CATION EXCHANGE CAPACITY, SELECTIVITY AND THE SORPTION COEFFICIENTS OF THE WATER BEARING SOIL MATERIALS AT INSHAS SITE IN EGYPT

N. H. M. Kamel ., A. S. Ibrahim., *H.F. Aly
Radiation Protection Department, Nuclear Research Center, Atomic Energy Authority
P. O. Box 13759 Cairo- Egypt , *Head of Atomic Energy Authority

ABSTRACT

The main source of drinking water in Egypt is the river Nile. Ismailia canal is considered as a part of the river Nile which is a fresh water way , it is adjacent to the Atomic Research Center at Inshas site . The canal water may pass through the soil layers and contribute to the groundwater.

For safety performance assessment of Inshas site, the interaction of dissolved radionuclides in the aqueous phase with the water bearing layer soil materials is very important . The present work dealing with sorption experiments which carried out on natural soil samples at different depths to more than 40 m down the surface of the ground . The soil materials was assumed as a weak cation exchange medium, the interaction of Cs-134 nuclide dissolved in the aqueous phase with natural soil samples was studied. The Cation Exchange Capacity (CEC) for natural soil samples was calculated using ammonia method . Selectivity coefficients of , Na-K, Na-Ca, Ca-K, and Mg-Ca for the exchangeable cations of Na, K, Mg and Ca were calculated. Na was found to be the domain cation in the aqueous phase followed by Ca, Mg, and K.. Sorption coefficients (Rd) of the soil samples was studied at different Cs ion concentrations
(0.0001,0.0005,0.005,0.001,and 0.01 mol/l). The Rd values were calculated for the soil samples from the selectivity coefficients measurements. The calculated values were compared with the results obtained experimentally. The resulting data indicated that, the calculated Rd values from selectivity calculations are in a good agreement with the experimental laboratory measurements.

INTRODUCTION

Groundwater is considered the most probable pathway for radionuclide to reach the biosphere, through different soil layers. Ismailia canal water is a fresh water stream and considered as the main source of groundwater, it is adjacent to the reactor site, Nuclear Research Center, the canal water may be eventually pass through the deep soil layers . In any natural soil-water system, particularly those containing clay minerals, the ion-exchange properties and exchange reactions of the minerals present are of fundamental and practical importance in understanding the water chemistry and the sorption behaviour (1). Water composition changes in soil-water interaction seemed to be indicative of cation exchange reaction. Cs-134 representing one of the hazardous radionuclide present in Low Level Radioactive Waste LLRW . The main parameters governing Cs-sorption are; the cation-exchange capacities of the soil material and the composition of the groundwater. The aim of this work is to study the exchange reaction

of Cs-134 radionuclide dissolved in the canal water with the natural soil mineral (water bearing soil materials) referring to Inshas site, surrounding the Nuclear Research Center NRC under the laboratory conditions using batch technique. Selectivity coefficients for the exchange reaction ,
Na-K, Na-Ca, Ca-K and Ca-Mg in different soil layers depth between 3 to 52 m down the surface of the ground at Inshas site were calculated. Cs distribution coefficient model was determined for the selected soil sample (water bearing soil sample) using experimental data was compared with Cs distribution coefficient determined from both the selectivity coefficient and the cation exchange measurements (1).

MATERIALS AND METHODS

Thirteen soil samples were collected by the Geological Survey Administration (GSA), from the selected drillhole E1/390 at depths between 3 to 52 m (E-1 to E-13) down the surface of the ground. Sample E-10 representing the water bearing layers was found at depth 37 m to 40 m down the surface of the ground. Chemical composition of the major oxides and the lithology of the thirteen soil samples has been previously investigated (2, 3). The natural soil samples were air-dried, thoroughly and grinded. The density of the soil samples was measured using pyknometer and the relative porosity was calculated from the density data measurements (4). The soluble cations were calculated from equilibration the soil sample with canal water, the water phases separated daily, the major cations, Na, K, Mg and Ca in the aqueous phases were measured until concentration of these cations are the same concentrations of the cations in the canal water. The soil samples dried and the Cation Exchange Capacity (CEC) was measured using ammonia method (2, 5). The soil sample (E-10) was sieved through 500, 400, 315, 160, 63, 56, 45, 36 and < 36 μm sieves and the fractional sample is calculated . 15 ml of the canal water filtered through 0.45 μm filter membrane. CsCl solution of concentrations 0.0001 to 0.01 mol/l is prepared using the filtered canal water as solvent traced by Cs-134 isotope, 0.5 g of soil samples was equilibrated in polyethylene bottles with CsCl solution with different concentrations (each sample was duplicated). The bottles were shaken at room temperature (30 ^{o}C) for seven days to attain equilibrium , then filtered through 0.45 μm membrane, the aqueous layer was extracted and was analyzed for the major cations, Na, K, Ca and Mg using liquid ion chromatography DIONEX. Cs-134 remained in the aqueous phases was counted using multichannel analyzers. In parallel some blank samples were also used to check for any looses on the container

RESULTS AND DISCUSSION

The soil mineralogical investigations are given in Table 1, in which , the mean diameter (M.D) in μm , geometrical standard deviation (G.S.D) $\mp \sigma$ for each soil sample were calculated (7). Soil mineralogical analyses shows that it consists of major, coarse and fine sand fractions mixed with minor silt and clay fractions. The data given in Table 1 showed that the percentage of fine sand fractions is higher than that of coarse sand fraction for samples E-1 to E-8. From sample E-8 to E-13 , the coarse sand fractions is more than the fine sand fractions and also the fraction of the fine sand decreased by increasing the sample depth (32- 52 m).

Table 1. The Mineralogy of the Soil Samples of the Borehole E1/390

Sample code No.	Depth (m)	The % Fractional Size Soil Sample				M.D (μm)	G.S. D (± σ)
		Clay (2 <μm)	Silt (2-50μm)	Fine Sand (50-200 μm)	Coarse Sand (> 200μm)		
E-1	3-5	0.85	7	60.09	32.06	27.03	2.39
E-2	4-5	0.6	13	64.44	22.28	16.03	2.58
E-3	9-11	2.64	4	50.06	43.3	28.39	2.53
E-4	12-14	8.57	10.5	45.15	35.78	7.72	3.18
E-5	14-17	6.33	25	52.17	16.5	2.94	3.42
E-6	17-21	3.28	20	50.21	26.51	3.54	3.42
E-7	21-25	3.07	12	64.91	20.02	20.79	2.48
E-8	25-32	0.2	0.25	78.6	20.95	77.64	1.85
E-9	32-37	1.24	8.85	43.5	45.66	8.64	3.1
***E-10**	37-40	3	13.96	38.11	44.93	7.57	3.22
E-11	42-44	1.07	3	34	61.93	37.63	2.57
E-12	44-46	0.39	1	27.97	51.84	0.14	5.66
E-13	46-52	0.25	0.2	20.29	78.32	26.99	2.81

***E-10** is water bearing soil layer, M.D is the mean diameter of the soil sample and σ is the geometrical standard deviation (G.S. D).

The true density of the soil samples ranged from 2.2 to 2.66 g/m^3 and the relative porosity is between 0.26 to 0.42 .

Table 2 gives the physical properties, the density and relative porosity of the soil samples.

The true density of the soil samples ranged from 2.2 to 2.66 g/m^3 and the relative porosity found to be between 0.26 to 0.42 .

The cation exchange capacities CEC of the soil samples were given in the previous work using ammonia method (5), the fractional occupancies of the cations Na, K, Ca and Mg ions was calculated from the CEC measurements and defined as (8)

Table 2 Physical Properties of the Soil Samples

Ample Code	True Density (g/m^3)	Bulk Density (g/m^3)	Relative Porosity
E-1	2.66	1.55	0.42
E-2	2.23	1.56	0.3
E-3	2.56	1.57	0.39
E-4	2.25	1.55	0.31
E-5	2.51	1.59	0.37
E-6	2.41	1.55	0.36
E-7	2.43	1.51	0.38
E-8	2.29	1.55	0.33
E-9	2.19	1.59	0.26
E-10	2.35	1.49	0.36
E-11	2.62	1.59	0.39
E-12	2.46	1.55	0.37
E-13	2.66	1.53	0.42

Fractional Occupancies of ion A=

$$\frac{Equivalen\ \ ion\ \ A\ \ per\ 100\,g\ \ of\ \ Inshas\ Soil\ Sample}{CEC\ (Equivalent\ \ per\ 100\,g\ \ of\ \ Soil)} \qquad \text{(Eq.1)}$$

Reversible cation exchange reaction involving the cations **A** and **B** with valences **za** and **zb**, respectively, can be expressed as;

$$\mathbf{zbxA + za\ B\ =\ za\ xB + zb\ A} \qquad \text{(Eq.2)}$$

where **x** denotes the amount of he exchangeable solid on the surface of the cation exchange medium A. **Kc** is the selectivity coefficient which can be obtained for the reaction (Eq.2) by direct application of the mass- action low:

$$\mathrm{Kc} = \frac{(Nb)^{za}[A]^{zb}}{(Na)^{zb}[B]^{Za}} \qquad \text{(Eq. 3)}$$

where *[A]* and *[B]* are the concentrations of the ions *A* and *B* in aqueous phase (canal water) (mol/l), *Na* and *Nb* are the fraction occupancies of the cations *A* and *B* on the solid phase.

Table 3 gives the concentrations of Na, K, Ca and Mg in natural Ismailia canal water.

Table 3 Major Cations concentrations of the natural Ismailia canal water.

Cation	Concentration (mg/l)	Concentration (mol/l)
Na	30.78	1.34 ×0.001
K	5.44	0.14×0.001
Mg	12.83	1.06×0.001
Ca	28.74	1.43×0.001

Table 4 gives Fractional occupancies of the cations Na, K, Ca and Mg and the calculated selectivity coefficients Kc for the exchange reaction of Mg-Ca, Na-K, Ca-Na and K-Na , for the soil samples E-1 to E-13 respectively, based on the cation exchange capacity(meq/100g) and the aqueous soluble cations concentrations (mol/l) from the interaction of the soil with canal water (given in Table 3) (2, 6).

Table 4. The Fractional Occupancies of the Cations and Selectivity Coefficients

Code No.	**Cation Exchange Reaction**							
	xCa+Mg=xMg+xCa		xK+Na=xNa+K		xNa+Ca=xCa+Na		xCa+K=xK+Ca	
	N(Mg)	Kc	N(Na)	Kc	N(Ca)	Kc	N(K)	Kc
E-1	0.03	0.11	0.63	4.67	0.33	1.06	0.01	98.57
E-2	0.06	0.23	0.58	1.2	0.35	1.32	0.05	9.13
E-3	0.07	0.34	0.64	6.04	0.28	0.85	0.01	159.68
E-4	0.09	0.49	0.66	6.85	0.24	0.68	0.01	193.21
E-5	0.1	0.61	0.56	0.52	0.23	1.1	0.11	1.54
E-6	0.12	0.7	0.65	4.5	0.22	0.68	0.02	85.87
E-7	0.15	0.77	0.56	3.63	0.27	1.04	0.02	75.47
E-8	0.15	0.67	0.51	2.12	0.31	1.46	0.03	30.91
E-9	0.19	0.96	0.5	1.36	0.27	1.36	0.04	13.38
E-10	0.28	0.96	0.29	0.81	0.39	5.95	0.04	14.11
E-11	0.16	0.41	0.29	1.43	0.53	8.06	0.02	43.81
E-12	0.2	0.91	0.47	1.39	0.29	1.64	0.04	15.77
E-13	0.26	0.71	0.23	0.31	0.5	12.5	0.08	3.18

The fractional occupancies given in Table 4 showed , that , Na is the domain cation for all investigated soil samples, followed by Ca, Mg and K. The calculated values of selectivity coefficients Kc of Na-K exchange reaction is greater than one for all soil samples except samples E-5 and E-10, this means that majority of the soil samples are more selective toward Na ion than K ion . and the values of selectivity coefficient KC of the exchange reaction for K-Na of samples E-9 to E-12 (close to the groundwater layer) is close to 1 indicating that this soil sample has no selectivtivity preference toward Na or K ions at this depths (32 to 46 m down the surface of the ground). Selectivity coefficients of Ca-Na reaction for smples E-1 to E-9 is close to unity, while it is found greater than unity for samples E10 to E-13 , indicating that these soil samples are more selective for Ca ion starting from the water bearing layer soil sample (E-10) and downward till the depth 52 m from the surface of the ground. Selectivity coefficient for Mg-Ca reaction is near unity at water bearing soil layer sample (E-10) which means that the sample has no selective preferred for Mg or Ca ions at this layers.

The reported selectivity coefficients values in the literature for the ion exchange reactions of Ca-Na for montomorillonite is 0.04-0.51, illite 0.033-0.44 and soils is 0.01-25 and selectivity coefficient for Ca-Mg for montmorillonite is 0.59-0.9 and soils is 0.59-4.9 (8, 9) which were in the same range of the experimentally obtained values for Kc.

As a result of the interaction of Cs-radionuclide dissolved in the groundwater along the water bearing soil layers, the mineral composition of the soil and the groundwater will changed. Cs exchange reaction using aqueous Cs concentrations of 0.0001 to 0.01 mol/l dissolved in the canal water with water bearing soil sample (E-10) was investigated. Cs sorption by the soil sample can be affected by the competitive effects of the monovalent cations of Na and K and the divalent cations of Ca and Mg present in the canal water. Selectivity coefficients of the exchange reaction of Cs-Na, Cs-K , Cs-Mg and Cs-Ca was calculated at initial aqueous Cs concentrations ranging from 0.0001 to 0.01 mol/l. Table 5 give the results of the fractional occupancies and the equilibrium cation concentrations of Na, K, Ca and Mg (mol/l) in the liquid phases of sample E-10 (water bearing soil sample) . The calculated selectivity coefficients of this soil sample is given in Table 6.

Table 5 Fractional Occupancies and the Equilibrium Cation Concentrations of Soil Sample E-10

Initial Cs Conc. (mol/l)	Fractional Occupancies (N)					Equilibrium Cation Concentrations (mol/l)				
	Na	K	Ca	Mg	Cs	[Na]	[K]	[Mg]	[Ca]	Cs
0.0001	0.08	0.03	0.27	0.06	0.27	0.0019	0.0003	0.0019	0.0015	0.0032
0.0005	0.08	0.02	0.22	0.04	0.21	0.002	0.0003	0.0018	0.0015	0.0013
0.001	0.16	0.02	0.013	0.02	0.13	0.0026	0.0003	0.0019	0.0015	0.0002
0.001	0.16	0.03	0.08	0.01	0.08	0.0026	0.0004	0.0019	0.0015	0.09
0.01	0.13	0.02	0.02	0.01	0.02	0.0024	0.0004	0.0019	0.0015	0.02

Table 6 The Calculated Selectivity Coefficient of the Soil Sample E-10

Initial Cs Conc. (mol/l)	Cation Exchange Reaction			
	xNa+Cs = xCs+Na	xK+Cs = xCs+K	xMg+Cs = xCs+Mg	XCa+Cs = xCs+Cs
	Selectivity Coefficient (Kc)			
0.0001	2.04	0.78	0.15	0.02
0.0005	4.06	2.5	9.97	8.08
0.005	10.29	8.59	15.28	9.87
0.001	15.6	12.08	6.56	5.71
0.01	19.9	22.45	0.031	0.024

Table 7, gives the calculated selectivity coefficient of the reactions of the monovalent cations of Na and K and the divalent cations of Ca and Mg at different Cs concentrations.

Table 7. Selectivity Coefficients for the monovalent and the divalent cations for Soil Sample E-10

Initial Cs Conc. (mol/l)	Cation Exchange Reaction	
	xNa+K = xK+Na	xMg+Ca = xCa+Mg
	Selectivity Coefficient (Kc)	
0.0001	2.675	0.791
0.0005	2.04	1.1
0.005	2.18	1.1
0.001	1.77	1
0.01	2.06	0.77

At all initial Cs concentrations (given in Table 7), the values of the selectivity coefficients Kc for the reactions between K and Na and nearly a constant value and greater than unity (the soil sample is more selective for K than Na and the selectivity ion, coefficient between Ca and Mg is nearly a unit value, the soil sample has no preference for Ca or Mg ion).

It is well Known from literature that Kc of Cs is affected by the presence of monovalent cation Na and K (1,2) and almost unaffected by the presence of divalent cation (Ca or Mg)

In order to calculate the distribution coefficient Rd for Cs by using the selectivity coefficient model, the fractional occupancies of Cs is NCs could be calculated from Kc(Cs-M) and Kc(Cs-B) and the CEC.

Cs sorbed by exchanging with the monovalent cations $[M^+]$ and divalent cation $[B^{2+}]$, where the monovalent cation

$[M^+] = [Na^+] + [K^+]$ (Eq.1) and ,

the bivalent cations $[B^{2+}] = [Mg^{2+}] + [Ca^{2+}]$ (Eq.2)

In general , selectivity coefficient of Cs exchange with monovalent cation Kc(Cs-M) and the selectivity coefficient of Cs exchange with the divalent cations Kc(Cs-B) can be defined as:

$$Kc(Cs\text{-}M) = \frac{NCs[M]}{NM[Cs]} \quad \text{(Eq.4)} \qquad \text{and } Kc(Cs\text{-}B) = \frac{N^2Cs[B^{2+}]}{NB[Cs]^2} \quad \text{(Eq.5)}$$

where [M] and [B] are the molar concentrations of the monovalent cations Na + K and concentrations of divalent cations of Ca + Mg respectively present in the aqueous phases.

The fractional occupancies of Na, K, Mg and Ca ions on the solid phase were given as

$N_M = N_{Na} + N_K$ (Eq.6) and $N_B = N_{Ca} + N_{Mg}$ (Eq.7)

Kc(Cs-Na) = $\frac{NCs[Na]}{NNa[Cs]}$ (Eq.8) and Kc(Cs-K) = $\frac{NCs[K]}{NK[Cs\}}$ (Eq.9)

therefore

$$N_{Na} + N_K = \frac{NCs}{[Cs]Kc(Cs-Na)}([Na]+Kc(K-Na)[K^+]) \qquad \text{(Eq.10)}$$

The fractional occupancies of the cations can be affected by the water composition and the selectivity coefficient.

Since NCs + NB + NM = 1 (Eq.11)

Assuming that; $\theta 1 = Kc(Cs-B)\frac{[Cs]^2}{[B]}$ (Eq.12)

and,

$$\theta 2 = Kc(Cs-M)\frac{[Cs]}{[M^+]} \qquad \text{(Eq.13)}$$

From Eq.2 –Eq.13, the root of the second order equation obtained is as follows;

$$NCs = \frac{-(\theta 1+\theta 1/\theta 2) \pm \sqrt{(\theta 1+\theta 1/\theta 2)^2 + 4\theta 1}}{2} \qquad \text{(Eq.14)}$$

$$Rd(Cs) = \frac{NCsCEC}{[Cs]} \qquad \text{(Eq.15)}$$

$$Rd = \frac{(C_o - C)}{C}.\frac{V}{m} \quad \text{(m/Kg)} \qquad \text{(Eq.16)}$$

The experimentally determined distribution coefficients Rd of Cs-radionuclide based on (Eq. 16) is compared by that calculated values obtained from the selectivity coefficients model (Eq.15).

where C_O is the initial Cs aqueous concentrations and C is the equilibrium concentrations of Cs in the aqueous phase (mol/l) , V is the volume of the aqueous solution (l), and m is the mass of the soil sample (Kg). Table 8 gives the values calculated for $\theta 1$ and $\theta 2$ and the corresponding fractional Cs occupancies NCs (Eq. 12-Eq.14.

Table 8. The Fractional Occupancies of Cs and the Other Factors .

N(Cs)	$\theta 1$	$\theta 2$
0.48	0.64	2.809
0.44	0.52	2.197
0.28	0.333	0.73
0.2	0.12	0.47
0.06	0.006	0.15

Fig.1 gives the relation between log Rd (l/Kg) for both theoretically calculated from Eq.15, and experimentally derived as a function of aqueous Cs concentration. The values are in a good agreement with the used selectivity model.

CONCLUSIONS

Cs sorption in soil-groundwater systems has been used to predict sorption isotherm for soil at Inshas site. The investigated soil samples consists of major fine and coarse sand mixed with minor clay and silt fractions. The cation exchange capacities of the therteen soil samples had been previously reported.

Sodium was found to be the domain cation present in the selected natural soil samples. The selectivity coefficients for the exchange reaction of, Na-K, Ca-Na, Mg-Ca and Ca-K were calculated. The investigated soil samples were more selective for Na than other cations. As a result of interaction of Cs-radionuclide dissolved in the canal water with soil sample (water bearing layer soil) , the composition of the water and the soil changed. , the soil samples were found more selective for K than Na ion, and it has no selectivity preference for Ca ion or Mg ion. Below the groundwater layer (from 32 to 52 m depth) , the investigated soil samples are more selective for Ca than other cations

The Experimental values of Cs distribution coefficients (Rd) were tested using a theoretical selectivity model , it was found to fit the model.

Cs sorption isotherm (log Rd , l/Kg , as a function of aqueous Cs concentration , mol/l, was found to be non-linear.

REFERENCES

1. M. BRADBURY, B. BAEYENS. "Sorption by Cation Exchange Model into Geochemical Computer Codes"TR 94-11, NAGRA, Switzerland (1994).
2. A. S. IBRAHIM and N. H. KAMEL, Proc. 6th Int. Conf. Advances in Energy and Environment. Cairo -Egypt V2, 621-630 (1998)
3. N. H.KAMEL and A. S. IBRAHIM, Paper accepted for publication ,Tunis, (1998)
4. F. A. GUMBS and B. P. WARKENTIN, Soil Sc.. Soc. Amer. Proc. 40: 28-33 (1976)
5. C. A. BLOCK "Methods of Soil Analysis" Chemical and Microbiological Properties. Part 2. (1995).

6. N. H.KAMEL and A. S. IBRAHIM, Paper under Publication (Cairo-Egypt)
7. J. M. DALLOVAL, "Fine Particle Measurement" New York. (1962)
8. M. H. BRADBURY "Laboratory Investigations in Support of the Migration Experiments at the Grimsel Test Sit" TR 88-23 (1989) Nagra, Switzerland.
9. H. G. M.BRUGGENWERT and A. KAMPHORST. "Soil Chemistry B. Physico-chemical Models"Chapter 5. G. H. Bold (Ed.). Elsevier, Amsterdam, (1982).
10. S. AKSOYOGLU, R. M. CORNELL, S. HASEIBECH, M. MANTOVANI, K. BLEIDISSEL, A. DIERCKX. " Marl Programs Progress report : Sorption of Cesium. Paul Scherre Institute, PSI 90-541 TM-43-90-53 Switzerland .
11. S. AKSOYOGLU, J of Radioanalytical and Nuclear Chemistry, Article, 140No. 2: 301-313 (1990)
12. A. A. TITLYANOVA, Soviet Soil Sci. (Engl. trans.), 12 1313- 1318 (1964)