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MINERAL AND SEDIMENT AFFINITY FOR RADIONUCLIDES

By

A. Sorathesn,^{*} G. Bruscia,^{**} T. T. Tamura
and E. G. Struxness

Abstract

In determining radionuclide sorption by clay minerals, shortcomings in the filtration technique for solid separation and in the contact times selected for testing were noted. Filters were found to have a high affinity for cesium and strontium when these elements are present in tracer-level concentrations. Sorption equilibrium was not established in 24 hours and the contact time was extended to 7 days.

The affinity of the clay minerals illite, kaolinite, montmorillonite and vermiculite for selected radionuclides were established after these shortcomings in the testing procedure were corrected. Illite exhibited a very high affinity for cesium 137 ($K_d = 200,000$ after 7 days contact); none of the clay minerals demonstrated exceptionally high affinity for strontium ($K_d = 4000$ for kaolinite which was the highest measured value). The behavior of cobalt and zirconium-niobium was complicated by the colloidal nature of the elements.

The uptake of the above radionuclides by a composited sample of Clinch River sediment showed that cesium and strontium behaved in accordance with the mineralogic character of the sediment. The sediment sorbed more cobalt than was accountable by the mineral composition; organic matter interactions with the cobalt is thereby suspected.

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Introduction

Since 1943 Oak Ridge National Laboratory has been releasing a portion of its low-level radioactive wastes into White Oak Creek which flows into the Clinch River. These radioactive wastes, after being discharged to the river, are diluted and dispersed downstream and, to some degree, reconcentrated in that environment. One of the reconcentrating agents is the sediment of the Clinch and Tennessee Rivers.^{1,2} It is of interest then to study the sediments to develop an understanding of their role in the accumulation and transport of radionuclides in this fresh water system.

Since fluviatile sediments reflect the composition of the soils from which they are derived and hence the clay minerals of the soils,³ knowledge of the mineral composition of the sediment will permit comparisons of radionuclide uptake of the sediment with that observed in pure minerals. Knowledge of the sorption and retention of radionuclides by pure minerals is particularly important in predicting interactions with sediments of known composition in other river systems or soils.

In addition to tests on the uptake of cesium, cobalt, strontium and zirconium-niobium by the minerals illite, kaolinite, montmorillonite and vermiculite, samples of bottom sediment from the uncontaminated portion of the Clinch River above White Oak Creek outfall were tested for radionuclide uptake. The techniques used in this study are described in detail because of the difficulties encountered.

Description of Samples and Sampling Procedure

River Bottom Sediments. Uncontaminated sediment from the bottom of the Clinch River was used as part of the initial studies. A Peterson dredge, an Ekman dredge, and a brass tube for coring into the river bed, were used to obtain a sample from the bottom of the river at a few places across the stream at CRM 22.5 which is about 2 miles upstream from the mouth of White Oak Creek. It was found that neither of the dredges nor the coring device picked up any of the bottom sediments. The mid-river bottom at this cross section was rocky and the water had scoured away all the clay deposits. The bottom of the river near the banks was more clayey and samples were taken from 3 different locations near the river bank of the stream. These samples were composited into a thick slurry and left to dry at room temperature. A portion of the dried samples was mechanically powdered and passed through a series of sieves ranging from mesh 35, 50, 100, 140, 170, 200 to 325. Only particles of mesh 140 were used in the sorption tests.

For determination of the mineral composition of the clay by x-ray diffraction, the other portion of the dried sample was mixed with water and left to settle for about half an hour before the liquid (with its suspended material) was decanted by pipette and placed on clean, degreased glass slides. Another portion of the decanted liquid was mixed with glycerol and dried on glass slides. Six of the slides so prepared were dried in air at room temperature and the other six were dried in an oven at 100°C over night before they were taken to the x-ray diffractometer for testing.

It was found that the sediment samples consisted of approximately:

60%	ILLITE
15%	KAOLINITE
10 to 15%	VERMICULITE
10 to 15%	QUARTZ

Standard Clays. Since illite, kaolinite and vermiculite were the principal constituents of the Clinch River sediments, standard clays such as those mentioned above and montmorillonite were used for comparison.

The standard clays used were:

ILLITE, Fithian, Illinois, No. 35, 140 Mesh

KAOLINITE, Macon, Georgia, No. 2, 140 Mesh

MONTMORILLONITE (BENTONITE), Clay spur, Wyoming,
No. 26, 140 Mesh

VERMICULITE (BO-B) Traveler's Rest, South Carolina.

With the exception of vermiculite the clays are well-characterized minerals. The vermiculite, which was donated by the Zonolite Company, is only 50% vermiculite, the remainder being biotite.

Tracer Radioisotopes. The radioisotopes used were (obtained from the Isotope Division, ORNL):

Cesium 137

Cobalt 60

Strontium 85

Zirconium-Niobium 95

Cs^{137} and Zr-Nb^{95} isotopes were carrier-free; the specific activity of Co^{60} was 13.6 mc/mg and for Sr^{85} , 8.09 mc/mg. Master solutions were made by mixing each of these isotopes with distilled water separately and in such amounts that the activity in each master solution was between 15,000 and 30,000 c/min/ml. The solutions were counted in a gamma scintillation-well counter at approximately 25% geometry.

Initial Testing Procedures

One gram of each standard clay was mixed with 100 ml of the master solution. The pH of one set of samples was adjusted to pH 6 and the other set of the same mix was adjusted to pH 9. They were shaken vigorously by hand and left standing in temperatures of 4°C, 12°C, and 20°C. After a period of 1 hour the mixtures were strained through Whatman filter paper no. 42 and three-1 ml samples from each of the filtrates were counted in the scintillation counter. The same procedure was repeated after the clays had been in contact with the master solution for a period of 12 hours and 24 hours.

The results obtained showed that the amount of activity removed from the master solutions was very high (80 to 99%), as in the case of illite with cesium and zirconium-niobium, and kaolinite with cobalt, strontium and zirconium-niobium. They also showed that time of contact (between 1 hr and 24 hrs) and temperature (between 4°C and 20°C) had no measurable effect on the capacity of the clays to sorb the radionuclides.

Concentration, Temperature and Time of Contact

Since, in the initial tests, there were only small variations in the clays' sorptive capacities with changes in time and temperature, more reliable data were needed. It was thought that such data could be obtained by lowering the concentration of the mixtures, by letting them stand at room temperature (20°C), and by lengthening the time of contact to 1 hr, 3 days and 7 days. The weight of each clay sample was reduced from 1 gm to 0.5 gm and 0.1 gm and the volume of the master solutions was increased from 100 ml to 200 ml and 300 ml. Table I shows sorption samples for illite and kaolinite due to variation in the concentration of the mixtures. Table II gives the corresponding K_d values. (See 11 for K_d definition).

Filtration Versus Centrifugation

During separation of the solid clay particles from the radioactive master solution by filtration, it was found that the filter paper itself absorbed an appreciable amount of activity from the solution. Various kinds of filters were tested and the results showed that:

Whatman Filter No. 42, 1 layer sorbs 23.2 % Cs;	73.8% Sr.
Whatman Filter No. 42, 4 layers sorbs 87.8% Cs;	74.4% Sr.
Fritted Disc (fine porosity) using vacuum pump sorbs 99.9% Cs;	25.4% Sr.
Millipore Filter (0.45 micron pore size) sorbs 41.1% Cs.	

Table I. Per Cent Radioactivity Sorbed, by Illite and Kaolinite Using Different Isotopes Under Selected Conditions

Clays	pH	Isotope	Concentration	Contact Time		
				1 hr	3 days	7 days
ILLITE	6	Cs^{137}	0.1 gm/100 ml	94.25 $\pm$.23	98.42 $\pm$.20	99.01 $\pm$.24
			0.1 gm/300 ml	89.99 $\pm$.25	97.92 $\pm$.23	98.39 $\pm$.23
	9		0.1 gm/100 ml	96.42 $\pm$.23	98.07 $\pm$.20	98.69 $\pm$.24
			0.1 gm/300 ml	90.48 $\pm$.25	98.60 $\pm$.23	98.55 $\pm$.23
ILLITE	6	Co^{60}	0.1 gm/100 ml	28.98 $\pm$.52	85.49 $\pm$.37	86.43 $\pm$.37
			0.1 gm/300 ml	18.69 $\pm$.82	48.96 $\pm$.31	44.93 $\pm$.31
	9		0.1 gm/100 ml	78.04 $\pm$.19	94.65 $\pm$.35	95.94 $\pm$.35
			0.1 gm/300 ml	70.77 $\pm$.21	66.67 $\pm$.23	65.63 $\pm$.23
ILLITE	6	Zr-Nb^{95}	0.1 gm/100 ml	89.55 $\pm$.19	95.17 $\pm$.18	96.99 $\pm$.18
			0.1 gm/300 ml	83.62 $\pm$.25	90.39 $\pm$.23	94.05 $\pm$.22
	9		0.1 gm/100 ml	94.87 $\pm$.20	92.37 $\pm$.18	92.87 $\pm$.18
			0.1 gm/300 ml	75.99 $\pm$.27	83.92 $\pm$.30	89.08 $\pm$.23
KAOLINITE	6	Co^{60}	0.1 gm/100 ml	81.28 $\pm$.19	86.52 $\pm$.37	87.67 $\pm$.37
			0.1 gm/300 ml	63.91 $\pm$.24	71.54 $\pm$.21	60.91 $\pm$.25
	9		0.1 gm/100 ml	86.70 $\pm$.18	92.17 $\pm$.36	79.41 $\pm$.39
			0.1 gm/300 ml	69.17 $\pm$.22	51.51 $\pm$.29	46.57 $\pm$.32
KAOLINITE	6	Sr^{85}	0.1 gm/100 ml	84.17 $\pm$.17	87.70 $\pm$.17	84.83 $\pm$.55
			0.1 gm/200 ml	62.77 $\pm$.25	67.49 $\pm$.23	66.43 $\pm$.24
	9		0.1 gm/100 ml	72.32 $\pm$.20	79.25 $\pm$.18	73.33 $\pm$.19
			0.1 gm/200 ml	71.24 $\pm$.22	68.55 $\pm$.23	66.27 $\pm$.24
KAOLINITE	6	Zr-Nb^{95}	0.1 gm/100 ml	91.64 $\pm$.18	95.43 $\pm$.18	96.60 $\pm$.15
			0.1 gm/300 ml	89.18 $\pm$.23	94.00 $\pm$.22	94.93 $\pm$.22
	9		0.1 gm/100 ml	86.94 $\pm$.19	90.91 $\pm$.19	91.77 $\pm$.19
			0.1 gm/300 ml	81.73 $\pm$.25	87.03 $\pm$.24	85.82 $\pm$.24

Table II. K_d Values with Different Isotopes Under Selected Conditions

Clays	pH	Isotopes	Concentration	Contact Time		
				1 hr	3 days	7 days
ILLITE	6	Cs^{137}	0.1 gm/100 ml	18,251	62,191	99,516
			0.1 gm/300 ml	26,965	141,010	183,402
	9		0.1 gm/100 ml	26,964	50,799	75,130
			0.1 gm/300 ml	28,522	217,815	205,014
	6	Co^{60}	0.1 gm/100 ml	408	5,891	6,372
			0.1 gm/300 ml	689	2,878	2,447
ILLITE	9		0.1 gm/100 ml	3,554	17,706	23,624
			0.1 gm/300 ml	7,263	5,921	5,728
	6	$Zr-Nb^{95}$	0.1 gm/100 ml	8,567	19,730	38,280
			0.1 gm/300 ml	15,310	28,241	47,437
	9		0.1 gm/100 ml	5,611	12,106	13,041
			0.1 gm/300 ml	9,497	15,659	24,470
KAOLINITE	6	Co^{60}	0.1 gm/100 ml	4,343	6,416	7,115
			0.1 gm/300 ml	3,541	5,028	3,117
	9		0.1 gm/100 ml	6,517	11,781	3,858
			0.1 gm/300 ml	4,486	2,124	1,744
	6	Sr^{85}	0.1 gm/100 ml	5,317	7,132	5,592
			0.1 gm/200 ml	3,372	4,152	3,959
KAOLINITE	9		0.1 gm/100 ml	2,612	3,819	2,750
			0.1 gm/200 ml	4,954	4,358	3,930
	6	$Zr-Nb^{95}$	0.1 gm/100 ml	10,966	20,891	28,423
			0.1 gm/300 ml	24,735	46,973	56,158
	9		0.1 gm/100 ml	6,660	10,004	11,149
			0.1 gm/300 ml	13,423	20,121	18,161

Because of high activity removal by the filter material, the method employed for the separation of this liquid from clay sediments was changed to centrifugation. After the mixtures were prepared and allowed to stand for 1 hr at room temperature, the top liquids were drawn off and centrifuged for 1 hr. The period of one hour was necessary for the separation of the colloidal particles from the liquids, especially in the cases of montmorillonite and kaolinite with cobalt and with other radioisotopes. Longer periods of centrifugation showed no improvement in separation.

The master solutions of cesium, cobalt, strontium, and zirconium-niobium were also separately centrifuged. The cesium and strontium did not show any difference between activity in the supernate and activity in the bottom of the centrifuge tube. However in the cases of zirconium-niobium and cobalt (probably colloidal), activities in the master solutions settled to the bottom of the tubes after centrifugation.

Table III shows the amount of radioactivity removed from the master solution in the bottom of the tubes after one-half hour of centrifugation.

Table III. Per Cent of Radioactivity Removed from Solution Through Process of Centrifugation for One-Half Hour.

<u>ZIRCONIUM-NIOBIUM</u>	pH 6	21.8%	
	pH 9	17.5%	
	pH 7.4	28.8%	(unadjusted pH of mixture)
	pH 7.4	63.3%	
for 1 hr at			
<u>COBALT</u>	pH 6	11.3%	
	pH 9	7.6%	
	pH 5.9	1.0%	(unadjusted pH of mixture)

Two samples of montmorillonite, one of pH 6 and the other at pH 9 were mixed with Zr-Nb and, after 1 hour, centrifuged for another hour. It was found that the amount of activity sorbed by the clay after centrifugation was only 14.4% at pH 6 and 26.3% at pH 9.

Thus, after 1 hr centrifugation, montmorillonite reduced removal by 7.4% to about 48.9% of the activities, depending on the pH and the length of time of centrifugation.

A three-day test also showed that 34.6% of the activity that had been centrifuged to the bottom of the centrifuge tubes had been repelled by the clay at pH 6 and 25.4% at pH 9. (These values were calculated from the amount of activity settled to the bottom at a mean pH of 7.4 and centrifugation time of 1 hour). This behavior shows that Zr-Nb is in a colloidal form at these pHs and suggests that Co is also colloidal.

pH of the Mixtures

The hydrogen ion concentration of each mixture varied with different clays and different radioisotopes. The required pH of 6 and 9 were obtained by adding HNO_3 or NaOH to the mixture. These adjusted pH values were checked after 3-day and 7-day periods and it was found that the pH values gradually changed to their mean values. Thus, pH 6 had changed toward 7 while pH 9 had decreased to about 8 or 7; this behavior is likely due to the buffering capacity of the clays. After 3 days the pH of the mixtures were again corrected to the required values before they were left to stand for the seven-day tests.

Amount of Radioactivity Sorbed by Clays

After establishing the concentration range of the mineral, the volume of radioactive solution to be used, the mineral-solution separation technique, and the sampling procedure with regard to time of contact, the study was carried on routinely. For gamma counting, three-1 ml supernate solution samples were taken from each centrifuged mixture of each clay and each radioisotope in contact for 1 hr, 3 days and 7 days and counted in the gamma scintillation well-counter for 1 minute. Background counts were subtracted and the counts of the 3 samples were averaged. Table IV, V, VI, and VII show the average percentage of activity of Cs, Co, Sr, and Zr-Nb sorbed by the various standard clays and by the river-bottom sediment.

The affinity of the clays to sorb the radioactivity can be expressed in terms of K_d or distribution coefficient value:

$$K_d = \frac{f_c/M}{f_s/V}$$

where:

- K_d = distribution coefficient
- f_c = fraction of activity sorbed by clay in counts per minute
- f_s = fraction of activity left in the solution in counts per minute
- M = weight of clay used in the mixture in grams
- V = volume of master solution used for the mixture in milliliter.

The K_d values are listed in the tables.

Table IV. Per Cent of CESIUM Sorbed by Clays

Standard Clays	Contact Time	% Activity Sorbed		K_d		Weight of Clay Used per ml of Master Solution
		pH 6	pH 9	pH 6	pH 9	
ILLITE	1 hr	89.99±.25	90.48±.25	26,965	28,522	0.1 gm/300 ml
	3 days	87.92±.23	98.60±.23	141,010	217,815	
	7 days	98.39±.23	98.56±.23	183,402	205,014	
KAOLINITE	1 hr	74.23±.28	93.19±.28	2,880	13,691	0.1 gm/100 ml
	3 days	73.96±.25	62.35±.27	2,840	1,656	
	7 days	68.47±.25	51.20±.44	2,171	1,049	
MONIMORILL- ONITE	1 hr	61.20±.34	58.26±.35	1,577	1,396	0.1 gm/100 ml
	3 days	55.14±.34	56.16±.35	1,229	1,281	
	7 days	49.95±.45	50.54±.45	998	1,022	
VERMICU- LITE	1 hr	96.63±.25	95.77±.42	1,433	1,132	1 gm/50 ml
	2 days	99.41±.24	99.64±.24	8,432	14,087	
	8 days	99.60±.24	99.76±.24	12,423	21,155	
RIVER SEDIMENT	1 hr	53.75±.42	61.31±.37	2,326	3,169	0.1 gm/200 ml
	3 days	96.17±.25	96.16±.25	50,152	50,152	
	7 days	97.78±.24	97.64±.24	88,048	82,769	

Table V. Per Cent of COBALT-60 Sorbed by Clays

Standard Clays	Contact Time	% Activity Sorbed		K_d		0.1 gram of Clay Per ml of Master Solution
		pH 6	pH 9	pH 6	pH 9	
ILLITE	1 hr	28.98±.52	78.04±.19	.408	3,554	0.1 gm/100 ml
	3 days	85.49±.37	94.65±.35	5,891	17,706	
	7 days	86.43±.37	95.94±.35	6,372	23,624	
KAOLINITE	1 hr	63.91±.24	69.17±.22	3,541	4,486	0.1 gm/300 ml
	3 days	71.54±.21	51.51±.29	5,028	2,124	
	7 days	60.92±.25	46.58±.32	3,117	1,744	
MONTMORILL- ONITE	1 hr	69.70±.21	56.38±.26	2,301	1,293	0.1 gm/100 ml
	3 days	63.91±.46	45.68±.60	1,771	841	
	7 days	62.36±.46	45.37±.60	1,657	831	
VERMICU- LITE	1 hr	70.63±.21	72.87±.21	120	134	1 gm/50 ml
	2 days	98.63±.16	84.62±.18	3,606	275	
	8 days	98.96±.16	89.80±.18	4,737	440	
RIVER SEDIMENT	1 hr	46.44±.33	71.91±.22	1,734	5,120	0.1 gm/200 ml
	3 days	93.34±.17	82.38±.19	28,017	9,354	
	7 days	97.28±.17	85.12±.18	71,567	11,445	

Above results were calculated from Centrifuged Master Solution.

Table VI. Per Cent of STRONTIUM-85 Sorbed by Clays

Standard Clays	Contact Time	% Activity Sorbed		K_d		0.1 gram of Clay per ml of Master Solution
		pH 6	pH 9	pH 6	pH 9	
ILLITE	1 hr	23.42±.62	31.67±.45	306	316	0.1 gm/100 ml
	3 days	26.69±.54	41.05±.34	364	696	
	7 days	26.88±.54	43.17±.33	368	760	
KAOLINITE	1 hour	62.77±.25	71.24±.22	3,372	4,954	0.1 gm/200 ml
	3 days	67.49±.23	68.55±.23	4,152	4,358	
	7 days	66.435±.24	66.28±.24	3,959	3,930	
MONTMORILL- ONITE	1 hr	70.85±.20	71.88±.20	2,430	2,555	0.1 gm/100 ml
	3 days	66.88±.21	68.65±.21	2,019	2,189	
	7 days	67.21±.21	68.67±.21	2,059	2,163	
VERMICU- LITE	1 hr	77.45±.22	67.14±.26	172	102	1 gm/50 ml
	2 days	96.95±.19	96.46±.19	1,590	1,364	
	8 days	97.33±.19	98.73±.19	1,821	3,874	
RIVER SEDIMENT	1 hr	21.42±.78	24.79±.67	545	659	0.1 gm/200 ml
	3 days	45.79±.36	63.87±.26	1,690	3,537	
	7 days	41.83±.39	66.80±.25	1,438	4,024	

Table VII. Per Cent ZIRCONIUM-NIOBIUM 95 Sorbed by Clays

Clays	Contact Time	% Activity Sorbed		K_d		0.1 gm of Clay Per ml of Master Solution
		pH 6	pH 9	pH 6	pH 9	
ILLITE	1 hr	83.62±.25	75.99±.27	15,310	9,497	0.1 gm/300 ml
	3 days	90.39±.23	83.92±.30	28,241	15,659	
	7 days	94.05±.22	89.08±.23	47,437	24,470	
KAOLINITE	1 hr	89.18±.23	81.73±.25	24,735	13,423	0.1 gm/300 ml
	3 days	94.00±.22	87.03±.24	46,973	20,121	
	7 days	94.93±.22	85.82±.24	56,158	18,161	
MONTMORILL- ONITE	1 hr	14.45±1.16	26.28±.63	169	356	0.1 gm/100 ml
	3 days	28.74±.57	37.90±.43	403	610	
	7 days	35.24±.46	42.07±.39	544	726	
RIVER SEDIMENT	1 hr	62.83±.32	54.37±.37	3,380	2,383	0.1 gm/200 ml
	3 days	82.69±.25	75.55±.27	9,554	6,181	
	7 days	86.56±.24	79.94±.25	12,886	7,970	

The above results were calculated from counts/ml of Zr-Nb.
Master Solution - well mixed and stirred but not centrifuged.

Discussion

Affinity

1. Cesium 137

An outstanding characteristic of cesium is its strong affinity for illite. The vermiculite samples also show a relatively high affinity for cesium; this is likely due to the biotite impurity in the sample. The biotite may be regarded as being identical to illite in structure. Note, too, that the K_d value of vermiculite may be the lower limit since the percentage sorbed is approaching 100%.

In Table IV, it is seen that illite and vermiculite uptakes for Cs increase with time, whereas with kaolinite and montmorillonite the capacity decreases as the contact time is increased. The bottom sediment also behaved in the same way as did illite and vermiculite.

This variation in uptake can be explained on the structural properties of the clays.⁴ The illite has a c-axis length of about 10.1 Å and is negatively charged, primarily at the internal faces of the cell. The size of the Cs ion is large compared to the size of the gaps existing between the cells of the illite, and Cs, being large, can be polarized and can enter the narrow gaps of the illite cells. Other radionuclides such as Sr, Co and Zr do not behave in this manner. Thus, when sufficient contact time is allowed, Cs will gradually work its way into the illite. It was known that the standard illite used in these experiments was not 100% pure. Indication through x-ray diffraction showed that there was

some montmorillonite impurity in it.

The vermiculite sample was about 50% pure and contained some percentage of illite.

The kaolinite has a c-axis length of 7.2 Å and the charges are negative, distributed only at the edges of the cells. Its narrow gaps are always closed and the absence of internal negative charges prevents the Cs ions from getting in between the cells. As shown in Table I and IV, kaolinite has less capacity to sorb Cs than illite at the same concentration.

The c-axis of montmorillonite is between 9.8 Å to 18 Å, depending on the number of layers of water sorbed. These wide-open gaps are probably not a desirable quality for Cs sorption; hence, montmorillonite did not sorb as much Cs as kaolinite. The open gaps would not prevent access of other ions to charge sites.

2. Strontium 85

With illite and vermiculite (also kaolinite at pH 6), the uptake for Sr^{85} increases with time, but, with kaolinite at pH 9 and montmorillonite, it decreases as the time of contact is increased. This behavior of strontium may be likened to that of cesium. The Sr would prefer wide-open gaps to narrow passages and, because the negative charges of illite are inside the clay cells (whose c-axis gaps are too narrow for Sr to get into), a much lower percentage of Sr (23.42%) than of Cs (95.25%) is sorbed by illite. Although more contact time was allowed, the increase in sorptive capacity was little improved.

The negative charges in kaolinite are on the edges of the cells making it more accessible for the positive charges of strontium. However, the lower exchange capacity would limit the amount sorbed. Also, strontium ions cannot easily exchange with H^+ ions; hence, the greater the hydrogen ion concentration in the solution (lower pH), the less Sr sorbed.

Montmorillonite showed less specificity for strontium than kaolinite (70.85 : 84.17%) at the same concentration, but these capacities seemed to level off after contact with the master solutions for three days. Since kaolinite has only about 1 to 10% of the capacity shown by montmorillonite, it is surprising that this mineral (kaolinite) sorbs so much strontium. It may be that, in the case of Sr removal, the ion exchange capacity of the clay is less important than the structural property of clays. This behavior is similar to that observed for cesium.

3. Cobalt 60

The sorptive capacity of illite and vermiculite for Co^{60} increases with time - but decreases when mixed with kaolinite and also with montmorillonite. The affinity of kaolinite and montmorillonite for cobalt in the first hour was high compared to that of illite; but it rose to almost the same level when they were left in contact with the mixture for three days or longer.

As mentioned earlier, cobalt behaved like a colloid at pH values between 6 and 9 and was probably in a complex form.

4. Zirconium-Niobium 95

The affinities of illite and kaolinite for Zr-Nb were much higher than that of montmorillonite. The river sediment sorbed a little less than the two former clay minerals. This may be due to the impurities present in the river bottom clay. In all cases, sorption increased with time. The results show that Zr-Nb was of colloidal form, negatively charged and repelled by some of the remaining negatively charged ions in the clay minerals and hydrolyzed, but not ion exchanged. The capacity of all the clays tested to remove these two radionuclides increased with time, suggesting that the Zr-Nb behaved as colloidal particles.

Effect of pH

The per cent of cesium activity sorbed by illite and vermiculite increased slightly when the pH of the mixtures was increased. Cesium can exchange with H^+ ions and better still with Na^+ ions. Thus, when the mixture is more basic (higher pH value), the affinity for cesium becomes greater. However, the major influence on cesium sorption is structure.³

Strontium exchanges with H^+ ions to a very limited degree, but it can replace Na^+ ions more easily. Thus, the higher the H^+ ion concentration or the more acid the mixture becomes, the less the clay can sorb Sr.

For cobalt with illite, the same conclusion may be drawn; but with kaolinite, montmorillonite and also vermiculite, it appears that at higher pH, the sorptive capacity is decreased.

Some peculiarity may be seen in that some percentages of sorption (such as kaolinite with cobalt at pH 6) began to increase from one hour to three days and later dropped to a level lower than it was originally. Perhaps the clay was not able to give up its H^+ ions fast enough to show the right pH at the time it was mixed and measured.

Note that for both cobalt and zirconium-niobium centrifugation removed less activity at pH 9 than at pH 6. This behavior was also noted when clays were added; the possible exception being illite with cobalt and montmorillonite with zirconium-niobium. This behavior of colloids at different pH values is well documented; with increasing hydroxyl concentration, the colloids deflocculate and suspend themselves in the media.

Conclusions

ILLITE - Illite has high specificity for cesium because this clay has the right structural properties. Time of contact between this clay and the radionuclides is important. Illite has very little affinity for strontium, probably due to the narrow spacing of this clay mineral. Time also plays an important role in the removal of Sr. Illite has less affinity for cobalt and Zr-Nb than for Cs.

KAOLINITE - Kaolinite has less affinity for cesium than illite. With an increase in time of contact the capacity to sorb Cs and Co is decreased, but with strontium at pH 6 and Zr-Nb at pH 6 and 9 the results are reversed. Kaolinite has a relatively high affinity for Sr and this is surprising in view of its low ion exchange property.

MONTMORILLONITE (Bentonite) - Montmorillonite has less specificity for Cs than illite and kaolinite even though it has the highest exchange capacity of the mineral tested. The rate of sorption of Cs and also of Co decreases as the time of contact is increased. The capacity of montmorillonite to sorb Sr is less than that of kaolinite (approximately 84% of the kaolinite) but is about 3 times as much as illite, which may be due to the wide spacing between cells of the bentonite. Montmorillonite has a low affinity for Zr-Nb; this may be due to the high negative charge of the clay repelling a negative colloid.

RIVER SEDIMENTS - The bottom sediments of the Clinch River at CRM 22.6 sorbed Cs, Co and Sr, and the per cent absorbed increased with time. The high cesium uptake is due to the high percentage of illite present in the bottom sediments. The higher-than-expected sorption of cobalt and strontium by sediment (on the basis of mineralogic composition) suggests that the sediment contains organic matter with ion exchange properties. The significance of this observation is that studies of this type may well serve to differentiate sorption by minerals and by organic components in sediments and soils.

From the K_d values for the river sediment, the distribution of radionuclides between the sediment and the liquid phase can be calculated over a range of sediment concentrations. It is to be remembered that the K_d value changes with different ionic strengths; at tracer level concentrations pH would be one of the more significant parameters. In Figures 1 and 2 the percentage of the radionuclide on the sediment as a function of the sediment concentration (ppm) and pH is shown. Note that cesium is insensitive to changes in pH; strontium sorption is favorably influenced by increasing pH. As discussed earlier, the lower removal of cobalt and zirconium-niobium at higher pH suggests that the principal mechanism of removal is filtration and not ion exchange. Thus, if the Clinch River contains 30 ppm of sediment of the type used here, over 70% of the cesium would be associated with the sediment but only about 5% of the strontium. Comparing these data with other data now available for the Clinch River sediment, these percentages appear to be in line with the earlier findings.⁵ These preliminary results for the sediment justify further research on K_d determinations of sediments collected at different localities along the Clinch and Tennessee Rivers.

General Observations

1. In considering tracer level sorption by clays, the ion exchange capacity of the clays is not as important a factor as their specificity. For example, consider the cases of cesium with illite and strontium with kaolinite: illite has a very high affinity for Cs and is a medium exchange

Radionuclide Distribution on Sediments as a Function of the Sediment Load in the River Under Different pH Conditions.

Fig. 1.

Radionuclide Distribution on Sediments as a Function
of the Sediment Load in the River Under Different pH
Conditions.

Fig. 2.

clay; kaolinite has high affinity for Sr and is a low exchange mineral.

2. Illite and vermiculite show an increase in sorption with time, while montmorillonite and kaolinite show a decrease in sorption with time. Hence, time is a very important variable in this type of sorption.

3. Zr-Nb and Co behave more like colloids and not as ions at these pH values. Therefore, the nature of the ion form is important.

4. Cobalt and Strontium uptakes by river sediment suggest an influence by the organic matter in the sediments. This should be considered in determining the mechanisms of accumulation and transport of radionuclides in the Clinch River Study.

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