Co radiotracer from different electrolytes as a function of the concentration of nitric, hydrochloric, perchloric, and sulfuric acid solutions in the 0.01–5 *M* range. The results are recorded in Fig. 3.

Studies were also conducted to examine the effects of adsorption behavior with shaking and stirring time. Figure 4 establishes that stirring and shaking has a relatively small influence on the rate and overall extent of adsorption.

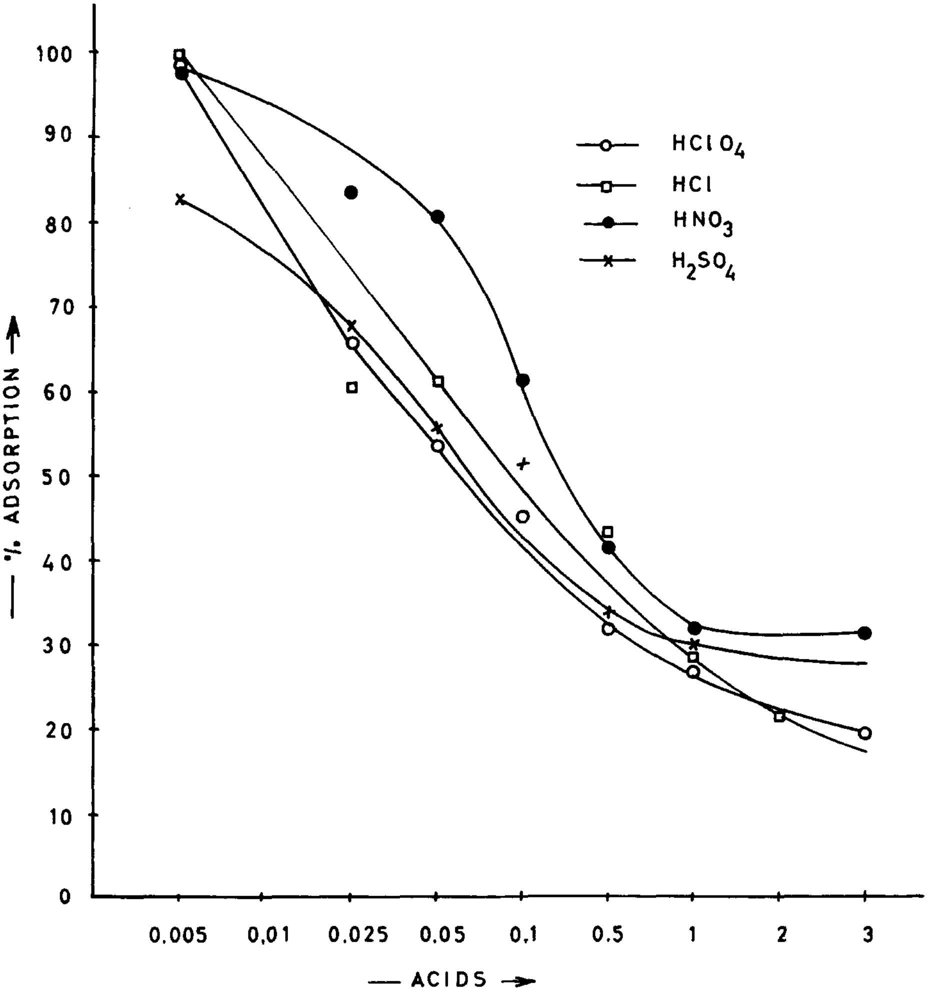

FIG. 3. Percent adsorption of ^{60}Co on the mineral mixture as a function of various acid concentrations.

Several mesh conformations were also investigated. The results, plotted in Fig. 5, show that a fine grain size has high adsorption, which is due to the availability of a larger area for adsorption. Thus, a fine mesh size was selected due to its high adsorption rate.

The effect of varying temperature is shown in Fig. 6.

The effect of additional anions in adsorption was studied from 0.01 *M* HNO_3 acid solution. Anions were added in the form of their sodium and

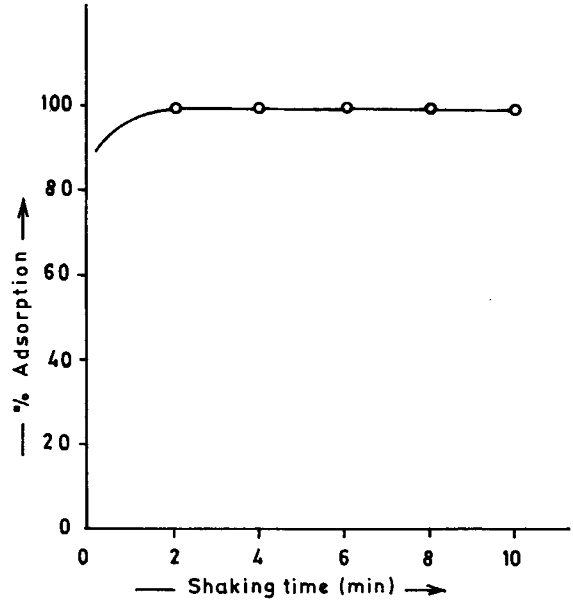

FIG. 4. Percent retention of ^{60}Co on the mineral mixture as a function of shaking time.

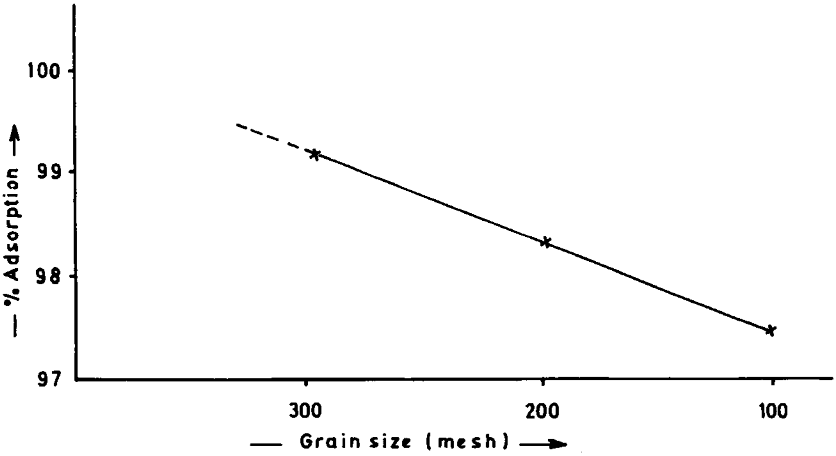

FIG. 5. Percent adsorption of ^{60}Co on the mineral mixture as a function of grain size.

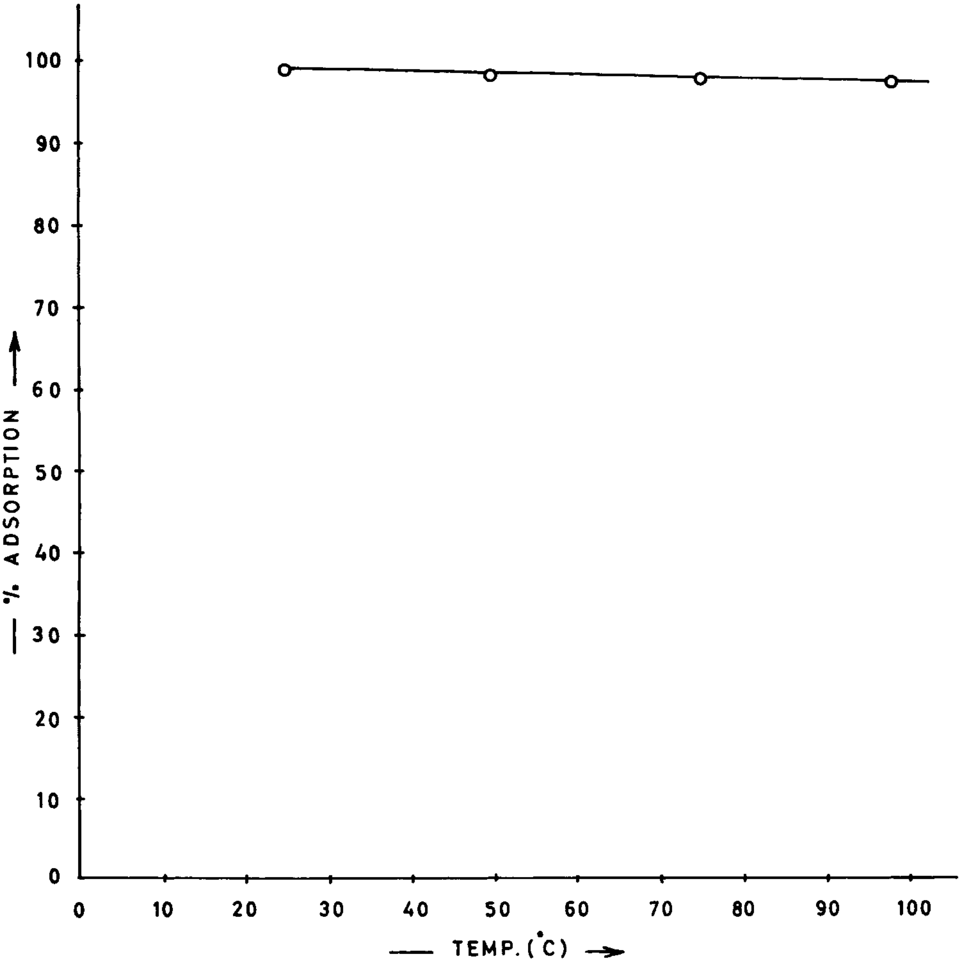

FIG. 6. Percent adsorption of ^{60}Co on the mineral mixture as a function of temperature.

potassium salts. All the anions, including organic complexing anions, do not interfere in the adsorption mechanism. Similarly, adsorption was measured in the presence of foreign cations of different valence stages as nitrates. The decrease in adsorption can be ascribed to the occupation of sites by foreign cations available for adsorption on the adsorbent surface.

The results shown in Fig. 3 indicate that ^{60}Co exhibits maximum adsorption at an acids concentration of 0.01 *M*, which corresponds to pH 2. This also correspond to other elements studied in our earlier publications

(*11*, *12*). It has been reported in the literature that certain elements form hydrolyzed positively charged colloidal species in aqueous medium, while iron-III oxide and iron-III hydroxide minerals (those that are present as major components of LM) possess a negative surface charge at low pH (*21*). It is therefore postulated that fixation may be mainly attributed to the mutual attraction of positively charged elemental species and negatively charged minerals surfaces. The decreasing adsorption trend with increasing acid concentration may be due to the existing competition between the excess H^+ in the medium and positively charged hydrolyzed species. More-

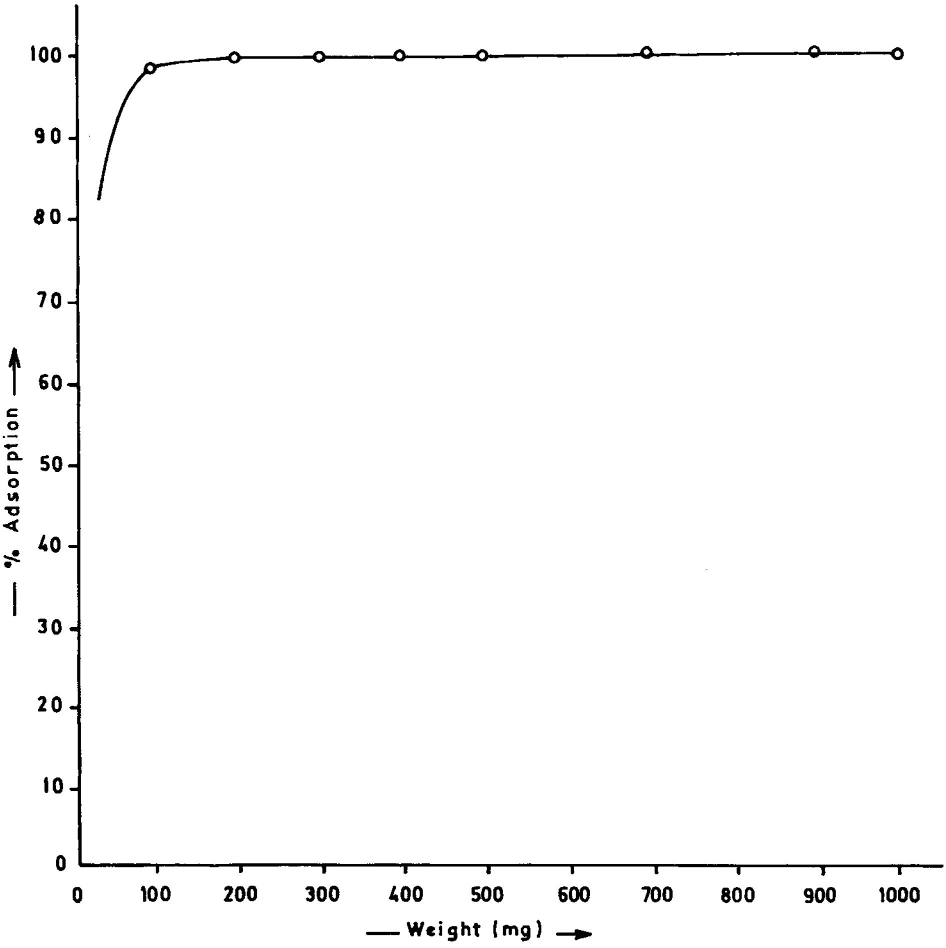

FIG. 7. Adsorption of ^{60}Co for different amounts of sorbent.

over, at higher acid concentrations the hydrolysis of the elements is suppressed, resulting in the low adsorption behavior of ^{60}Co. Similar adsorption in different acid solutions at 0.01 *M* indicates that in any acid solution, ^{60}Co species are essentially not influenced by the nature of the anion present. This characteristic is advantageous as long as the acid concentration is around 0.01 *M*, because liquid waste can be in any medium.

The dependence of ^{60}Co sorption on different amounts of lateritic minerals was studied in the 10 mg to 5 g range, and the results are shown in Fig. 7. The percent adsorption yield increases with an increasing amount of adsorption, reaching a maximum value (100%) at around 200 mg. The percentage adsorption remains almost constant above 200 mg. Therefore, all subsequent studies were carried out with 200 mg LM.

The fast contact time reported earlier (*11*, *12*) established the fact that there is a surface reaction. In fact, this is a hydrolytic adsorption which can be considered to be a simple condensation reaction between the hydrolytic product of the metal ions and the sorbent-carrying OH group. Thus, an oxygen bridge is formed between Fe(III) minerals and the ion (*3*, *22*, *23*). The adsorption variations of ^{60}Co radiotracer with different solution concentrations (10^4–10^2 *M*) were studied to calculate the loading capacity of LM. Figure 8 shows that a loading capacity up to 55 g/kg can be achieved, which is similar to our previous findings under optimum

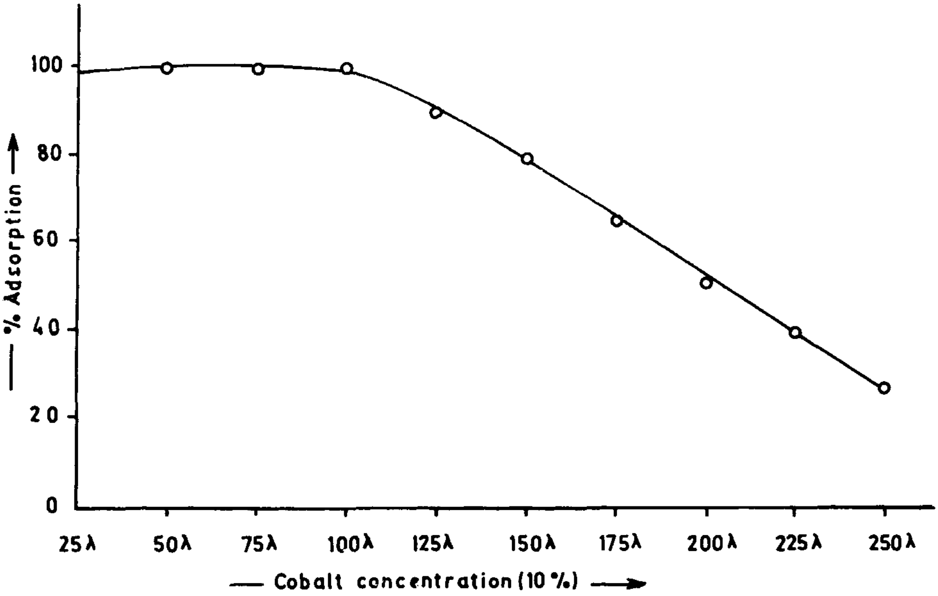

FIG. 8. Percent adsorption of ^{60}Co on the mineral mixture as a function of radiotracer concentration.

conditions. Leaching experiments were performed on pellets made from the loaded adsorbent material, and they were also heated in a furnace at 700°C for one day. The results indicate no leaching. The pellets were also exposed for 1 week to a 4000 Ci ^{60}Co source to observe any radiation damage. After exposure, leaching experiments were repeated, and no change in activity or strength was observed.

In the light of these observations, it is concluded that fixation of ^{60}Co can be achieved in a very short time period in a wide range of pH values without the need for any prior chemical treatment or time-consuming adjustments. This study also shows that untreated, naturally occurring inexpensive minerals can be effectively used for the monitoring and removal of ^{60}Co from nuclear industry effluents. They can also be used for long-term storage in reduced solid brick form.

Acknowledgments

The authors gratefully acknowledge the technical assistance of A. K. Rana, M. Daud, and F. Nahid. We are also grateful to the Reactor Operation Group for arranging the irradiation of the target samples.

REFERENCES

1. B. Kahn, *Environ. Int.*, *4*, 333 (1981).
2. R. E. Jervis et al., *J. Radioanal. Nucl. Chem.*, *110*, 379 (1987).
3. K. H. Lieser, *Sorption and Filtration Methods for Gas and Water Purification* (NATO Advance Study Institute Series), Nardloff, Byden, 1975.
4. S. Music, *J. Radioanal. Nucl. Chem.*, *100*, 185 (1986).
5. Al. Cecal, N. Bilba, and G. Iancu, *Ibid.*, *85* (1984).
6. E. Djurova, I. Slefanova, and G. Grader, *Ibid.*, *30*, 425 (1989).
7. C. A. Mawson, *Processing of Radioactive Waste,* IAEA, Vienna, 1961.
8. C. B. Amphlett, *Treatment and Disposal of Radioactive Waste,* Pergamon, Oxford, 1961.
9. *Proceedings of the Symposium on Monitoring of Radioactive Effluent from Nuclear Facilities,* IAEA, Vienna, 1978.
10. *Use of Local Minerals in Treatment of Radioactive Waste* (Tech. Rep. Ser. 136), IAEA, 1972.
11. S. Ahmad and I. H. Qureshi, *Sep. Sci. Technol.*, *24*, 569 (1989).
12. S. Ahmad and I. H. Qureshi, *J. Radioanal. Nucl. Chem.*, *130*, 347 (1989).
13. C. L. Tsena and J. M. Lo, *Radiochem. Radioanal. Lett.*, *33*, 315 (1978).
14. S. M. Hasany et al., *Int. J. Appl. Radiat. Isot.*, *32*, 747 (1981).
15. C. L. Tsena, M. H. Yang, and C. C. Lin, *J. Radioanal. Nucl. Chem.*, *85*, 253 (1984).
16. S. Ahmad and D. F. C. Morris, *Min. Mag.*, *42*, 143 (1978).
17. S. Ahmad and D. F. C. Morris, *Analyst*, *103*, 17 (1977).
18. S. Ahmad and D. F. C. Morris, *Ibid.*, *102*, 395 (1977).
19. J. Eakins, *Symp. AERE,* Jarwell, UK, 1966.
20. J. A. Davis et al., *J. Colloid Interface Sci.*, *63*, 480 (1979).
21. W. Faubel, *Radiochem. Acta*, *40*, 49 (1986).
22. S. Music, M. Geasener, and R. H. Wolf, *J. Radioanal. Chem.*, *50*, 90 (1979).
23. K. H. Lieser, *Radiochim. Acta*, *40*, 33 (1986).

Received by editor February 8, 1991