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ADSORPTION EQUILIBRIA BETWEEN EARTH MATERIALS AND RADIONUCLIDES, CAPE THOMPSON, ALASKA

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ABSTRACT

The concept and the derivation of a distribution coefficient are developed. Ion exchange and the nature of competition among cations are given. Distribution coefficients for carrier-free cesium, strontium, and iodine were determined on 17 samples collected during July, 1961, in the vicinity of Cape Thompson, northwestern Alaska. High percentage uptake of these ions was measured under the test conditions. Cesium adsorption, at 1 day, was found to be represented by the mass-action equation. The distribution coefficients for cesium adsorption were so large that, in all but a few cases, very little of this nuclide would remain long in solution in the natural waters of the area. Strontium adsorption was found to be a function of the calcium-plus-magnesium concentration and to be independent of the sodium concentration. In most samples, its equilibrium is reached in less than 1 day. Iodine sorption varied with percent organic matter in the samples. If the iodine were in contact with organic matter for several days, a substantial part of it probably would be removed from solution in the natural waters.

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SOME PRINCIPLES OF ADSORPTION AND ION EXCHANGE

General aspects of the distribution coefficient

When waters containing a dissolved radionuclide come in contact with earth materials some of that radionuclide will be sorbed by the earth material. Such sorption results from a variety of chemical reactions. For example, strontium might become incorporated in insoluble calcium carbonate or calcium phosphate, or it might be attached to clay minerals or decomposing organic matter by ion exchange. Ion exchange is a common mechanism for sorption of ions, because natural materials such as clay minerals and organic matter have high exchange capacities and are widely distributed in nature.

Regardless of the mechanism by which an ion is retained by earth material, the distribution of the substance between water and the earth material can be described by the distribution coefficient K_d, formulated by Tompkins and Mayer (1947). Thus, if f_s represents the fraction of the substance that is sorbed by the earth material and $1-f_s$ represents the fraction remaining in solution, then

$$K_d = \frac{f_s}{1-f_s} \cdot \frac{V}{M}, \qquad (1)$$

where V is the volume of solution in milliliters and M is the mass of earth material in grams.

K_d represents the ratio of the amount of substance sorbed per gram of earth material to the amount of substance per milliliter of solution. The amounts may be expressed in any convenient unit. When $\frac{V}{M}$ is changed, $\frac{f_s}{1-f_s}$ changes but the distribution coefficient, K_d, remains constant (Thompkins and Mayer, 1947). Hence, values of K_d measured at one $\frac{V}{M}$ ratio can be applied to systems having other $\frac{V}{M}$ ratios. For example, for a distribution coefficient of 100, the percent sorbed under changing values of $\frac{V}{M}$ would vary as follows:

V/M	1	10	100	1,000	10,000
Percent sorbed	99	91	50	9.1	0.99

Thus, for a stream with a suspended-sediment concentration of 100 ppm (parts per million) $\frac{V}{M}$ is 10,000, and, under a K_d of 100, only about 1 percent of the radionuclide would be sorbed on the suspended sediment.

Although it remains constant as the ratio of volume of solution to mass of earth material varies, the distribution coefficient, K_d, usually changes as the composition of the solution varies. If the process of radionuclide adsorption is that of ion exchange, the effect of changes in composition of the solution can be predicted from one of the equations describing ion-exchange equilibria. Some of these equations are reviewed below.

Ion exchange and the equilibrium constant

When the exchanging ions have the same valence, all theories of ion exchange yield the same equation. Thus, if adsorbed sodium is replaced by cesium the reaction may be represented by

$$Na^+_{(adsorbed)} + Cs^+_{(solution)} \rightleftharpoons Cs^+_{(adsorbed)} + Na^+_{(solution)} \qquad (2)$$

and the equilibrium constant, K, for the reactions may be expressed by

$$K = \frac{(Cs^+)_a \ (Na^+)_s}{(Cs^+)_s \ (Na^+)_a} \qquad (3)$$

where the brackets represent activities and the subscripts "a" and "s" refer to the adsorbed and solution phases respectively.

The equilibrium constant, K, may be expected to differ according to the type of exchange sites at which the ions are adsorbed--for example, carboxyl groups of organic matter and the surfaces of clay minerals. Unless they are substantial, however, the differences among the values of K for the several types of sites in a given earth material may not be detectable.

Several equations have been proposed to describe the equilibria when the exchanging ions do not have the same valence. For the reaction,

$$2\ \mathrm{Na}_s^{+} + \mathrm{Sr}_a^{++} \rightleftarrows \mathrm{Sr}_s^{++} + 2\ \mathrm{Na}_a^{+}\ , \tag{4}$$

the mass-action equilibrium constant may be expressed as

$$K = \frac{(\mathrm{Sr}^{++})_s\ (\mathrm{Na}^{+})_a^2}{(\mathrm{Sr}^{++})_a\ (\mathrm{Na}^{+})^2_s}\ . \tag{5}$$

For this reaction (4), another equation has been derived by Krishnamoorthy and Overstreet (1949), as follows:

$$K = \frac{(\mathrm{Na}^{+})^2_a\ (\mathrm{Sr}^{++})_s}{(\mathrm{Na}^{+})^2_s\ (\mathrm{Sr}^{++})_a\ (\mathrm{Na}^{+} + 1.5\ \mathrm{Sr}^{++})_a}\ . \tag{6}$$

The equation derived by Eriksson (1952) on the basis of Donnan theory is

$$K = \frac{(\mathrm{Na}^{+})^2_a\ (\mathrm{Sr}^{++})_s\ C}{(\mathrm{Na}^{+})^2_s\ (\mathrm{Sr}^{++})_a\ (\mathrm{Na}^{+} + 2\ \mathrm{Sr}^{++})_a}\ . \tag{7}$$

In these equations the quantities of the ions adsorbed are expressed in moles per gram of exchanger and the concentration of the solution in moles per liter. If the concentration of diffusable anions in the exchanger phase is very small, the factor $(\mathrm{Na}^{+} + 2\ \mathrm{Sr}^{++})_a$ is approximately equal to the exchange capacity C; under these conditions Eriksson's equation (7) becomes identical to equation (5).

Eriksson (1952) also derived an equation based on the Gouy theory of the diffuse double layer. This equation, as formulated by Bolt (1955) expresses the ratio between the sodium adsorbed and the exchange capacity of a sodium-strontium system; thus

$$R = \frac{(Na^+)_a}{(Na^+ + Sr^{++})_a} = \frac{r}{\Gamma\sqrt{B}} \sinh^{-1} \frac{\Gamma\sqrt{B}}{r + 4\, V_c \sqrt{(Sr^{++})_s}} \tag{8}$$

where the amounts of adsorbed ions are expressed in milliequivalents per gram, r is the ratio $\frac{(Na^+)_s}{\sqrt{(Sr^{++})_s}}$ with the concentrations expressed in moles per liter, Γ is the cation-exchange capacity per unit surface area (surface charge density) expressed in milliequivalents per square centimeter, B is a constant equal to 1.06 x 10^{15} centimeters per millimole at 20°C, and V_c is related to the degree of interaction between the clay particles and for most cases can be taken as unity. According to this equation the ratio of sodium to strontium adsorbed is (Lagerwerff and Bolt, 1959)

$$\frac{(Na^+)_a}{(Sr^{++})_a} = \frac{R}{1-R} = \frac{\frac{1}{\Gamma\sqrt{B}} \sinh^{-1} \frac{\Gamma\sqrt{B}}{r + 4\, V_c \sqrt{(Sr^{++})_s}}}{1 - \frac{r}{\Gamma\sqrt{B}} \sinh^{-1} \frac{\Gamma\sqrt{B}}{r + 4\, V_c \sqrt{(Sr^{++})_s}}} \; \frac{(Na^+)_s}{\sqrt{(Sr^{++})_s}} \tag{9}$$

so that

$$\frac{(Na^+)_a}{(Sr^{++})_a} \approx \frac{k\ (Na^+)_s}{\sqrt{(Sr^{++})_s}} \tag{10}$$

This is the Gapon equation, in which k is an "exchange constant."

Bolt (1955) found that experimental results for sodium-calcium exchange on illite could be fitted quite well to this equation using a value of 0.0125 for "k" when the concentrations of the ions in the equilibrium solution were expressed in milliequivalents per liter. In addition, Lagerwerff and Bolt (1959) found that theoretical values of "k" calculated from the double-layer equation, equation (10), agreed well with experimental values for potassium-calcium exchange on montmorillonite but not with those on illite.

Certain clay minerals of the montmorillonite and illite types are known to "fix" potassium, rubidium and cesium. These elements, presumably because of their ionic radii, fit into the hexagonal spaces between silicate layers in such a configuration as to make their removal very difficult. Thus, in the case of potassium-calcium exchange on illite, the theoretical and experimental values of "k" deviated widely, presumably owing to such fixation of potassium by illite. The double-layer equation also has been reported to describe sodium-calcium exchange in soils (Richard and others, 1954). For a large number of soils the exchange constant averaged 0.015.

Competition among cations

Natural water commonly contains several cations; sodium and calcium usually predominate. A radionuclide dissolved in such a water must compete against all these cations simultaneously for exchange sites on earth materials. To simplify consideration of this phenomenon, little error should be introduced ordinarily by treating all the natural monovalent cations as sodium and all the natural divalent cations as calcium. However, this generalization may not be valid when the earth material contains an appreciable amount of clay minerals such as illite, which "fix" potassium in a nonexchangeable form.

Assuming that the Gapon equation (10) with an exchange constant of 0.015 is applicable, the relative competition with radionuclides for exchange sites on earth materials, by sodium and by calcium, can be evaluated. Thus, for an earth material having a cation-exchange capacity of 20 milliequivalents per 100 grams, the percentage of exchange sites occupied by sodium among several concentrations of sodium and calcium, would be as follows:

Composition of solution (equivalents per million)		Percent sodium saturation
Calcium	Sodium	
0.04	0.2	2
.2	.2	1
1.0	1.0	2
2.0	2.0	3

In natural fresh waters of the area considered later in this report, the concentration of all cations generally is less than 4 epm, and in most of them the concentration of calcium is greater than that of sodium. According to the preceding calculation, therefore, less than 3 percent of the exchangeable cations should be sodium. Evidently the adsorption of radioactive cations onto earth materials depends primarily on the concentration of calcium, or of calcium plus magnesium, in the waters of the area.

The effect of calcium concentration on the distribution coefficient for strontium adsorption under competitive ion exchange can be derived for the reaction

$$Ca_a^{++} + Sr_s^{++} \rightleftharpoons Sr_a^{++} + Ca_s^{++} \tag{11}$$

using the mass-action expression

$$K = \frac{(Sr^{++})_a(Ca^{++})_s}{(Sr^{++})_s(Ca^{++})_a} \tag{12}$$

To ensure that K will be constant the activities of the ions in solution and of those adsorbed must be used. In dilute solutions the activity corrections for strontium and calcium ions will cancel each other; so that the concentrations of the ions may be inserted in the preceding equation. For the adsorbed ions, however, there is no generally acceptable method of calculating activity coefficients. Because of this and other uncertainties--in particular, the possible variation in K for different types of exchange material--it seems advisable and permissible to replace the equilibrium constant, K, with an "equilibrium coefficient," K', and to use concentrations rather than activities, recognizing that K' cannot be expected to remain strictly constant.

For strontium adsorption the equation would be

$$K_d = \frac{f_s}{1-f_s} \cdot \frac{V}{M} = \frac{(Sr^{++})_a}{(Sr^{++})_s} \tag{13}$$

where the ratio $\frac{Sr^{++}_a}{Sr^{++}_s}$ is in milliliters per gram, and

$$K' = \frac{(Sr^{++})_a (Ca^{++})_s}{(Sr^{++})_s (Ca^{++})_a} \tag{14}$$

where the parentheses represent the concentrations of the ions. Then

$$K' = K_d \frac{(Ca^{++})_s}{(Ca^{++})_a} \, . \tag{15}$$

This can be transformed to

$$K_d = \frac{K'C}{(Ca^{++})_s + K' \, (Sr^{++})_s} \, , \tag{16}$$

that is, the sum of the exchangeable cations in which C represents the cation-exchange capacity of the earth material.

$$C = (Ca^{++})_a + (Sr^{++})_a$$

The concentration of strontium in natural waters ordinarily is small and much less than the concentration of calcium; also, the value of K' should not be much greater than unity. Under these conditions, the term K' $(Sr^{++})_s$ relatively is so small that it may be neglected and equation (16) reduces to

$$K_d = \frac{K'C}{(Ca^{++})_s} \tag{17}$$

for a homovalent system such as a calcium-strontium system.

A similar transformation for a calcium-cesium system would start with

$$K_d = \frac{f_s}{1-f_s} \cdot \frac{V}{M} = \frac{(Cs^+)_a}{(Cs^+)_s} \tag{18}$$

in milliliters per gram, and

$$K' = \frac{(Cs^+)_a^2 \quad (Ca^{++})_s}{(Cs^+)_s^2 \quad (Ca^{++})_a} \tag{19}$$

Then

$$K' = \frac{(K_d)^2 \quad (Ca^{++})_s}{(Ca^{++})_a} \tag{20}$$

which, using $C = (Ca^{++})_a + (Cs^+)_a$, can be transformed to

$$(K_d)^2 = \frac{K'C}{(Ca^{++})_s + K' \; (Cs^+)_s^2} \tag{21}$$

As for strontium, the concentration of cesium in natural waters ordinarily is much less than that of calcium and the term $K' \; (Cs^+)_s^2$ may be neglected. Thus, equation (21) reduces to

$$(K_d)^2 = \frac{K'C}{(Ca^{++})_s} \tag{22}$$

In logarithmic form, equation (17) becomes

$$\log K_d = \log K'C - \log \; (Ca^{++})_s . \tag{23}$$

Accordingly: (1) The value of K_d for adsorption of strontium in competition with calcium becomes virtually independent of the strontium concentration and becomes a function of the calcium concentration in the solution and the exchange capacity of the solid-phase material. (2) The K_d for radioactive strontium that may be added to the natural system should not be affected appreciably by the concentration of strontium in that natural system. (3) A plot of log K_d for strontium adsorption against log $(Ca^{++})_s$ should give a straight line with a slope of -1.

Likewise, for cesium adsorption, equation (22) becomes

$$2 \log K_d = \log K'C - \log (Ca^{++})_s \ , \tag{24}$$

which may be rewritten as

$$\log K_d = \tfrac{1}{2} \log K'C - \tfrac{1}{2} \log (Ca^{++})_s \tag{25}$$

Accordingly, a plot of log K_d against log $(Ca^{++})_s$ should give a straight line with a slope of $-\frac{1}{2}$. Hence, variation of calcium concentration in the solution should have even less effect on cesium adsorption than on strontium adsorption.

Adsorption of anions

Just as cations may be adsorbed at negatively charged sites on earth materials, so anions may be adsorbed at positively charged sites. In most soils the capacity to sorb anions is small but in some soils the sorption of anions may be substantial (Thomas, 1960). At certain pH values, iron and aluminum precipitates can form in soils; Schofield (1950) has shown that these precipitates can sorb anions such as chloride under acid conditions. Other sources of positive charge may be broken edges of clay minerals and organic matter. Phosphate ions are strongly retained by most soils through the formation of insoluble iron and aluminum phosphates in acid soils, and calcium phosphates in neutral and alkaline soils. When radioactive anions are adsorbed by anion exchange the adsorption should be dependent on the concentrations of natural anions in the system just as the adsorption of radioactive cations is dependent on the concentration of natural cations.

EXPERIMENTAL WORK

Lamar (1960) summarizes the chemical composition of natural waters in northwestern Alaska as two principal types, low-chloride and high-chloride. The high-chloride waters in the area are mostly sea water or those associated with sea water. This type of water was not considered in these studies. Among the low-chloride waters, (1) total cation concentrations generally ranged from 0.25 to 4 equivalents per million, (2) the ratio of the calcium-plus-magnesium ion concentration to the sodium-plus-potassium ion concentration ranged from 0.33 to 40, and (3) the ratio of bicarbonate ion to sulfate ion ranged from 0.3 to 10.

Nine solutions were prepared to simulate the range in composition of the natural low-chloride waters; their chemical composition is given in table 1. Among these solutions, total cation concentration was 0.2, 1.0, or 4.0 equivalents per million. At each of these three concentrations, the ratio of calcium-plus-magnesium ion concentration to sodium ion concentration was 0.5, 2, or 5.

The salts used for preparing these solutions were calcium sulfate, magnesium sulfate, and sodium bicarbonate. No chloride ion was added to the solutions because only low-chloride waters were simulated. Chloride ion was not expected to have an effect greatly different from that of sulfate and bicarbonate ions on the adsorption of carrier-free cesium, strontium, or iodine by the earth-material samples.

The geology in the vicinity of Cape Thompson has been described by Kachadoorian and others (1960). The information required to plan the sampling of the vegetation and earth materials was drawn from this background material. The samples--of bedrock, talus, soil and tundra--were collected July 8-18, 1961, by Reuben Kachadoorian and A. M. Piper in connection with hydrologic investigation of the area. Locations and characteristics of the samples are presented in table 2.

Table 1.--Composition of solutions, in equivalents per million, used for the measurement of distribution coefficients for adsorption of carrier-free cesium, strontium, and iodine.

Solution number	Calcium (Ca^{++})	Magnesium (Mg^{++})	Sodium (Na^{+})	Total cations	$\frac{(Ca^{++} + Mg^{++})}{(Na^{+})}$	Bicarbonate (HCO_3^{-})	$\frac{(HCO_3^{-})}{(SO_4^{--})}$
1	1.1×10^{-1}	5.4×10^{-2}	3.3×10^{-2}	0.2	5	3.3×10^{-2}	0.2
2	8.9×10^{-2}	4.4×10^{-2}	6.7×10^{-2}	.2	2	6.7×10^{-2}	.5
3	4.4×10^{-2}	2.2×10^{-2}	1.3×10^{-1}	.2	.5	1.3×10^{-1}	2.0
4	5.4×10^{-1}	2.8×10^{-1}	1.1×10^{-1}	1.0	5	2.7×10^{-1}	.2
5	4.4×10^{-1}	2.2×10^{-1}	3.3×10^{-1}	1.0	2	3.3×10^{-1}	.5
6	2.2×10^{-1}	1.1×10^{-1}	6.7×10^{-1}	1.0	.5	6.7×10^{-1}	2.0
7	2.2×10^{0}	1.1×10^{0}	6.7×10^{-1}	4.0	5	6.7×10^{-1}	.2
8	1.8×10^{0}	8.9×10^{-1}	1.3×10^{0}	4.0	2	1.3×10^{0}	.5
9	8.9×10^{-1}	4.4×10^{-1}	2.7×10^{0}	4.0	.5	2.7×10^{0}	2.0

Table 2.--Description and location of samples from vicinity of Cape Thompson

Sample number	Description	Location
61 AKd 1	Limestone from bedrock outcrop	165°48'00"W.,68°06'22"N., Cape Crowbill
61 AKd 2	Limestone talus	165°48'00"W., 68°06'22"N., Cape Crowbill
61 AKd 3	Soil derived from limestone	165°48'00"W., 68°06'22"N., Cape Crowbill
61 AKd 4	Vegetation, sphagnum moss	165°48'00"W., 68°06'22"N., Cape Crowbill
61 AKd 5	Vegetation, includes sphagnum moss and grasses	165°48'00"W., 68°06'22"N., Cape Crowbill
61 AKd 6	Vegetation, chiefly dry	165°48'00"W., 68°06'22"N., Cape Crowbill
61 AKd 7	Vegetation, chiefly moss	165°42'28"., 68°11'33"N.,
61 AKd 8	Vegetation, tussock grass	165°42'28"W., 68°11'33"N.,
61 AKd 9	Wind-blown sand and silt	165°42'28"W., 68°11'33"N.,
61 AKd 10	Silt and sand from frost boil	165°42'28"W., 68°11'33"N.,
61 AKd 11	Vegetation collected from pond in 6 inches of water	165°42'28"W., 68°11'33"N.,
61 AKd 112	Mudstone	165°43'44"W., 68°06'09"N., Chariot site
61 AKd 113	Silt and sand from frost boil	165°43'55"W., 68°06'30"N., Chariot site
61 AKd 114	Do.	165°43'55"W., 68°06'29"N., Chariot site
61 AKd 115	Do.	165°43'56"W., 68°06'28"N., Chariot site
61 AKd 116	Do.	165°43'56"W., 68°06'26"N., Chariot site
61 AKd 117	Do.	165°43'56"W., 68°06'25"N., Chariot site
61 AKd 118	Wind-blown sand and silt from frost boil	165°43'56"W., 68°06'24"N., Chariot site

The organic content of the samples was determined by the procedure of chromic acid oxidation and ferrous sulfate titration (Peach and others, 1947, p. 5). The cation-exchange capacity of the samples was determined by the radio-cesium method (Beetem and others, 1962); results follow:

Sample number	Organic matter (percent)	Exchange capacity (meq/100 g)
61 AKd 3	3.5	23
61 AKd 9	16.2	28
61 AKd 10	16.5	--
61 AKd 11	55.5	40
61 AKd 113	8.6	28
61 AKd 114	5.0	30
61 AKd 115	10.5	26
61 AKd 116	10.6	20
61 AKd 117	7.3	18
61 AKd 118	11.8	24

Distribution coefficients for the sorption of carrier-free cesium, strontium, and iodine were measured on each of the 18 samples of rock, moss, and soils. Ten microcuries per liter of carrier-free cesium-137, strontium-85, or iodine-131 was added to portions of each of the 9 solutions simulating the composition of natural waters near the sample sites. The samples were equilibrated with those solutions and aliquots of the equilibrated solution were removed after 1 day and 6 days. The percent of the radioactive isotope remaining in solution was measured in these aliquots.

Each type of sample (rock, moss, tussock, and soil) was treated in a different manner. Rock samples weighing between 55 grams and 115 grams were placed in polyethylene beakers and equilibrated with 100 ml of solution 1. Moss-sample portions weighing 1 gram (fresh weight) were placed in polyethylene bottles and equilibrated with 20 ml volumes of solutions 1 and 3; these samples were run in duplicate. The tussock was divided into two parts, root-mat and crown. Portions of each, weighing between 21 grams and 46 grams, were placed in polyethylene beakers and equilibrated with 200 ml of solution 2.

Duplicate 1-gram (fresh weight) portions of the soil samples were dried at 110°C for 24 hours and then equilibrated with 20 ml of each of the nine solutions in polyethylene bottles. The dry weights were used in calculating the K_d's. The results for the moss and the tussock were expressed on a basis of fresh-sample weight. The weight of rock samples used for the K_d calculations was on the air-dried basis. The rocks received no special treatment.

The distribution coefficients for the adsorption of carrier-free cesium, strontium, and iodine by these samples, after 1 day and after 6 days, are presented in tables 3-5. They were calculated from equation (1),

$$K_d = \frac{f_s}{1-f_s} \cdot \frac{V}{M}$$

Table 3.--Distribution coefficients for adsorption of carrier-free cesium by J. H. Baker, W. A. Beetem, R. S. Dewar, M. C. Goldberg, R. A. Sample, and J. S. Wahlberg.

Sample number	Description	Solution number								
		1	2	3	4	5	6	7	8	9
					One-day					
61AKd 3	Soil from limestone	6,590	13,000	14,950	1,320	4,320	5,280	2,760	3,350	1,880
61AKd 9	Wind blown silt	2,000	2,620	31,740	3,320	2,620	10,460	1,620	3,750	4,500
61AKd 11	Organic bottom sludge, west pond	3,980	3,570	6,440	1,630	3,620	5,300	2,400	2,750	2,250
61AKd 116	Frost boil	1,640	2,340	4,170	1,730	2,560	2,630	2,150	2,320	3,000
61AKd 4	Moss	594	--	4,040	--	--	--	--	--	--
61AKd 5	Moss	1,520	--	1,650	--	--	--	--	--	--
61AKd 6	Moss	1,780	--	1,240	--	--	--	--	--	--
61AKd 7	Moss	99	--	168	--	--	--	--	--	--
61AKd 8a	Grass	--	8.3	--	--	--	--	--	--	--
61AKd 8b	Root mat	--	164	--	--	--	--	--	--	--
					Six-day					
61AKd 3	Soil from limestone	12,800	10,560	27,460	5,060	14,130	40,160	11,900	21,900	8,200
61AKd 9	Wind blown silt	3,970	5,420	16,550	5,070	7,380	53,130	8,320	8,370	17,300
61AKd 11	Organic bottom sludge west pond	4,320	4,300	5,790	3,170	5,480	14,730	4,140	4,940	2,590
61AKd 116	Frost boil	2,120	3,980	8,620	5,660	9,000	49,130	6,990	9,070	11,180
61AKd 4	Moss	1,820	--	5,540	--	--	--	--	--	--
61AKd 5	Moss	4,160	--	2,640	--	--	--	--	--	--
61AKd 6	Moss	2,200	--	3,380	--	--	--	--	--	--
61AKd 7	Moss	1,370	--	4,150	--	--	--	--	--	--
61AKd 8a	Grass	--	13	--	--	--	--	--	--	--
61AKd 8b	Root mat	--	138	--	--	--	--	--	--	--

Table 4.--Distribution coefficients for adsorption of carrier-free strontium determined by J. H. Baker, R. S. Dewar, R. A. Sample, R. W. Vernon, E. Villasana, and J. S. Wahlberg.

Sample number	Description	Solution number								
		1	2	3	4	5	6	7	8	9
		One-day								
61AKd 3	Soil from limestone	577	697	757	166	222	440	47	55	155
61AKd 9	Wind blown silt	207	496	1,407	91	141	285	22	33	666
61AKd 10	Frost boil	141	305	1,230	55	104	859	14	26	1,980
61AKd 11	Organic bottom sludge, west pond	1,984	2,210	5,360	364	616	12,210	73	131	7,320
61AKd 113	Frost boil	249	425	1,260	66	131	2,150	15	26	1,100
61AKd 114	Frost boil	333	586	1,980	80	130	3,650	20	27	624
61AKd 115	Frost boil	216	371	1,420	54	104	1,450	12	23	1,750
61AKd 116	Frost boil	221	407	1,060	64	118	2,170	14	31	1,210
61AKd 117	Frost boil	282	493	1,480	76	139	2,410	16	31	918
61AKd 118	Wind blown debris off frost boil	227	377	1,100	88	131	1,040	19	29	888
61AKd 4	Moss	1,260	--	3,720	--	--	--	--	--	--
61AKd 5	Moss	696	--	940	--	--	--	--	--	--
61AKd 6	Moss	495	--	631	--	--	--	--	--	--
61AKd 7	Moss	713	--	2,620	--	--	--	--	--	--
61AKd 8a	Grass	--	53	--	--	--	--	--	--	--
61AKd 8b	Root mat	--	86	--	--	--	--	--	--	--
61AKd 1	Limestone	.85	--	--	--	--	--	--	--	--
61AKd 2	Limestone talus	2.8	--	--	--	--	--	--	--	--
61AKd 112	Tiglukpuk rocks	38	--	--	--	--	--	--	--	--
		Six-day								
61AKd 3	Soil from limestone	585	620	914	245	385	730	60	65	3,400
61AKd 9	Wind blown silt	222	222	482	101	124	507	22	39	4,940
61AKd 10	Frost boil	128	142	341	60	107	710	21	32	4,130
61AKd 11	Organic bottom sludge, west pond	992	948	1,190	369	452	4,180	73	127	10,700
61AKd 113	Frost boil	150	205	550	68	115	1,480	16	26	3,100
61AKd 114	Frost boil	236	300	702	85	153	2,700	27	37	2,439
61AKd 115	Frost boil	136	178	480	54	91	3,480	13	22	2,700
61AKd 116	Frost boil	131	190	630	70	118	1,900	18	28	4,100
61AKd 117	Frost boil	230	300	855	80	132	2,100	16	32	3,200
61AKd 118	Wind blown debris off frost boil	150	144	300	75	107	875	22	36	2,200
61AKd 4	Moss	450	--	1,600	--	--	--	--	--	--
61AKd 5	Moss	560	--	930	--	--	--	--	--	--
61AKd 6	Moss	380	--	440	--	--	--	--	--	--
61AKd 7	Moss	348	--	670	--	--	--	--	--	--
61AKd 8a	Grass	--	43	--	--	--	--	--	--	--
61AKd 8b	Root mat	--	98	--	--	--	--	--	--	--
61AKd 1	Limestone	.80	--	--	--	--	--	--	--	--
61AKd 2	Limestone talus	3.1	--	--	--	--	--	--	--	--
61AKd 112	Tiglukpuk rocks	75	--	--	--	--	--	--	--	--

Table 5.--Distribution coefficients for adsorption of carrier-free iodine determined by J. H. Baker, R. S. Dewar, R. A. Sample, R. W. Vernon, E. Villasana, and J. S. Wahlberg.

Sample number	Description	Solution number 1	2	3	4	5	6	7	8	9
		One-day								
61AKd 3	Soil from limestone	4.5	12	7.2	14	7.0	12	2.8	6.5	4.7
61AKd 9	Wind blown silt	95	22	12	30	45	53	20	42	56
61AKd 10	Frost boil	16	11	1[illegible]	11	12	24	8.5	14	11
61AKd 11	Organic bottom sludge, west pond	235	71	150	97	122	188	31	240	66
61AKd 113	Frost boil	6.4	10	3.4	16	7.8	7.1	5.6	3.6	3.5
61AKd 114	Frost boil	1.9	3.3	.9	5.6	3.4	1.2	2.6	1.5	1.6
61AKd 115	Frost boil	1.9	10	.0	5.8	3.5	2.8	2.4	1.6	2.0
61AKd 116	Frost boil	7.6	12	4.1	13	6.8	11	6.0	4.6	7.2
61AKd 117	Frost boil	3.6	9.4	4.1	12	4.4	5.4	4.4	2.2	3.2
61AKd 118	Wind blown debris off frost boil	22	8.1	10	21	14	47	18	8.1	9.4
61AKd 4	Moss	68	--	26	--	--	--	--	--	--
61AKd 5	Moss	67	--	64	--	--	--	--	--	--
61AKd 6	Moss	40	--	23	--	--	--	--	--	--
61AKd 7	Moss	26	--	21	--	--	--	--	--	--
61AKd 8a	Grass	--	8.4	--	--	--	--	--	--	--
61AKd 8b	Root mat	--	2.7	--	--	--	--	--	--	--
61AKd 1	Limestone	.29	--	--	--	--	--	--	--	--
61AKd 2	Limestone talus	.12	--	--	--	--	--	--	--	--
61AKd 112	Tiglukpuk rocks	.04	--	--	--	--	--	--	--	--
		Six-day								
61AKd 3	Soil from limestone	51	216	216	232	60	75	12	52	11
61AKd 9	Wind blown silt	1,090	345	976	448	1,090	862	58	881	630
61AKd 10	Frost boil	159	92	277	1,040	139	274	60	133	53
61AKd 11	Organic bottom sludge, west pond	3,970	1,900	2,450	3,440	3,100	2,070	1,100	4,050	1,950
61AKd 113	Frost boil	50	80	73	100	34	58	12	20	86
61AKd 114	Frost boil	14	26	16	28	24	7.2	12	12	14
61AKd 115	Frost boil	14	32	19	23	16	19	6.4	9.0	26
61AKd 116	Frost boil	40	126	56	90	38	54	12	30	93
61AKd 117	Frost boil	29	113	38	94	40	40	10	13	19
61AKd 118	Wind blown debris off frost boil	273	218	175	260	20	115	198	175	89
61AKd 4	Moss	282	--	267	--	--	--	--	--	--
61AKd 5	Moss	540	--	568	--	--	--	--	--	--
61AKd 6	Moss	288	--	233	--	--	--	--	--	--
61AKd 7	Moss	728	--	905	--	--	--	--	--	--
61AKd 8a	Grass	--	23	--	--	--	--	--	--	--
61AKd 8b	Root mat	--	4.1	--	--	--	--	--	--	--
61AKd 1	Limestone	.60	--	--	--	--	--	--	--	--
61AKd 2	Limestone talus	1.2	--	--	--	--	--	--	--	--
61AKd 112	Tiglukpuk rocks	.017	--	--	--	--	--	--	--	--

DISCUSSION OF RESULTS

Adsorption of cesium

The distribution coefficients for adsorption of cesium by several samples showed large experimental scatter. However, as suggested by equation (25'), in theory they should be a function of the square root of the calcium-plus-magnesium ion concentrations. Figure 1 is a plot of the logarithms of the 1-day cesium distribution coefficients against the logarithms of the calcium-plus-magnesium ion concentrations. Lines of best fit have a slope of $-\frac{1}{2}$. Figure 2 is a corresponding plot of the 6-day cesium distribution coefficients. The two plots suggest that, for the adsorption of cesium on these particular earth-material samples, the mass-action equation defines a limiting case, at least.

Values of the equilibrium constant (K') were computed from equation (22) for samples 61 AKd 3, 61 AKd 9, 61 AKd 11, and 61 AKd 116 and for certain clay minerals (after Wahlberg and Fishman, in press). These values are:

Material	Equilibrium constants (K')	
	1-day	6-day
61 AKd 116	2,100 - 72,100	3,610 - 3,720,000
61 AKd 9	2,190 - 128,000	8,750 - 3,400,000
61 AKd 11	4,360 - 50,000	5,610 - 171,000
61 AKd 3	6,220 - 78,500	62,800 - 5,220,000

American Petroleum Institute standard clays	Equilibrium constant (K')
Kaolinite no. 4	2,000
Montmorillonite no. 21	7,700
Montmorillonite no. 11	82,200
Halloysite no. 12	5,260,000

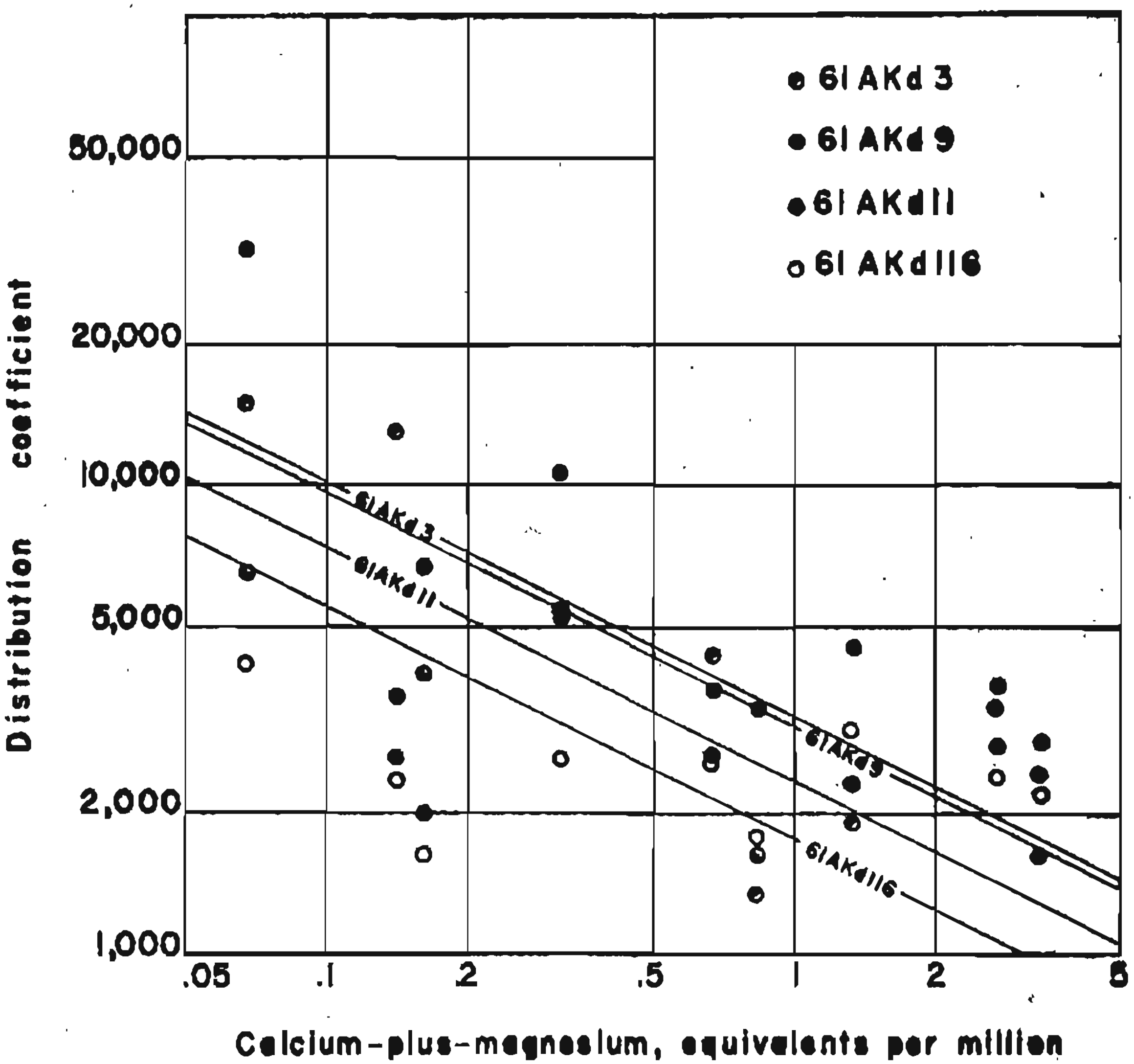

Figure 1.—— Distribution coefficients for cesium adsorption v. calcium-plus-magnesium ion concentration after one day

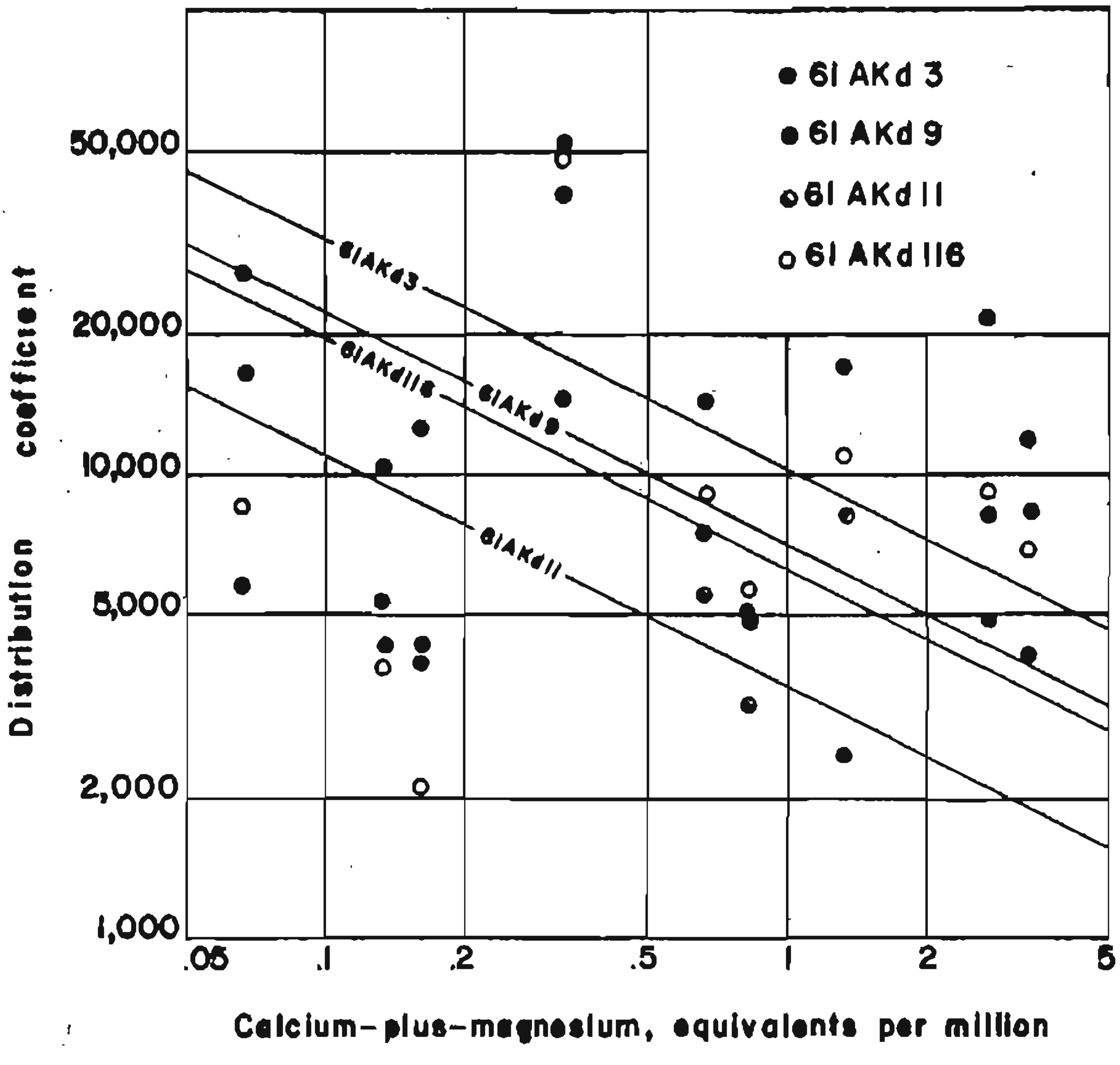

Figure 2.—— Distribution coefficients for cesium adsorption v. calcium-plus-magnesium ion concentration after six days

The above values of K' for the earth-material samples from Alaska range about as widely as those for "standard clays." For the earth materials, the relatively large increase between 1 day and 6 days can be best explained through "fixation" of cesium by 2:1 clay minerals. In such minerals, a small fraction of the adsorbed cesium is slowly converted to a nonexchangeable form, the mass-action equilibrium does not apply to that fraction, and a new distribution is established for the residual exchangeable cesium. At any given time, therefore, only a pseudoequilibirum exists. With passage of time, the percentage of cesium sorbed continues to increase. Given enough time for the "fixation" to proceed to completion, the amount of cesium adsorbed by 2:1 (montmorillonite-illite) clay minerals will depend only upon the cesium concentration and will be independent of the calcium-magnesium concentration.

Table 6 illustrates the relative removals of cesium in 1 day for several $\frac{V}{M}$ ratios of earth material to solution. Thus, under field conditions equivalent to those of the one-day tests, the movement of cesium ions through or over earth material will be slow indeed.

Table 6.--Percentage of carrier-free cesium removed from solution in one day

Sample number	Solution number	Sample weight (g)	Volume of solution (ml)	K_d	Percent Cs removed		
					$\frac{V}{M}$ as in laboratory	$\frac{V}{M} = 1$	$\frac{V}{M} = 100$
61 AKd 3	1	0.79	20	6,590	99.6	99.98	98.5
61 AKd 11	1	.17	20	3,980	96.9	99.97	97.5
61 AKd 116	1	.75	20	1,640	98.8	99.94	94.3
61 AKd 1	1a/	55.5	100	3.0	62.2	75.0	2.9
61 AKd 2	1a/	107.5	100	6.7	87.8	87.0	6.3
61 AKd 112	1a/	72.0	100	26.4	95.0	96.4	20.9
61 AKd 5	1	1.0	20	1,520	98.3	99.93	93.8
61 AKd 7	1	1.0	20	99	82.4	99.0	49.7
61 AKd 8a	2	35.5	200	8.3	51.7	89.2	7.7
61 AKd 8b	2	35.5	200	164	96.7	99.4	62.1

a/ The solution containing cesium that was equilibrated with the rock samples had a pH of 3.

Adsorption of strontium

Figures 3 and 4 show respectively the 1-day and 6-day distribution coefficients for strontium adsorption on samples 61 AKd 3, 61 AKd 11, and 61 AKd 117 v. the calcium-plus-magnesium concentration. The dashed lines in the two figures were calculated from the theoretical relation, by modifying equation (17) to

$$K_d = \frac{K' C}{(Ca^{++})_s + (Mg^{++})_s} \quad . \tag{26}$$

The equilibrium constant was assumed to be unity; the exchange-capacity values were those listed on page 14. These theoretical lines (dashed) and the lines of best fit (unbroken) agree in slope; this agreement shows, as would be expected, that strontium adsorption from the solutions was independent of the sodium concentration. Calculation of the sodium-adsorption ratio (Bower and others, 1954, p. 26) for these solutions indicates that negligible amounts of sodium would be adsorbed. Hence, sodium ions in the solutions would not be expected to influence strontium adsorption. Although strontium adsorption by the organic bottom sludge (61 AKd 11) was almost exactly as predicted from equation (26), the results for most samples from frost boils were lower than would be predicted from that equation. The reason for this difference is not known.

Adsorption of strontium from solutions 6 and 9 was greater than would be expected from the results from the other seven solutions. The results from solutions 6 and 9 may be in error although no source of error has been isolated.

The adsorption of strontium was rapid and the reaction was apparently complete after 1 day. In the more dilute solutions, however, the distribution coefficients after 6 days were less than after 1 day. This is likely the result of soluble substances dissolving from the earth material and then replacing adsorbed strontium. The results for the more concentrated solutions, except solution 9, did not change with time.

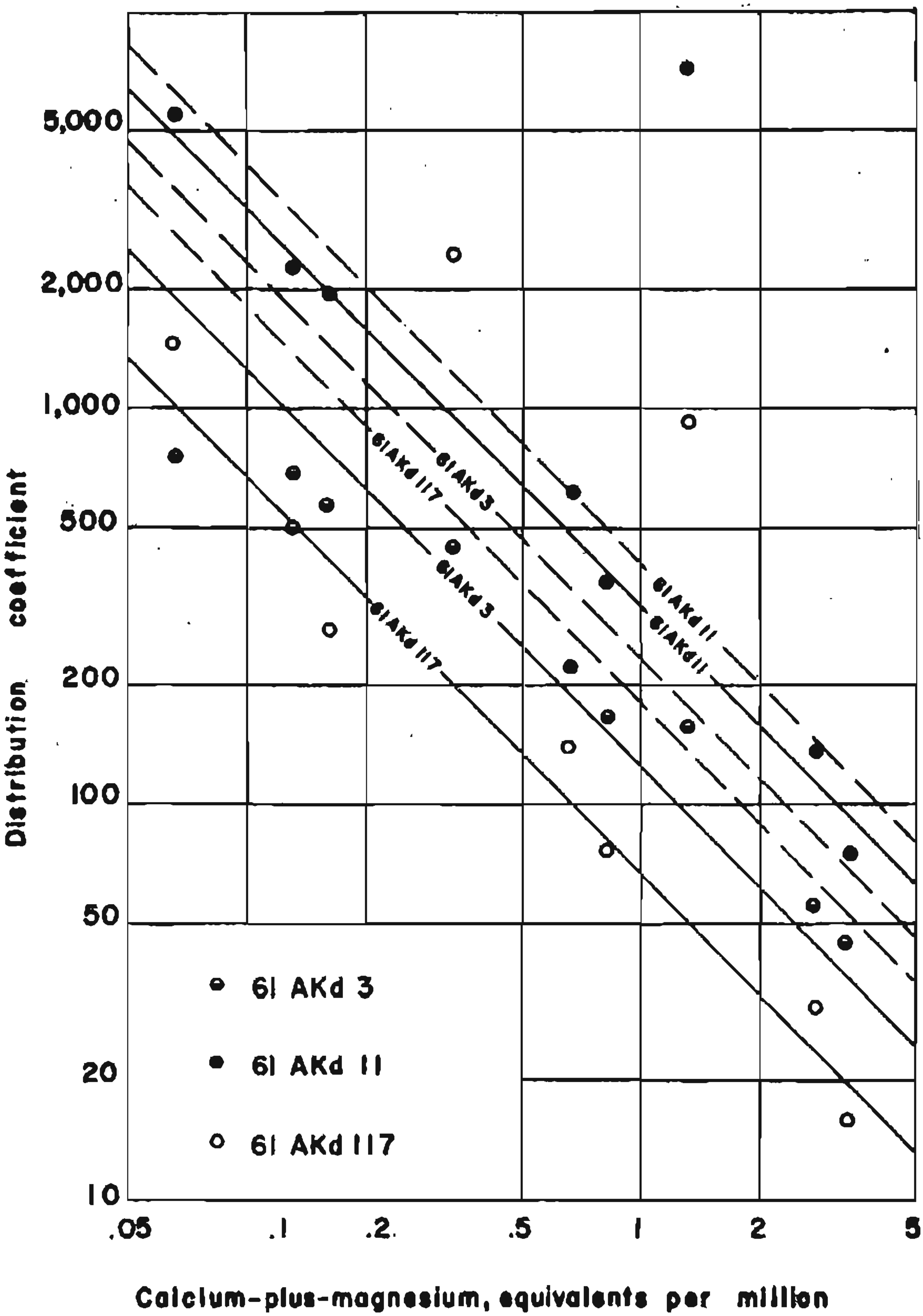

Figure 3.—— Distribution coefficients for strontium adsorption v. calcium-plus-magnesium ion concentration after one day

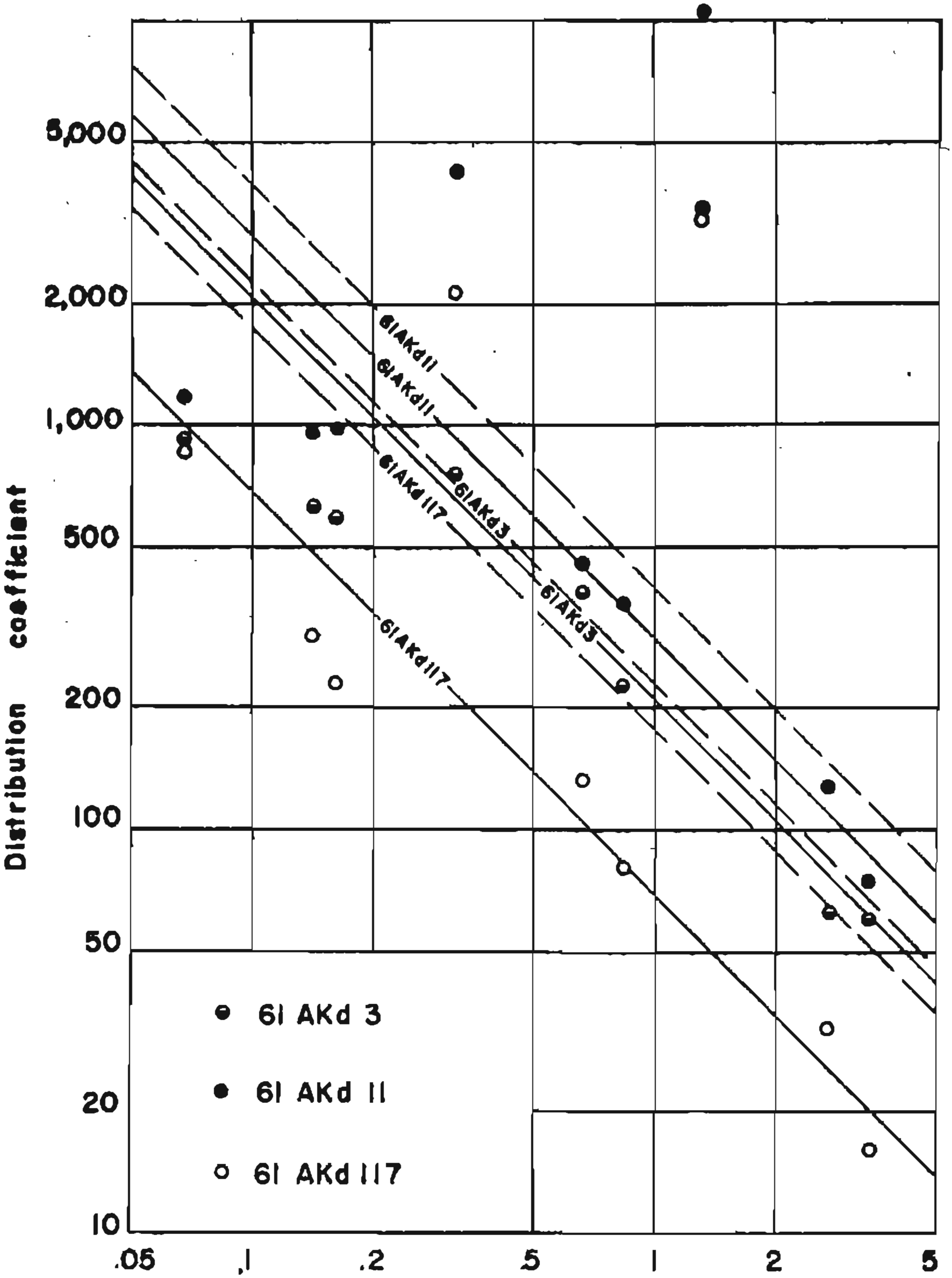

Figure 4.-- Distribution coefficients for strontium adsorption v. calcium-plus-magnesium ion concentration after six days

The distribution coefficients for adsorption of strontium by the rocks were smaller than those for the other materials, probably because the surface-to-volume ratio of the rock samples was relatively small. Even so, the sample of the Ogotoruk rock (61 AKd 112) weighing 87 grams removed 97 percent of the strontium from 100 milliliters of solution in 1 day and 73 grams of the limestone talus (61 AKd 2) removed 67 percent of the strontium from 100 milliliters of solution in 1 day. Table 7 shows the percentage removal of carrier-free strontium in one day by all the samples tested--at the $\frac{V}{M}$ ratio of the tests, $\frac{V}{M} = 1$, and $\frac{V}{M} = 100$.

Adsorption of iodine

The adsorption of iodide ions by the soil samples did not vary systematically with solution composition, and the distribution coefficients for many of the samples increased approximately tenfold between one day and 6 days. The samples of moss and organic sludge (AKd 5 and AKd 11) had relatively high distribution coefficients. Figure 5 plots the percent organic matter in 10 samples against mean 1-day distribution coefficient for iodine sorption; figure 6, against the 6-day values. Both figures show a definite relation between adsorption of iodine ions and organic content of the samples. Two reactions may be involved: (1) anion exchange at a limited number of sites on the earth-material samples, and (2) fixation of part of the iodine by reaction with organic matter. In the first reaction, the K_d would depend on total anion concentration, so that a plot similar to figure 3 should show whatever interdependency exists. In the second reaction, the K_d would be nearly independent of concentration of the solutions but would depend on percent organic matter, lapse of time, and temperature. The adsorption of iodine from solutions probably combines the two reactions, with the second becoming dominant with passage of time. Table 8 further shows the effects of reaction time.

Table 7.--Percentage of carrier-free strontium removed from solution in one day

Sample number	Solution number	Sample weight (g)	Volume of solution (ml)	K_o	Percent Sr removed		
					$\frac{V}{M}$ as in laboratory	$\frac{V}{M} = 1$	$\frac{V}{M} = 100$
61 AKd 3	1	0.79	20	577	95.7	99.8	85.2
61 AKd 11	1	.17	20	1,080	94.4	99.95	95.2
61 AKd 116	1	.75	20	221	88.5	99.6	68.8
61 AKd 1	1	94.0	100	.85	44.4	45.9	.8
61 AKd 2	1	73.0	100	2.8	67.1	73.7	2.7
61 AKd 112	1	87.5	100	38	97.1	97.4	27.5
61 AKd 5	1	1.0	20	696	97.2	99.9	87.4
61 AKd 7	1	1.0	20	713	97.2	99.9	87.7
61 AKd 8a	2	26.3	200	53	87.5	98.1	34.6
61 AKd 8b	2	30.0	200	86	92.8	98.8	46.2

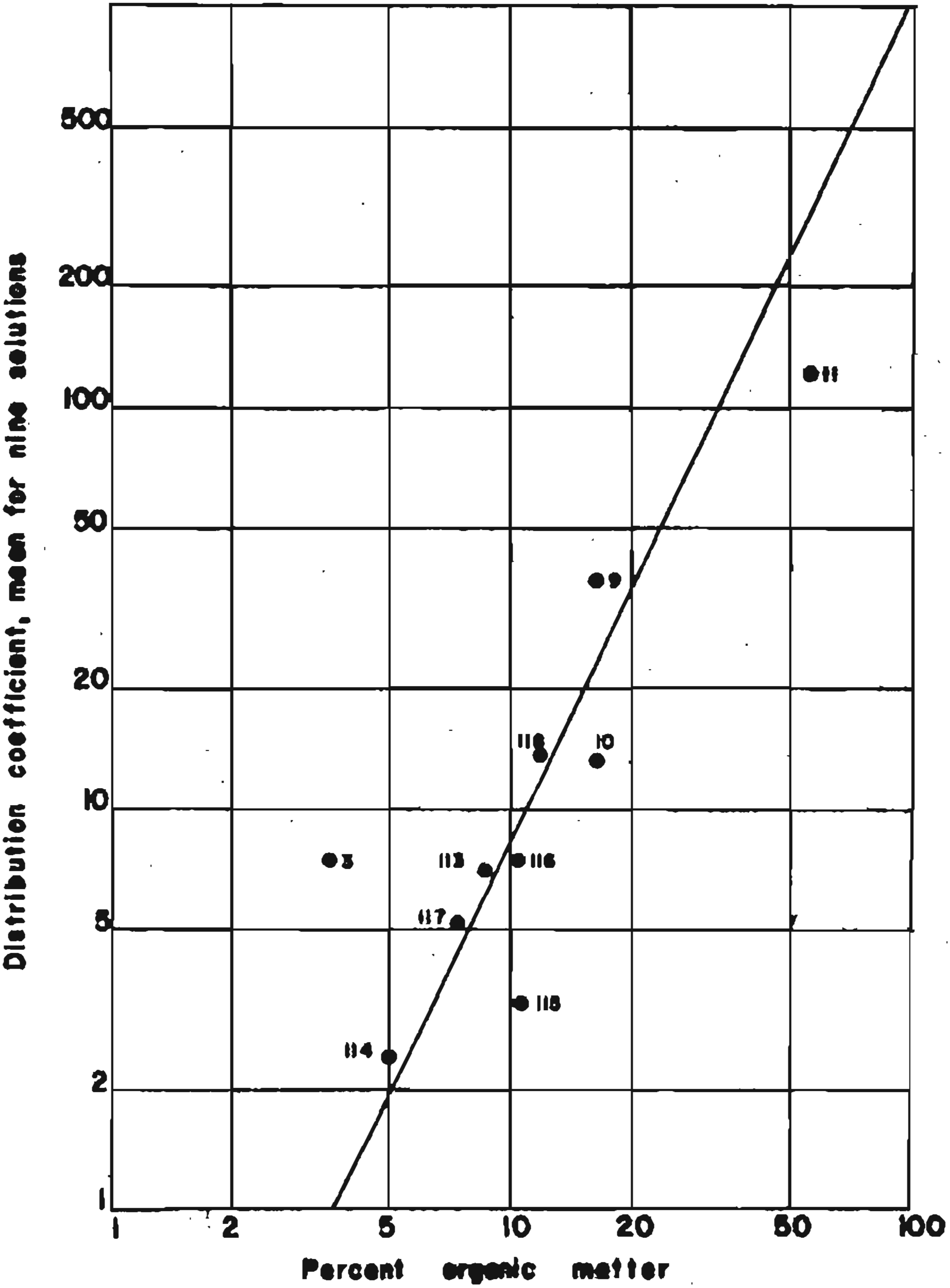

Figure 5.-- Iodine sorption v. percent organic matter for ten samples after one day.

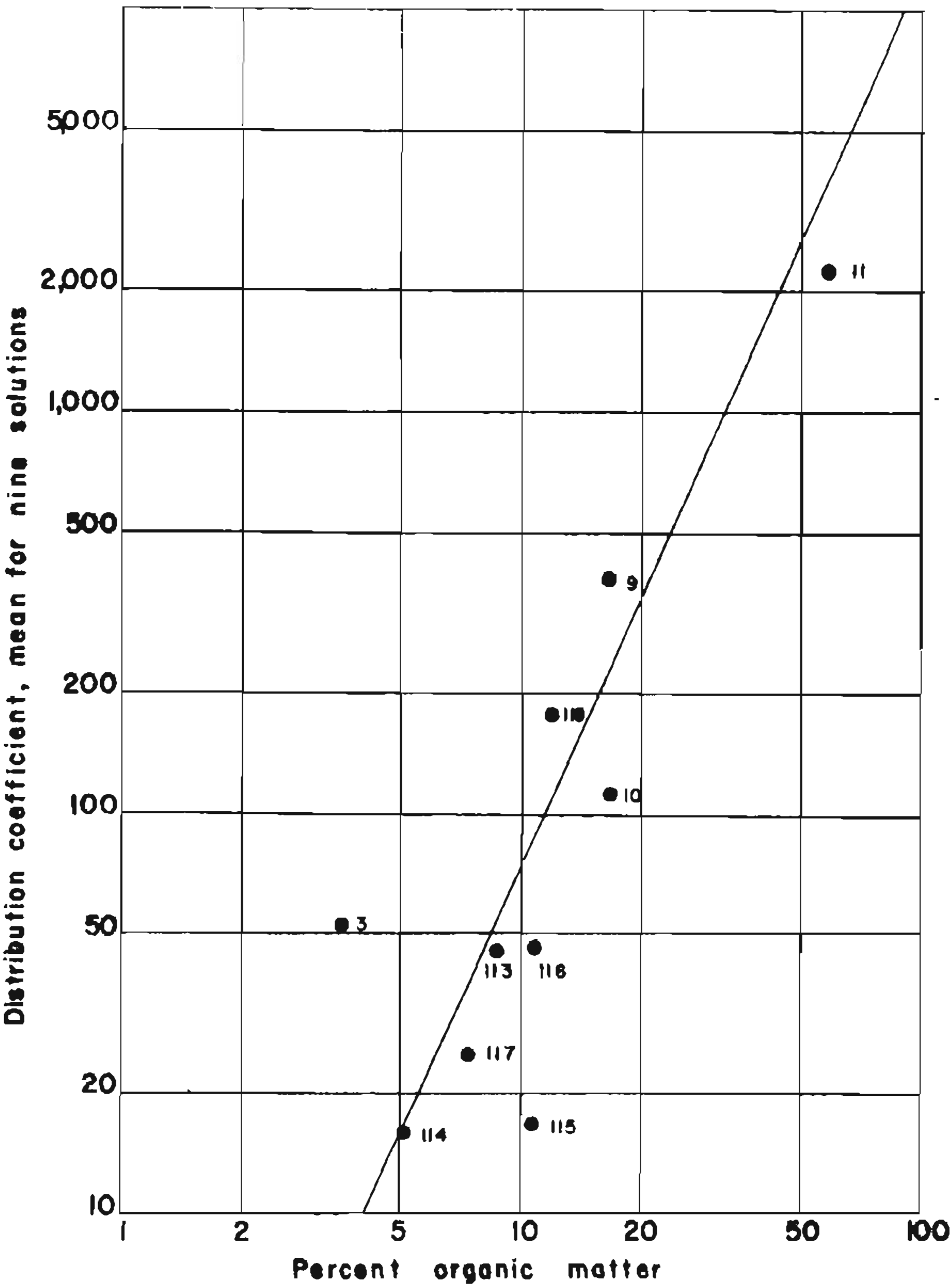

Figure 6.-- Iodine sorption v. percent organic matter for ten samples after six days.

Table 8.--Percentage of carrier-free iodine removed from solution

Sample number	Solution number	Sample weight (g)	Volume of solution (ml)	K_d		Percent I removed			
						$\frac{V}{M} = 100$		$\frac{V}{M} = 1$	
				One-day	Six-day	One-day	Six-days	One-day	Six-days
61 AKd [illegible]	1	0.79	20	4.5	51	4.3	33.8	81.8	98.1
61 AKd 11	1	.17	20	235	3,970	70.1	97.5	99.6	99.97
61 AKd 116	1	.75	20	7.6	40	7.1	28.6	88.4	97.6
61 AKd 1	1	76.4	100	.29	.60	.29	.60	22.5	37.5
61 AKd 2	1	54.5	100	.12	1.2	.12	1.19	10.7	54.5
61 AKd 112	1	114.7	100	.04	.016	.04	.02	3.8	1.7
61 AKd 5	1	1.00	20	67	540	40.1	84.4	98.5	99.8
61 AKd 7	1	1.00	20	26	728	20.6	87.9	95.3	99.9
61 AKd 8a	2	21.0	200	8.4	23	7.7	18.7	89.4	95.8
61 AKd 8b	2	46.5	200	2.7	4.1	2.6	3.9	73.0	80.4

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