Interaction of cesium and strontium with two Indian loams

Z. A. KHAN*, SATYA BRAT* AND B. M. MISRA**
*Waste Management Division and **Desalination Division
Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

Abstract

The sorption and desorption of Cs^+ and Sr^{2+} on a silty loam and a silty clay loam from India were carried out at different times of contact and at different temperatures. The activation energy of uptake E_a and pseudo-thermodynamic parameters ΔH°, ΔG° and ΔS° were calculated. These showed that the silty clay loam immobilised cations more than the silty loam. The cation exchanger in the silty clay loam preferred Cs^+ more than that in the silty loam, whereas Sr^{2+} was preferred more by the silty loam.

Key words: Silty loam, silty clay loam, sorption, desorption, retardation, immobilised, thermodynamic parameters.

1. Introduction

Various ionic and non-ionic substances dissolved in natural aqueous streams as well as industrial, agricultural and domestic effluents interact with the soil while moving through it. Depending on the nature of interaction of these species with the soil matrix, whereby affecting its quality, they are either retained or migrate towards ground-water sources.

A number of investigators[1-10] have reported wide-ranging studies on the uptake and migration of different species in rocks, soils and synthetic minerals. Fission products like Cs^+ and Sr^{2+} are a potential source of ground water/soil pollution from the point of view of radioactive waste management. The details of their interactions with a silty loam and a silty clay loam from India are presented in this paper. Since energy exchange plays a key role in any reaction, the phenomena have been investigated in thermodynamic terms.

2. Materials and methods

2.1 Materials

A silty loam (s. loam) from the Gangetic plain (sampled to six feet depth) and a silty clay loam (s.c. loam) from coastal Maharashtra (to bed rock at five feet depth) were used. The soils were oven-dried at 310 K to ensure moisture content at normal field conditions.

Their general physico-chemical characteristics like silt and clay contents were determined (sedimentation method[11]), organic matter percentage (H_2O_2 oxidation method[12]), cation exchange capacity (Jackson method[12]) and surface area (BET method[13]). Soil minerals were identified[14] by differential thermal, thermogravimetric, X-ray and chemical analyses.

Cs^+ and Sr^{2+} solutions of 10^{-2} M concentration were prepared by dissolving AR grade CsCl and $SrCl_2$ in distilled water. These were respectively tagged with ^{137}Cs and $^{85,89}Sr$. The pH of the solutions was adjusted to around 7.

2.2   Methods

The s. loam and Cs^+-spiked solutions were suspended at a 1:10 solid-liquid (w/v) ratio in eight 250 ml-capacity plastic bottles and shaken in an end-to-end shaker at room temperature (303 K). The shaker was operated at 100 oscillations a minute. After half-an-hour, two bottles were removed, centrifuged at 3000 rpm for 15 minutes and the solid-liquid phases were separated. Distilled water was added to each bottle containing the centrifugate to give a 1:10 solid-liquid ratio. The bottles were vigorously agitated (by hand) for about a minute, then for half-an-hour in the shaker, centrifuged at 3000 rpm and the solid-liquid phases were separated as before. The ^{137}Cs activity in the initial solution, in the reacted supernatant and in the distilled water wash was determined by counting in triplicate with a well type NaI(Tl) gamma scintillation detector attached to a single channel analyzer. Duplicate count rates agreed to within $\pm 1\%$. From these, the sorption and desorption of Cs^+ were calculated, and hence the retention values. The sorption and desorption experiments were repeated at 1, 2 and 4 hours contact time. This process was repeated with the s.c. loam and with the sorption and desorption reactions of Sr^{2+} with both the loams. All the above experiments were repeated at 333 K (± 0.1 K).

2.2.1.   Arrhenius energy of activation and thermodynamic parameters

The Arrhenius energy of activation E_a for sorption can be calculated[15] using the equation $K = Ae^{-E_a/RT}$, by plotting the rate of uptake (K) against $1/T$. Alternatively it can also be calculated by determining the uptake at two temperatures using equations (1), (2) and (3) (Singhal *et al*[16]).

$$F_{T_1} = Ae^{-E_a/RT_1} \tag{1}$$

$$F_{T_2} = Ae^{-E_a/RT_2} \tag{2}$$

$$E_a = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{F_{T_2}}{F_{T_1}} \tag{3}$$

where F_{T_1}, F_{T_2} are uptakes in time t at temperatures T_1 and T_2 respectively, R the universal gas constant, and A another constant.

The sorption and desorption data were treated by equations for both the first- and second-order reactions. Statistical analyses indicated the best fit for the first-order

reaction whose rate constants were calculated using the rate expression

$$K_t(K_1 \text{ or } K_2) = 2.303/t = \log a/a - x$$

where K_1 and K_2 are the rate constants for sorption and desorption respectively, t, the time in seconds, a, the amount of ionic species added, and x, the amount taken up in time t.

The ratio of the reaction rate constants K_1/K_2 gives the equilibrium constant K for the overall sorption and desorption reaction. This enabled us to calculate the pseudo-thermodynamic parameters[17,18] for the physico-chemical equilibrium between the species and the soils. The Gibbs free-energy change $\Delta G''$ was calculated by the equation

$$\Delta G' = -RT \ln K. \tag{4}$$

The standard enthalpy change ($\Delta H''$) was calculated from Van't Hoff isochore

$$\ln K_{I_2} = -\frac{\Delta H}{R} (1/T_2 - 1/T_1). \tag{5}$$

The standard entropy change ($\Delta S''$) was finally determined from the relationship:

$$\Delta G'' = \Delta H'' - T \Delta S''.$$

3. Results and discussion

3.1 Characterisation of soils

Some physico-chemical properties of the soils are given in Table I. It is concluded from mineralogical studies that the s. loam contains mostly amorphous silica and crystalline silica resembling quartz along with traces of illite and montmorillonitic structures, while the s. c. loam contains about 30% montmorillonite and the remainder as amorphous and crystalline silica.

Table I
Physico-chemical characteristics of the loams

	s. loam	s.c loam
Sand (<2000, >60 micron)%	55·00	10·91
Silt (<60, >2 micron)	36·55	52·14
Clay (<2 micron)	8·15	36·95
Organic matter (%)	0·59	8·01
CEC (μeq/g)	163·30	474·80
Surface area (m^2/g)	78·30	396·80
Surface charge density (μeq/m^2)	2·09	1·20

3.2 *Sorption, desorption and retention*

From the physico-chemical and mineralogical characteristics of the soils, it is
expected[5, 19, 20-22] that there will be more sorption of Cs^+ and Sr^{2+} on the s.c. loam than
on the s. loam.

Figures 1 and 2 show percentages sorption and desorption of Cs^+ and Sr^{2+} with
respect to their amount in original solution by the s. and s.c. loams, respectively, at
different times of contact and at the two temperatures. It is seen that at the selected solid-
liquid ratio, the sorption of Cs^+ is around 48 and 83% for the s. and s.c. loams, res-
pectively, at 303 K and 55 and 86% at 333 K. It is further noted that desorption in
both the soils increases slightly with the rise in temperature resulting in less retention.
This indicates that interaction of Cs^+ in both the soils is governed by ion exchange
phenomenon followed by trapping in the lattice of illitic structure.

The sorption of Sr^{2+} by s. and s.c. loams at 303 K is around 14 and 58% respectively,
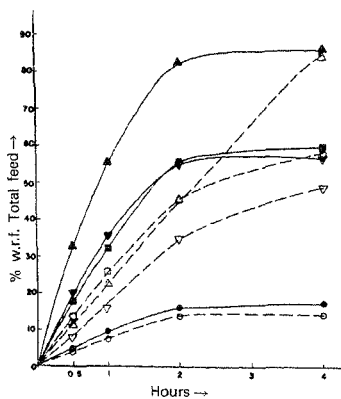but at 333 K, it increases marginally to around 17% for the s. loam and remains almost

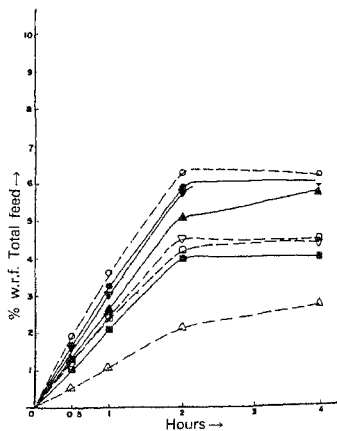FIG. 1   Uptake of Cs^+ and Sr^{2+} by the soils

FIG. 2.   Leaching of Cs^+ and Sr^{2+} from the soils.

	Cs^+-Silty	Cs^+-Clayey	Sr^{2+}-Silty	Sr^{2+}-Clayey
303 K	▽	△	⊙	⊡
333 K	▼	▲	●	■

constant for the s.c. loam. The desorption is found to decrease slightly with the rise in temperature, more so in the case of s. loam. Thus, there is more retention at the higher temperature. It appears that both chemisorption and adsorption are equally contributing towards total adsorption. With the rise in temperature, the increase in the value of the first is balanced by the decrease in the value of the second. The higher sorption of Cs^+, compared to Sr^{2+}, is probably due to its ionic size, ionic potential, chemical activity[23] and more electro-positivity[24,25].

3.3 Energy of activation for sorption and pseudo-thermodynamic parameters

The Arrhenius energy of activation (E_a) for the sorption of Cs^+ and Sr^{2+} by the soils near the equilibrium stage (4 hours contact time) was found to be:

$$Cs^+ - s.c. \text{ loam} > Sr^{2+} - s.c. \text{ loam} > Cs^+ - s. \text{ loam} > Sr^{2+} - s. \text{ loam}$$
$$0.014 \qquad\qquad 0.038 \qquad\qquad 1.063 \qquad\qquad 1.336$$

(all in K cal/mol)

Thus, the ease of reaction of Cs^+ and Sr^{2+} with both the soils will be in the above order. The E_a values indicate that Cs^+ and Sr^{2+} will interact well with both these soils. The values of E_a in all the four cases are too small as compared to those reported by Singhal et al[16] and others[26]. This is possible as the virgin soils used in our studies contain organic matter and broken bonds on their surfaces. On treatment with any chemical, both these are usually removed and thus more energy is involved in the interaction phenomenon.

The sorption and desorption reactions could be regarded as equilibrium processes, the point of equilibrium being dictated by the relative energies of the reactants and the products. These could therefore be defined in terms of thermodynamic quantities. Since it is difficult to eliminate diffusion completely, particularly at macro and micro levels in the soil systems[27] and as our experimental conditions are chosen to resemble field conditions, we could calculate only pseudo-thermodynamic parameters with the help of reaction rate constants of uptake and leaching near equilibrium conditions. The pseudo-thermodynamic parameters for the interaction of Cs^+ and Sr^{2+} with the soils are given in Table II.

It is noted that apparent equilibrium constant (K) is greater than unity in all the cases, indicating that both Cs^+ and Sr^{2+} will interact well with the soils and sorption in all the cases is faster than desorption. The values of the equilibrium constants for $Cs^+ - s.c.$ loam are greater than for $Cs^+ - s.$ loam; thus Cs^+ will react more with the s.c. loam than with the s. loam.

The value of K for $Cs^+ - s.$ loam is greater at 333 K than at 303 K, a fact in accordance with ΔH° and ΔG° values at the two temperatures. $K_{333} < K_{303}$ is observed in the case of interaction of $Cs^+ - s.c.$ loam, which is exothermic reaction. The K values for $Sr^{2+} - s.c.$ loam are many times higher than for $Sr^{2+} - s.$ loam and are found to increase with rise in temperature in accordance with the endothermic nature of

Table II
Thermodynamic parameters of interaction

Soil	Cations	$\triangle H^\circ$ K cal/ mol	303 K			333 K		
			K Equilibrium constant	$\triangle G^\circ$ K cal/ mol	$\triangle S$ cal/ mol/degree	K Equilibrium constant	$\triangle G^\circ$ K cal mol	$\triangle S^\circ$ cal/ mol/degree
S. loam	Cs⁺	1 641	5 845	− 1·063	8·924	7 473	− 1·330	8·922
	Sr²⁺	1·496	1 880	− 0·380	7·459	2 352	− 0·566	7·105
S. c. loam	Cs⁺	− 3·797	13·665	− 1·573	− 7 340	7·741	− 1·354	− 7·336
	Sr²⁺	1·933	8·520	− 1 289	10·634	11·380	− 1·609	10·637

interaction. Sr^{2+} will therefore interact more with s.c. loam compared to s. loam and the rise of temperature will enhance the interaction in both the cases. The K values, *i.e.* $\triangle G$ values, further indicate that sorption of Cs^+ and Sr^{2+} on the soil surface at the two temperatures is in the order:

$$Cs^+ - s.c. \text{ loam} > Sr^{2+} - s.c. \text{ loam} > Cs^+ - s. \text{ loam} > Sr^{2+} - s. \text{ loam at } 303 \text{ K};$$

$$Sr^{2+} - s.c. \text{ loam} > Cs^+ - s.c. \text{ loam} > Cs^+ - s. \text{ loam} > Sr^{2+} - s. \text{ loam at } 333 \text{ K}.$$

As $\triangle G^\circ = -RT \ln K$, the above is obvious. The negative values of $\triangle G^\circ$ indicate the possibility of spontaneity of interaction[28] in all the cases. However, with the $Cs^+ - s.$ loam, $Sr^{2+} - s.$ loam and $Sr^{2+} - s.c.$ loam, it is spontaneous only at the higher temperature (+ve $\triangle H^\circ$, − ve $\triangle G^\circ$ and +ve $\triangle S^\circ$). On the other hand, the $Cs^+ - s.c.$ loam interaction is always spontaneous as indicated by the negative values for all the three parameters. The magnitude of $\triangle G^\circ$ values in the range − 0·380 to − 1·609 K cal/mol further indicates the dominance of adsorption in the interaction of Cs^+ and Sr^{2+} with the loams.

4. Conclusions

Adsorption, absorption and ion exchange all contribute to the interaction of Cs^+ and Sr^{2+} with soils, which is generally dominated by diffusion in normal field conditions. However, the contribution of the three factors varies depending upon the physico-chemical and mineralogical characteristics of the soils and the nature of the interacting species. The values of the thermodynamic parameters evaluated indicate that Cs^+ will interact more with these formations as compared to Sr^{2+}. The magnitude of $\triangle G^\circ$ values indicate the dominance of adsorption in the interaction of Cs^+ and Sr^{2+} with the loams. Silty clay loam as compared to silty loam provides a better retardation for the immobilisation of these waste species. The quality of ground water will be more affected by these species in silty loam formation as compared to the silty clay loam. Thermodynamic studies because of the diffusion phenomena can only give an approximate idea about the behaviour of these species in soil-water systems.

References

1. ANDERSSON, K., TERSTENFELT, B AND ALLARD, B.   *IAEA-SM-257/20*, Vienna, 1982, 111–131

2. FOWLER, E. B, ESSINGTON, E. H AND POLZER, W. L.   *Soil Sci.*, 1981, **132**, 2–12.

3. SCHWEICH, D. AND SARDIN, M.   *J. Hydrology*, 1981, **50**, 1–33

4. NISHITA, H. AND HAMILTON, M   *Soil Sci* 1981, **131**, 56–61.

5. GOULDING, K. W. T. AND TALIBUDEEN, O.   *J. Soil Sci.* 1984, **35**, 397–408.

6. SADIQ, M. AND ZAIDI, T. H.   *Water, air and soil pollutants*, 1981, **16**, 293–299

7. BANSAL, O. P.   *J. Soil Sci.*, 1982, **33**, 63–71.

8. SPARKS, D. L. AND JARDINE, P. M.   *Soil Sci.*, 1984, **138(2)**, 115–122.

9. OGWADA, R. A. AND SPARKS, D. L   *Soil Sci. Soc. Am. J.*, 1986, **50(2)**, 300–305.

10. BRAT, S.   *Indian J. Tech.*, 1985, **23**, 345–347.

11. BAVER, L. D., GARDNER, W. H. AND GARDNER, W. R   *Soil Physics* John Wiley, 1972, p. 40.

12. JACKSON, M. L.   *Soil Chemical Analysis* Asia Publishing House, Bombay, 1962, p. 64.

13. MARSHALL, C. E.   *The physical chemistry and mineralogy of soils*, Vol. I, John Wiley, 1964, p. 189.

14. GRIM, R. E.   *Clay mineralogy* McGraw-Hill, 1968, 125.

15. LAIDLER, K. J.   *Chemical kinetics*, Tata McGraw-Hill, Bombay, 1965, p. 89.

16. SINGHAL, J. P., KHAN, S. AND, BANSAL, O. P.   *Indian J. Chem*, 1978, **16A**, 945–948.

17. MOORE, W. J.   *Physical chemistry*, Orient Longmans, New Delhi, 1969, p. 299.

18. SPARKS, D. L. AND JARDINE, P. M.   *Soil Sci. Soc. Am. J.*, 1981, **45**, 1094–1099.

19. TARE, V. AND BOKIL, S. D.   *J. Environmental Quality*, 1982, **11**, 596–602.

20. GOULDING, K. W. T. AND TALIBUDEEN, O.   *J. Soil Sci.*, 1984b, **35**, 409–420.

21. BROWMAN, M. G. AND SPALDING, B. P.   *J. Environmental Quality*, 1984, **13**, 166–172.

22. WILLIAMS, J, PREBBLE, R. E., WILLIAMS, W. T. AND HIGNETT, C. T.   *Aust. J. Soil Res.*, 1983, **21**, 15–32.

23. BOHN, H. L., McNEAL, B. L.   *Soil chemistry*, Wiley-Inter Science, 1979, p. 117.
    AND O'CONNOR, G. A.

24. ESSINGTON, E. H.,   *Soil Sci*, 1981, **132**, 13 18.
    FOWLER, E. B. AND
    POLZER, W. L

25 POLZER, W L.,   *Soil Sci.*, 1981, **132**, 19 24.
    FOWLER, E. B. AND
    ESSINGTON, E. H

26. GRIFFIN, R A AND   *Soil Sci. Soc. Am. Proc*, 1973, 37, 869 872
    JUTINAK, J. J

27 SKOPP, J.   *J Environmental Quality*, 1986, **15**, 205 213

28 SAMUEL, D. F. AND   *Chemistry of natural waters*, Ann Arbor Science, Michigan, 1981, 66.
    OSMAN, M. A