A STUDY OF CATION EXCHANGE WITH VERMICULITE

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by

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Abstract

Ion-exchange techniques are favored for the removal of some of the more hazardous fission products from nuclear wastes. Vermiculite has a high cation exchange capacity and is selective toward the sorption of cesium. A modified ion-exchange procedure was developed for these investigations using a sodium chloride saturating solution and an ammonium acetate leaching solution; the released sodium was determined by flame photometry. The rate of saturation was found to be greater for 5N than 1N NaCl and also increased when the temperature was changed from 25° to 80° C. Sodium ions were leached with 1N and 5N ammonium acetate at approximately equal rates. Vermiculite which is finer than 100 mesh was saturated at a greater rate than 20 mesh size. The ion-exchange capacities of eight vermiculites as determined by the modified procedure ranged from 120 to 172 milliequivalents per 100 grams. Attainment of complete saturation for the different vermiculites required from 1 day to 3 weeks.

Cesium-137 was used as a tracer in some experiments. Vermiculite was found to sorb cesium firmly at pH values above 3 but this exchange reaction was reversed by hydrogen ions below a pH of 1. The interference of aluminum with the cesium exchange in vermiculite was removed largely by using a sodium saturated vermiculite at pH 12.6

I. INTRODUCTION

The new and as yet unsolved problems introduced by the production of large quantities of fission products and radioactive isotopes from the nuclear energy industry present mankind with a most complex technical, health economic and political problem. Attending the use of the fission process to produce energy is the problem of controlling the dangerous products of fission for periods of time measured in terms of many hundreds of years.

In the nuclear fuel cycle wastes are produced in each step: from the mining of the ore, the production of fuel elements, the operation of reactors, the chemical reprocessing of fuels, and from the research activities associated with each of these steps. The wide variety of wastes produced can be categorized into two classes: "low-level" and "high-level" wastes. Their major difference lies in the order of magnitude of their activities.

"Low-level wastes" (1) are defined as those having a radioactivity concentration up to one microcurie per gallon (up to 3.7×10^4 disintegrations per second). By way of contrast high-level wastes may have concentrations of hundreds or thousands of curies per gallon. Billions of gallons of low-level wastes are produced each year whereas the volume of high-level wastes is considerably less. Although the nuclear energy industry has developed in less than 15 years, 65 million gallons of high-level wastes have accumulated, all of which are stored in tanks (1).

The disposal of conventional industrial wastes and sewage usually involves methods of returning them to the environment in such form and concentration that they do not represent hazards to plant and animal life.

The disposal of radioactive wastes presents a different and more difficult problem in that radioactive isotopes can be removed from nature only by their natural decay. As a result, all that can be accomplished by waste disposal techniques is to provide a relatively safe place and form while the radionuclides decay. Inasmuch as most of the radioactive fission products have short half-lives it is entirely feasible to allow these to disappear during storage before any process is undertaken.

Table 1 characterizes several of the aqueous wastes for selected solvent extraction processes. The procedures for the chemical separation of fissionable materials involve solution in nitric acid or nitric acid with mecuric nitrate followed by solvent extraction. The extraction solvents used are as follows (2):

a) Redox process - hexone (methyl isobutyl ketone)

b) Purex process - 30% tributyl phosphate in a hydrocarbon base

c) TBP "25" - 5% tributyl phosphate in a hydrocarbon base

Table 1

Characterization of First Cycle High Level Aqueous Wastes From Selected Solvent Extraction Processes(a)

	Approximate Chemical Composition (molarity) Exclusive of Fission Products and Heavy Elements						Waste Volume gal/g U^{235} Consumed	Waste Activity (b) curies/gal
Process	H	Al	Na	Hg	NO_3	SO_4		
Redox	-0.2	1.2	0.46		4.1		0.27	1720
Purex	2.5-7.0				2.5-7.0		0.34	1320
TBP-"25"	0.5	1.6		0.01	5.5	0.02	0.11-0.22	2580-5160

a) Extracted from table in "Status Report on the Disposal of Radioactive Wastes", ORNL-CF-57-5-114 (revised).

b) After 100 days decay cooling from time of reactor discharge.

From the standpoint of waste disposal the fission products of most interest possess relatively long half-lives and have a high hazard potential for man as defined by their allowable limits in the human body. The most significant fission products are shown in Table 2.

Cesium^{137} and strontium ^{90} are two of the most dangerous waste fission products. With their removal much high-level waste could be reduced to intermediate levels and the problem of disposing of the main volume of waste could be greatly reduced.

Although the occurrence of radioactive wastes as aqueous solutions is convenient from the standpoint of transport within a processing facility the attendant properties of mobility and chemical reactivity render liquid wastes especially hazardous. A substantial reduction in the long-term hazards associated with disposal could be achieved by conversion of radio-isotopes into solid form from which they could not easily be removed. These solids could then be stored in suitable areas.

A possible process for the handling of nuclear wastes is the ion exchange of waste fission products by various minerals which possess high cation exchange capacities.

Many clay minerals possess the property of cation exchange. This property arises from unbalanced electrical forces within the clay structures. Two structural units are involved in their atomic lattices: alumina octahedra and silica tetrahedra. Clay minerals are built up from layer-lattice structures which are stacked parallel to each other in a sandwich fashion, normal to the c-axis of the crystal. The different types of clay structures result from variations in the pattern of stacking and from variations in the chemical composition of the layers themselves. Because of the selectivity of vermiculite for cesium and the irreversible nature of this ion exchange, vermiculite was chosen from among clay minerals for experimental studies.

Table 2

Principal fission products of interest in waste-disposal operations(a)

Radionuclide	Half life(b)	Approximate percent of total activity after decay of		
		100 days	5 years	30 years
Strontium 90	28.0 y	< 2	15	~ 49
Cesium 137	26.6 y	< 2	15	~ 49
Promethium 147	2.6 y	5	15	< 1
Cerium-praseodymium 144	290.0 d	45	50	
Krypton 85 (gas)	10.3 y	< 1	1	< 1
Iodine 131 (gas)	8.1 d	< 1		
Zirconium-niobium 95	65.0 d	35		
Barium-lanthanum 140	12.8 d	< 1		
Ruthenium-rhodium 103	41.0 d	5		
Ruthenium-rhodium 106	1.0 y	2	3	
Strontium 89	54.0 d	7		
Xenon 133 (gas)	5.3 d	< 1		

a) Culler, F. L., "Nature of Radioactive Wastes", ORNL-CF-59-1-106, January 26, 1959.

b) d = days, y = years.

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II. HISTORICAL AND GENERAL

The name "Vermiculite" derived from the Latin, <u>vermiculari</u> (to breed worms), was given by T. H. Webb (3) in 1824 to a mineral occurring at Milbury, Massachusetts, in allusion to its curious property of exfoliating into long worm-like forms on heating.

Vermiculite is a clay mineral produced by the alteration of biotite mica. Unlike most clay minerals, it is not restricted to small particles and may form large crystals. The mineral exists in a wide range of colors from black through various shades of brown and yellow; its lustre is usually pearly to bronze-like. The habit is platy but frequently irregular. Vermiculites crystallize in the monoclinic system and have perfect basal cleavage. In distinction to biotite and muscovite the plates of vermiculite are soft and pliable.

Until the work on the structure of vermiculite by Gruner (4) and later by Hendricks and Jefferson (5), it was not known whether vermiculite was a distinct mineral. It is now recognized that there is a true vermiculite with a characteristic structure. According to Gruner, vermiculite consists of sheets of trioctahedral mica or talc separated by layers of water molecules occupying a definite space (4.98 A) which is about the thickness of two water molecules.

Vermiculite inherits its trioctahedral character from the biotite from which it originates. Trioctahedral is the term used to indicate that all three positions for cations in the octahedral layer are filled. This is in contrast to the dioctahedral condition in which only two-thirds of the positions in the octahedral layer are filled as in muscovite and illite.

The vermiculite structure is electrically unbalanced chiefly by the substitution of trivalent aluminum for quadrivalent silicon. These substitutions may be partially balanced by other substitutions within the mica lattice but there is always a residual net-charge deficiency. This charge deficiency is satisfied by cations which occur chiefly between the mica layers and are frequently exchangeable. In the natural mineral the balancing cations are magnesium, sometimes accompanied by calcium.

In biotite the sheets are held together by potassium ions which give electrical neutrality and prevent the entry of water. In vermiculite as shown in Figure 1, the potassium ions have been replaced by magnesium ions and water molecules with consequent interlayer expansion. This separation of the sheets allows solutions to enter and cation exchange to take place.

The wide range in chemical composition is shown in Table 3 which gives analyses of vermiculites used in the present experiments. The fact that vermiculite is seldom found in the pure state should be emphasized. X-ray examination by Daphne Ross, U. S. Geological Survey, showed that these samples contained the minerals listed in Table 4.

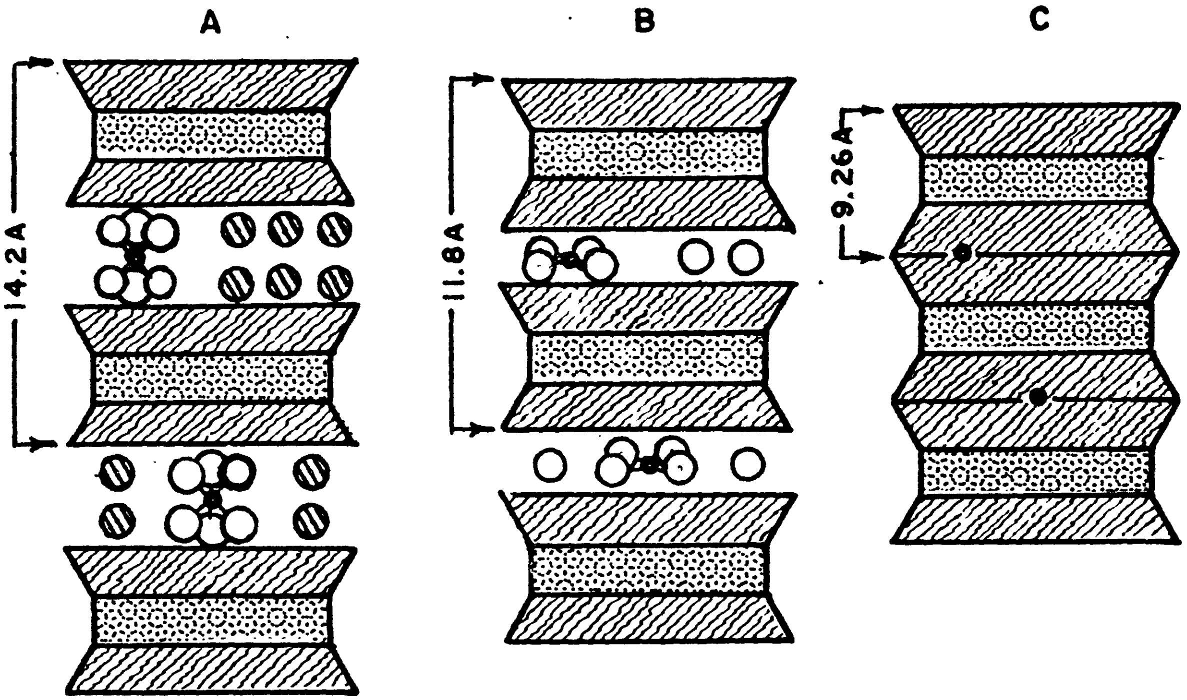
Table 3

Chemical Analyses of Vermiculite (percent)*

Sample Number	1	2	3	4	5	6	7	8	Average of 8 analyses	Range
SiO_2	36.4	32.8	29.3	41.3	43.3	36.7	38.4	38.4	37.1	29.3-43.3
Al_2O_3	12.2	17.7	10.0	11.0	12.9	12.2	9.8	9.4	11.9	9.4-17.7
Fe_2O_3	7.3	14.7	4.5	5.8	6.5	8.0	2.6	4.6	6.8	2.6-14.7
FeO	0.50	1.9	0.22	0.72	1.3	0.76	0.29	0.50	0.77	0.22-1.9
MgO	19.7	10.6	19.0	20.1	17.9	20.0	27.2	26.2	20.1	10.6-27.2
CaO	2.1	1.4	4.2	1.2	1.3	1.6	0.00	0.61	1.6	0.00-2.1
Na_2O	0.14	0.10	0.18	0.18	0.27	0.14	0.04	0.06	0.14	0.04-0.27
K_2O	2.0	2.4	0.10	3.4	5.1	2.5	0.04	4.2	2.5	0.04-5.1
H_2O	17.4	15.8	17.7	11.9	9.3	16.4	20.9	12.7	15.3	9.3-20.9
TiO_2	1.0	2.2	1.3	1.6	1.7	1.0	0.28	0.72	1.2	0.28-2.2
P_2O_5	0.05	0.11	0.12	0.68	0.33	0.05	0.03	0.02	0.17	0.02-0.68
MnO	0.10	0.19	0.10	0.08	0.13	0.10	0.02	0.02	0.09	0.02-0.19
CO_2	0.2	0.1	2.3	<.1	0.11	0.1	0.1	0.9	0.48	<0.1-2.3
$BaSO_4$			10.0							

* Analyses by Rapid Rock Analysis Laboratory of the U. S. Geological Survey

FIGURE I.



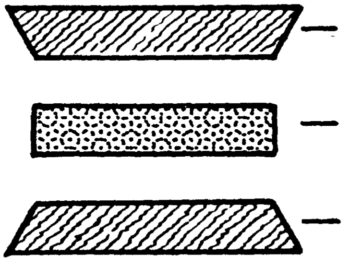
A. Fully hydrated.

B. About half hydrated after removal of unbound water. Of the six water molecules in original hydration shell of magnesium (See A) only four are now in actual contact with the ion.

C. Fully dehydrated with magnesium in holes in silicate layer.

▨ "Unbound" water
○ "Bound" water
● Magnesium ion

MICA UNIT



Tetrahedral sheet (silica)

Octahedral sheet (alumina)

Tetrahedral sheet (silica)

Legend

CONFIGURATION OF INTERLAYER WATER IN VERMICULATE (diagrammatic)

Table 4

X-Ray Description

Sample No.	U. S. National Museum No.	Location	Minerals Found by X-ray Examination
1	92,626	Libby, Montana	Vermiculite, vermiculite-montmorillonite mixed layer, mica-vermiculite mixed-layer, and calcite.
2	93,359	Spruce Pine, North Carolina	Vermiculite and mica-vermiculite mixed-layer
3	107,474	Hillside, Col.	Vermiculite and mica-vermiculite mixed-layer
4	108,799	Langford Station South Carolina	Mica-vermiculite mixed-layer and traces of quartz
5	.....	Travellers Rest, South Carolina	Vermiculite, a montmorillonite mineral, mica-vermiculite mixed-layer, biotite, quartz, and possible amphibole
6	97,399	Libby, Montana	Mica-vermiculite mixed-layer, vermiculite and mica
7	101,935	Franklin, North Carolina	Possibly chlorite or dioctahedral vermiculite and mica-vermiculite mixed-layer
8	106,779	South Africa	Mica-vermiculite mixed-layer or chlorite-mica mixed-layer with a trace of chlorite

A number of theoretical formulae have been proposed for vermiculite. Gruner, from the average of seven true vermiculites from different parts of the United States gave the following formula (4):

$$(OH)_2(Mg, Fe)_3(Si, Al, Fe)_4O_{10} \cdot 4H_2O$$

Barshad (6) proposed the formula for vermiculite as:

$$(H_2O)_x(Mg, Ca)_y(Al, Fe, Mg)_z(Si, Al, Fe)_4O_{10}(OH)_2$$

where x represents the moles of H_2O, y, the interlayer ions which may ranges from 0.22-0.36, and z, the octahedral ions, 3 or less. In contrast to Gruner's formula, this formula distinguishes between the exchange ions, and the atoms in the octahedral and tetrahedral layers.

As noted in the introduction vermiculite possesses the property of cation exchange; Grim (7) reports that the cation exchange capacity for this mineral ranges from 100 to 150 milliequivalents per 100 grams. Inasmuch as the exchange capacity of a given mineral may vary with many factors, capacity values are rigorously comparable only if they are obtained by the same standard procedure.

Early experiments on cation exchange indicated that under a given set of conditions various cations were not equally replaceable and did not have the same replacing power. As cation-exchange reactions were studied it became apparent that there is no single universal replaceability series. This is the result of interactions of a number of factors (7):

1) The nature of the cation. Other things being equal, the higher the valence of an ion the greater is the replacing power and the more difficult it is to displace. Hydrogen ions behave anomalously. Among cations of the same valence, replacing power increases with atomic number.

2) The concentration of the cation. In general, increased concentration of the replacing cation results in greater exchange by that ion.

But the effect of concentration also depends on the particular cation being replaced. The complexity of the factor of concentration is brought out by Kelly (8):

> With cation pairs of similar replacing power and of the same valence, such as K^+ *vs* NH_4^+ or Ca^{++} *vs* Ba^{++}, dilution has relatively little effect on exchange, while with cations of different replacing power and different valence, for example, Na^+ *vs* Ca^{++}, or NH_4^+ *vs* Ca^{++}, dilution produces marked effect on exchange.

3) *The population of exchange positions.* Jenny and Ayers (9) have shown that the ease of release of an ion depends not only on the nature of the ion itself but also upon the nature of the complementary ions filling the remainder of the exchange positions. For example, as the amount of exchangeable calcium on a clay mineral becomes less, the calcium becomes more difficult to release. Sodium, however, tends to become easier to release as the degree of saturation with sodium ions becomes less.

4) *The nature of the exchange mineral.* All other factors being equal the replaceability of various cations varies with the nature of the exchanging mineral. Careful work by Schachtschabel (10) on pure kaolinite, muscovite and montmorillonite clearly demonstrates that there is not a single replacement series characteristic of all minerals possessing ion exchange properties. When a mixture of montmorillonite and muscovite is treated with solutions containing both calcium and ammonium acetate the muscovite adsorbs relatively more of the NH_4^+, and the montmorillonite adsorbs more of the Ca^{++}.

Barshad (6), in his investigations of the cation exchange characteristics of vermiculite, showed that the exchange process is reversible between Na^+, Ca^{++}, Mg^{++}, and K^+ but is not completely reversible between K^+, NH_4^+, Rb^+, and Cs^+. The latter ions tend to become fixed and relatively non-replaceable.

As stated in the introduction cesium ^{137} is one of the more hazardous fission products. Inasmuch as it has a long half life and vermiculite is selective toward the sorption of cesium, experiments were made on the cation exchange properties of vermiculite.

III. EXPERIMENTAL

Cation exchange can be represented by the equation

$$AX + B^{+} \rightleftharpoons BX + A^{+}$$

where A^{+} and B^{+} represent solution cations of equal change and AX and BX represent the exchange material saturated with A^{+} and B^{+}, respectively. When the exchange material has only one kind of exchangeable cation, the material is said to be saturated with that ion. The total amount of exchangeable cations is usually expressed as milliequivalents per 100 grams (meq/100 g) and this quantity is called the cation exchange capacity.

This study was made to develop a procedure for the determination of cation exchange capacities of vermiculites, to characterize the cation exchange properties of several vermiculites, and to determine the ion exchange behavior of cesium with vermiculite with a view towards application to the waste disposal problem.

A procedure was desired for determining the cation exchange capacity of vermiculite so that later experiments might indicate how capacity values were affected by such factors as the hydrogen ion and aluminum concentration on the sorption of cesium. Because cesium salts are relatively expensive it was decided to determine the cation exchange capacity using some other ion.

Two procedures for the determination of cation exchange capacities were tried on a single vermiculite. The method of Bower and Troug (11) employed a manganese (II) chloride saturating solution whereas the method of Barshad (6) used a sodium chloride solution. The first method seemed attractive in that it offered a simple colorometric determination; the latter method was attractive from an economic view.

According to the method of Bower and Troug the clay mineral is treated with six fresh portions of a 0.50 M manganese (II) chloride at pH 7 for a total of thirty minutes. The excess manganese is washed out with methanol and the residue containing exchanged manganese ions is leached with 1 N $NH_4C_2H_3O_2$ also at pH 7. The leached manganese ions are oxidized to permanganate and determined colorimetrically. The author found several objections to this procedure, namely:

1) at pH 7 a manganese (II) chloride solution is unstable leading to the formation of a brown precipitate, which could possibly be precipitated in the sample and thus cause a mechanical problem in washing out unexchanged ions.
2) the exchange capacity value obtained from the designated saturation time was only about 20 % of the total capacity as determined by subsequent experiments.

This last factor was less objectionable in that the saturation time could be extended but the instability of the saturating solution made the method appear unreliable.

By the method of Barshad a lightly ground sample is treated with 1 N NaCl. Fresh portions of saturating solution are added every three to four hours for ten days after which the sample is washed free of excess salt solution with absolute methanol. The sodium saturated sample is then leached with an ammonium acetate solution and the sodium is determined.

Experiments according to Barshad's method proved to be simple but suffered from the prolonged time necessary for saturation. It should be noted that in this process a divalent ion, Mg^{++}, in the vermiculite is being replaced by a monovalent one. Also the exchange capacity value obtained was only about 60% of the total value.

The latter method, however, was chosen for a more detailed study to find the best conditions for determining the cation exchange capacity of a vermiculite. It was desirable to experiment with such factors as the washing reagent, temperature, particle size, concentration of saturating and leaching solutions, and the time necessary for complete saturation and leaching. Also, it was desirable to ascertain the effect of exfoliation on the exchange capacity. These pilot experiments were made on vermiculite No. 5 because of its availability.

A. Experiments to Determine Optimum Conditions for Cation Exchange

In each of the following experiments the weighed sample (0.5000 to 1.0000 g) was placed in a fifteen milliliter glass-stoppered centrifuge tube. A fifteen milliliter portion of saturating solution was added and sample was agitated gently at intervals of time. After three hours the sample was centrifuged and the supernatant liquid discharged. Fresh portions of saturating solution were added and the procedure repeated. After saturation, the excess saturating ions were washed free and the exchanged ions leached with fifteen milliliter portions of leaching solution. Again the sample was centrifuged and leachings were filtered and added to a volumetric flask. This procedure was repeated until leaching was complete, after which the leachates were made to volume and the leached-ion concentration determined by flame photometry.

Washing Procedure. First it was necessary to adopt some standard method for washing out excess unexchanged ions. The procedure employing absolute methanol was tested to determine its effectiveness in washing a sodium saturated fine-grained sample. Four 2 gram samples of acid-washed, 100 mesh, white sand were "soaked" with 5 N NaCl. The samples were then washed with ten 15 milliliter portions of absolute methanol after which a negative test for the chloride ion was obtained with acidified silver nitrate solution. The alcohol washed samples were next leached with distilled water and the sodium concentration of leachings determined. The results indicated that absolute methanol is an effective washing agent for the sand. To determine whether methanol was satisfactory for vermiculite, samples were treated with 5 N NaCl for six hours. The vermiculite samples were washed as above. Upon leaching with distilled water the equivalent of 3 milliequivalents of sodium per 100 grams of vermiculite was obtained. Based on the minimum exchange capacity of any of the encountered vermiculites this would amount to as much as a 2.5% error. However, it is questionable whether the sodium leached with water was the result of inefficient washing by methanol. Perhaps the hydrogen ion concentration of the water was responsible. It was felt that absolute methanol was an adequate washing reagent for the experiments at hand and consequently was adopted.

<u>Temperature Effect</u>. To check the effect of temperature on cation exchange four portions of a given vermiculite were saturated simultaneously with a sodium chloride solution. Two of the samples were kept at approximately 25° C. and the other two at 70° to 80° C. during saturation. The higher temperature was obtained with a sand bath; no thermostat was used. In each case higher exchange values were obtained at the elevated temperature. Therefore, all succeeding experiments were carried out at 70° to 80° C.

<u>Saturation and Leaching</u>. It was desired to determine the effect of concentration of saturating solution on the rate of exchange for two different particle sizes. It was also considered desirable to check the effect of the concentration of leaching solution on these two different particle sizes for any given length of time.

Five sets of eight samples of a given vermiculite were treated in increments of twenty-four hours. Of the eight samples of a single set, four were 100 mesh and four were 20 mesh particle size; A pair of the 100 mesh samples was treated with 1 N NaCl, and the other with 5 N NaCl saturating solution. The 20 mesh samples were treated in similar fashion. Half of all the samples (20 and 100 mesh) treated with 1 N NaCl were leached with 1 N $NH_4C_2H_3O_2$ (NH_4Ac) and the remaining half with 5 N $NH_4C_2H_3O_2$ (NH_4Ac). See Table 5.

Table 5

Saturation and Leaching Experiment

Saturation Time	100 Mesh				20 Mesh			
	1 N NaCl		5 N NaCl		1 N NaCl		5 N NaCl	
Days	1 N NH_4Ac	5 N NH_4Ac	1 N NH_4Ac	5 N NH_4Ac	1 N NH_4AC	5 N NH_4Ac	1 N NH_4Ac	5 N NH_4Ac
	Milliequivalents per 100 grams*							
1	58	60	72	72	47	48	59	56
2	59	62	78	80	50	51	61	61
3	60	62	86	88	52	54	67	67
4	65	64	92	91	55	53	73	75
5	67	67	94	91	55	56	76	79

* Table gives final leaching values.

It was apparent that the 100 mesh vermiculite was saturating more easily than the 20 mesh samples and that 5 N NaCl was more efficient than the 1 N NaCl for a rapid approach to complete saturation.

Conclusion Concerning Leaching Solution. The 5 N $NH_4C_2H_3O_2$ gave exchange values approximately similar to the 1 N $NH_4C_2H_3O_2$ as a leaching solution for the same length of time. The exchange values given in Table 5 are those obtained after complete leaching. It was found that for the 100 mesh samples the sodium was completely leached in 24 hours; the 20 mesh samples required considerably longer time. One of the following experiments demonstrates this. It was concluded that the 5 N $NH_4C_2H_3O_2$ offered no particular advantage over the 1 N $NH_4C_2H_3O_2$ for the leaching of sodium ions. Nevertheless for all further experiments a 2 N $NH_4C_2H_3O_2$ leaching solution was adopted as a safety measure.

Conclusion Concerning Saturating Solution. It was desired to establish the relationship between the time necessary for complete saturation and particle size. Experiments were continued along the same lines as described in the preceding paragraph. The 100 mesh vermiculite treated with 5 N NaCl was saturated within 3 weeks as indicated by no further increase in exchange capacity value. The 100 mesh sample which was treated with 1 N NaCl, however, was only 63% saturated in 3 weeks and 90% in 6 weeks. At the end of 6 weeks the 20 mesh samples, one of which was treated with a 5 N NaCl and the other with a 1 N NaCl, were 80% and 56% saturated respectively.

From the above results in which one sample was only 56% saturated after 6 weeks saturation the author concluded that a 1 N NaCl was impractical as a saturating solution and consequently adopted a 5 N NaCl for further experiments.

Leaching Rate. It was next desirable to investigate the relationship between time necessary for complete leaching and particle size. In these experiments samples which had been saturated with 5 N NaCl were leached. One sample was a 100 mesh and the other was a 20 mesh vermiculite. The leachings, after varying time intervals, were collected in separate volumetric flasks. The sodium concentration of the different flasks was determined; the combined values are given in Tables 6a and 6b. The tables show the 100 mesh sample is leached more rapidly.

Table 6a

Rate of Leaching for 100 Mesh Vermiculite

Leaching time hours	Meq/100 g leached	Percent of complete leaching
2	98	82
4	114	96
6	118	99
30	119	100

Table 6b

Rate of Leaching for 20 Mesh Vermiculite

Leaching time	Meq/100 g leached	Percent of complete leaching
2 hrs.	57	66
4 hrs.	70	82
6 hrs.	76	89
2 days	81	95
5 days	83	97
6 days	85	100

Exfoliation. Natural vermiculite has the peculiar property that it exfoliates when heated rapidly. This property is considered to result from the interlayer water in the structure which upon heating causes the expansion of the structure by the entrapped steam. See Figure 1. Very finely ground vermiculite may not show this property due to the rapid escape of the generated steam. Vermiculites have been reported (12) to expand as much as 19 times their original volume upon exfoliation.

A test was run on two different particle sizes of vermiculite to determine the effect of exfoliation upon cation exchange capacity. Table 7 gives information obtained for both the 100 mesh and the 20 mesh vermiculite in both the crude and exfoliated state.

Samples were treated simultaneously with 5 N NaCl with no view to complete saturation. Exfoliation was produced by heating samples for 2 minutes in a 900° C. furnace.

Table 7

Effect of Exfoliation on Cation Exchange Properties

State of Vermiculite	Meq./100 g
Crude vermiculite 100 mesh	69
Exfoliated vermiculite 100 mesh	23
Crude vermiculite 20 mesh	57
Exfoliated vermiculite 20 mesh	21

Little trouble was experienced with the washing of the crude vermicules - 10 washings with absolute methanol were quite adequate. For the exfoliated samples, and more particularly the 20 mesh exfoliated one, more than 20 washings were required. The chloride was leached in large quantities until finally a negative test was obtained.

Other difficulties were encountered; the exfoliated vermiculite, having a low density, floated on top of the saturating solution. Decanting the supernatant liquid after centrifugation proved to be quite a problem. It was concluded that exfoliation of the vermiculite did not improve its exchange capacity and, indeed, introduced a mechanical problem.

Particle Size. At this point it was deemed expedient to restrict the experimental variables with regard to particle size. It was found that more time is required for the saturation and leaching of a coarser-grained sample. On the basis of information given by Barshad (6), in which he reports that the exchange capacity of vermiculite is independent of particle size, the experiments on the 20 mesh vermiculite were discontinued. Further experiments were restricted to 100 mesh particle size.

Sodium Determination. So far no reference has been made concerning the method for determining the sodium concentration of the leachates. Standard solutions of sodium were prepared containing $NH_4C_2H_3O_2$ in concentrations equal to those found in diluted leachings. It was found that the curve which resulted from plotting percent transmission vs ppm sodium was not linear, particularly at the higher sodium concentrations. Therefore, solutions were diluted so that the sodium concentrations remained at less than 20 ppm sodium - closer to 10 ppm at which concentration the curve is more nearly linear. The percent transmission was measured with a Beckman D. U. Spectro-flame photometer using a 589 mu wave length.

Summary of Ion Exchange Procedure. The weighed vermiculite sample (0.5000 to 1.0000 g) is placed in a fifteen milliliter glass-stoppered centrifuge tube. Fifteen milliliters of 5 N NaCl saturating solution are added. The sample is agitated gently at intervals of time and after three to four hours at 70° to 80° C. the sample is centrifuged and the supernatant liquid is discarded. Fresh portions of saturating solution are added until saturation is complete. The sample is then washed with absolute methanol until a negative chloride test is obtained with acidified silver nitrate solution. The sample is then leached with a fifteen milliliter portion of 2 N $NH_4C_2H_3O_2$; during leaching procedure sample is agitated gently at intervals of time. After approximately two hours the sample is centrifuged and the supernatant liquid is filtered into a volumetric flask. Additional fifteen milliliter portions of leaching solution are used until leaching is complete. The sodium concentration of the combined leachings is determined by flame photometry.

Application of Ion Exchange Procedure to Seven Additional Vermiculites

It was desired to test this ion exchange procedure on a group of vermiculites. Seven additional vermiculite samples were obtained from the United States National Museum. These samples were analyzed and X-rayed (See Tables 3 and 4).

The purpose of checking seven additional samples was to ascertain their manner of saturating and leaching as compared to the original sample (vermiculite No. 5). It should be noted that the original sample was used in this experiment as a reference and as a precision check.

Saturation of six 0.5000 g portions of each of the eight vermiculites was started simultaneously. The cation exchange values for the various sample portions were determined after saturation time increments of one week with the exception of the first set of samples whose ion exchange values were determined at the end of twenty-four hours. Table 8 gives the ion exchange capacities after specified saturation time. It should be noted that while some samples (# 3 and # 7) are essentially saturated in a single day others take as much as 3 weeks.

Table 8

Cation Exchange Values, Meq/100 grams

Saturation Time	Vermiculite Sample Number							
	1	2	3	4	5*	6	7	8
1 day	143	102	139	100	69	137	159	110
1 week	159	121	143	139	93	159	160	147
2 weeks	163	123	143	147	107	159	163	167
3 weeks	165	125	143	150	119	161	163	171
4 weeks	163	128	143	150	121	161	163	172
5 weeks	163	127	143	150	120	163	161	173

* This vermiculite sample was used for all previous experiments.

Samples of the eight vermiculites which were completely sodium-saturated were leached. Leachings were collected after increments of 2 hours for the first 6 hours and then after a total of 24 hours. See Table 9 for the results.

Table 9

Leaching Values, Meq/100 grams

Leaching Time (hours)	Vermiculite Sample Number							
	1	2	3	4	5	6	7	8
2	147.83	117.39	126.09	139.13	100.00	150.00	143.48	147.83
4	13.22	9.56	15.13	9.74	13.22	13.91	15.30	20.87
6	0.17	0.17	1.56	0.17	1.74	0.35	1.22	2.78
24	0.00	0.00	0.70	0.00	1.04	0.00	0.70	1.56
Total Exchange Capacity	161 (22)	127.(12)	143 (48)	149 (04)	116 (00)	164.(26)	160.(70)	173.(04)

In order to determine the accuracy of the cation exchange a cross-check was desired. This was achieved by means of a Kjeldahl procedure. Sodium saturated samples were leached with ammonium acetate; the sodium concentration of the leachings was determined, and the cation exchange capacity calculated. The vermiculites were then washed free of excess ammonium acetate and transferred to Kjeldahl flasks. Distillation was carried out using approximately 2 grams of barium hydroxide as the alkali. A blank containing distilled water and barium hydroxide was distilled similarly. Fifty milliliters of the distillate were collected in a volumetric flask containing 4% boric acid. After adjustment of the volume an aliquot was taken; a methyl red-bromocresol green indicator was added to sample and blank. The sample was titrated to the color of the indicator blank with 0.100 N HCl and the exchange capacity calculated. Table 10 gives the cation exchange capacities obtained by the sodium determination and the Kjeldahl method. The results seem to be in good agreement. It may be concluded that the exchange capacity for sodium is equivalent to that for ammonium.

Table 10

Comparison of Cation Exchange Capacity Values by Two Methods, Meq/100 g

Sample Number	Sodium Determination	Kjeldahl Determination
1	163	161
2	127	134
3	143	140
4	150	150
5	120	120
6	163	163
7	161	163
8	173	171

Barshad (6) has stated that the ion exchange process is not completely reversible between potassium and ammonium ions. This statement prompted a test on the effectiveness of several alkalis in the Kjeldahl procedure. With no attempt at complete saturation, three portions of a single vermiculite were treated with ammonium acetate solution. The samples were then washed free of excess ammonium ions and Kjeldahls were run using three different alkalis: barium, sodium, and potassium hydroxides. The sample treated with barium hydroxide boiled quietly; the sample treated with sodium hydroxide had a slight tendency to "bump", and the sample treated with potassium hydroxide boiled like a volcano erupting at approximately twenty second intervals. Certainly the potassium hydroxide reacted with the ammonium vermiculite differently. The tabulated results are given below.

Table 11

Kjeldahl Distillation with Several Alkalis

Alkali	Milliequivalents per 100 Grams
1 N $Ba(OH)_2$	47
1 N NaOH	48
1 N KOH	8

The cation exchange value obtained from the potassium hydroxide distillation was less than 20% of the values obtained by the barium and sodium hydroxide distillations. Barshad (13) called the difference between the two values the "fixed" ammonium.

Inasmuch as ion exchange is an equilibrium reaction it was important to know the effect of mass action on the saturation of vermiculite. Two sets of the eight different vermiculite samples were treated, one with a single fifteen milliliter portion of 5 N NaCl and the other with sixty fifteen milliliter portions of 5 N NaCl. After one month's saturation the samples were washed and leached and the sodium determined. Table 12 gives the results.

Table 12

Effect of Mass Action

Vermiculite	Milliequivalents per 100 Grams	
Sample Number	15 Ml. 5 N NaCl	900 Ml. 5 N NaCl
1	134	161
2	87	127
3	130	143
4	83	150
5	57	120
6	*	164
7	155	161
8	101	173

* Sample lost

After one month the set of samples which was treated with single fifteen milliliter portions of saturating solution was drained. These solutions drained were analyzed and found to contain predominantly magnesium and calcium cations.

Previous experiments showed that for these samples, under the prevailing conditions, one month is sufficient time for complete saturation.

The results for the samples treated with only fifteen milliliters of saturating solution may be attributed to the fact that the mass action is insufficient to drive the reaction to completion.

B. Ion Exchange Experiments with Cesium

Having characterized the ion exchange properties of several vermiculites it was considered desirable to experiment with cesium using these samples. Because cesium is relatively expensive, the following experiments were conducted on a reduced scale.

The pH Effect on the Adsorption of Cesium. It was desired to provide sufficient cesium for the complete saturation of vermiculite No. 2 whose exchange capacity was found to be 127 meq./100 g. Portions of vermiculite weighing 0.2000 g were placed in glass-stoppered Erlenmeyer flasks containing 0.300 meq. cesium (as chloride) plus 0.30 μ curie cesium^{137} in twenty-five milliliters of solution at various pH values. The flasks were placed on an electrical shaker at room temperature (25° C.). After one month the samples were centrifuged and the radioactivity of the supernatant liquid measured using a sodium iodide (thallium activated) crystal scintillator counter. The radioactivity was compared with standard solutions and the cesium adsorbed by the vermiculite calculated. Table 13 gives the results. It is apparent that pH values 3 and above favor the sorption of cesium.

Table 13

Effect of pH on Cesium Sorption

pH	Meq./100 g
1.0	9.3
3.0	80.
5.0	79.
7.0	80.
9.0	79.
11.0	84.
12.5	77.

The pH values of solutions were measured before and after exposure to vermiculite with a Model G Beckman pH meter. Due to the lack of buffering action pH measurements were made with some difficulty, but the data seemed to indicate that the pH of the solutions did not change sensibly by their action on vermiculite.

The pH Effect on the Reversibility of Cesium Exchange. Four samples containing 10 mg. of exchanged cesium were treated with nitric acid solutions at various pH values. Table 14 gives the results, which indicate that the ion exchange of vermiculite with cesium is reversed by pH values less than 1.00.

Table 14
Reversibility as a Function of pH

pH	Milligrams of Cesium Released	Percent of 10 Milligrams Retained
0.00	10.0	0
0.10	7.1	29
0.22	5.9	41
0.52	3.3	67
1.00	1.8	82

The Effect of Aluminum on Cesium Exchange. Aluminum is commonly present in nuclear wastes. Therefore it was considered desirable to determine the effect of aluminum on the exchange of cesium by vermiculite. Because of the amphoteric nature of aluminum, experiments were restricted to those pH values in which aluminum is soluble. Preliminary experiments indicated that at pH 3 the cesium exchange by vermiculite is depressed. It was hoped that if aluminum existed as the anion, AlO_2^-, that the interference by aluminum would be removed.

Inasmuch as sodium aluminate was not immediately available it was necessary to prepare it. This preparation was accomplished by dissolving metallic aluminum in a measured quantity of carbonate-free sodium hydroxide solution. In order to achieve the desired pH of 12.6, nitric acid solution was added. During the addition of nitric acid some aluminum hydroxide precipitated out. After precipitation was complete the precipitate was filtered off and the sodium aluminate solution standardized.

The standardization consisted of first removing any silica after prior dehydration with hydrochloric acid solution. The solution was then made 5% with respect to ammonium chloride and ammonium hydroxide was added until methyl red turned yellow (pH ~ 5). A double precipitation was made. The aluminum hydroxide precipitate was dried, ignited and weighed. The aluminum concentration was found to be 0.27 M and according to a flame photometric determination the sodium concentration was 1.4 M.

Because the standardized aluminate solution was 1.4 M in sodium it was necessary not only to determine the effect of various concentrations of the aluminate ion but also the effect of this concentration of sodium. Table 15 gives the results which show that both the sodium and the aluminate ions at the given concentrations depress the cesium exchange, but the aluminate ion does so to a greater extent. The sodium concentration being 1.4 M as compared to cesium being 0.04 M might, because of mass action, compete for the exchange positions.

Table 15

Effect of Na^+ and AlO_2^- on Cesium Exchange by Natural Vermiculite at pH 12.6

(0.300 Meq. Cesium + 0.30 μ Curie Cesium^{137})/25.00 ml. plus	Meq./100 g
Nothing	77
35 millimoles Na^+	60
3.43 millimoles AlO_2^- + 17.5 millimoles Na^+	46
6.86 millimoles AlO_2^- + 35. millimoles Na^+	36

Wright and Monahan (14) found that the ion exchange efficiency of vermiculite, containing exchangeable magnesium ions, is impaired by the precipitation of magnesium hydroxide in the exchanger matrix when ion exchange reaction is carried out at pH 11.5 to 12.0.

Following the recommendation of Wright and Monahan, samples were converted to the sodium form, and the previous experiments were repeated at pH 12.6 to determine the effect of AlO_2^- and Na^+ on cesium exchange. Table 16 gives the results.

Table 16

Effect of Na^+ and AlO_2^- on Cesium Exchange by Sodium Vermiculite at pH 12.6

(0.300 Meq. Cesium + 0.30 μ Curie Cesium^{137})/25.00 ml Plus	Meq./100 g
Nothing	101
35 millimoles Na^+	103
3.43 millimoles AlO_2^- + 17.5 millimoles Na^+	102
6.86 millimoles AlO_2^- + 35 millimoles Na^+	110

The results were gratifying! Apparently at the concentrations used, the aluminum as the aluminate and/or the sodium cause very little depression on the vermiculite exchange with cesium. As far as the author knows this is the first time tests have been made with cesium in the presence of sodium aluminate on a sodium vermiculite.

Effect of Cesium Concentration. It was desired to test the effect of the concentration of cesium on the saturation of vermiculite at a given temperature. For reasons of simplicity room temperature was chosen (25° C.). Twelve 0.2000 g portions of vermiculite No. 5 were treated with twenty-five milliliters of solutions at pH 7 with cesium concentrations ranging from 2.4×10^{-5} N to 1.2×10^{-2} N; solutions were spiked with cesium ^{137}. The changes in activity of the solutions were measured after a one month exposure to the vermiculite and the cesium adsorbed calculated. Table 17 gives the results. If the percent saturation of the vermiculite vs the concentration of the cesium saturating solution is plotted a linear relationship is found up to the concentration of 2.4×10^{-3} N after which the percent saturation tapers off until at 7.2×10^{-2} N it reaches 56.7% and then remains constant. This 56.7% saturation represents 44 meq./100 g of vermiculite.

Table 17

Effect of Cesium Concentration on Saturation

Normality of Solution	Meq. Cesium Initially in Solution	Meq. Cesium Taken Up	Percent Saturation*
2.4×10^{-5}	.00060	0.00060	0.25
1.2×10^{-4}	.0030	0.0030	1.25
2.4×10^{-4}	.0060	0.0060	2.5
4.8×10^{-4}	.012	0.012	5.0
7.2×10^{-4}	.018	0.018	7.5
1.2×10^{-3}	.030	0.030	12.6
2.4×10^{-3}	.060	0.058	24.0
4.8×10^{-3}	.120	0.082	34.3
7.2×10^{-3}	.180	0.088	36.7
9.6×10^{-3}	.240	0.089	36.7
1.2×10^{-2}	.300	0.089	36.7

$$* \text{ Percent Saturation} = \frac{\text{Meq. Cesium Adsorbed/100 grams}}{\text{Total exchange capacity}} \times 100$$

Time Study of Cesium Saturation. As the final experiment it was desirable to determine the kinetics of the saturating operation. Twenty-three 0.2000 g portions of vermiculite No. 3 were each treated with twenty-five milliliters of a solution at pH 7 containing 0.200 meq. cesium plus 0.20 μcurie cesium^{137}. Saturation of individual portions was discontinued after varying intervals of time. After centrifugation of the samples the activity of the decanted supernatant liquid was measured and compared with standard solutions. Figures 2 and 3, which are plots of the reciprocal of the unexploited exchange capacity vs time, indicate three consecutive second-order reactions. See Table 18 for data. This

FIG. 2.

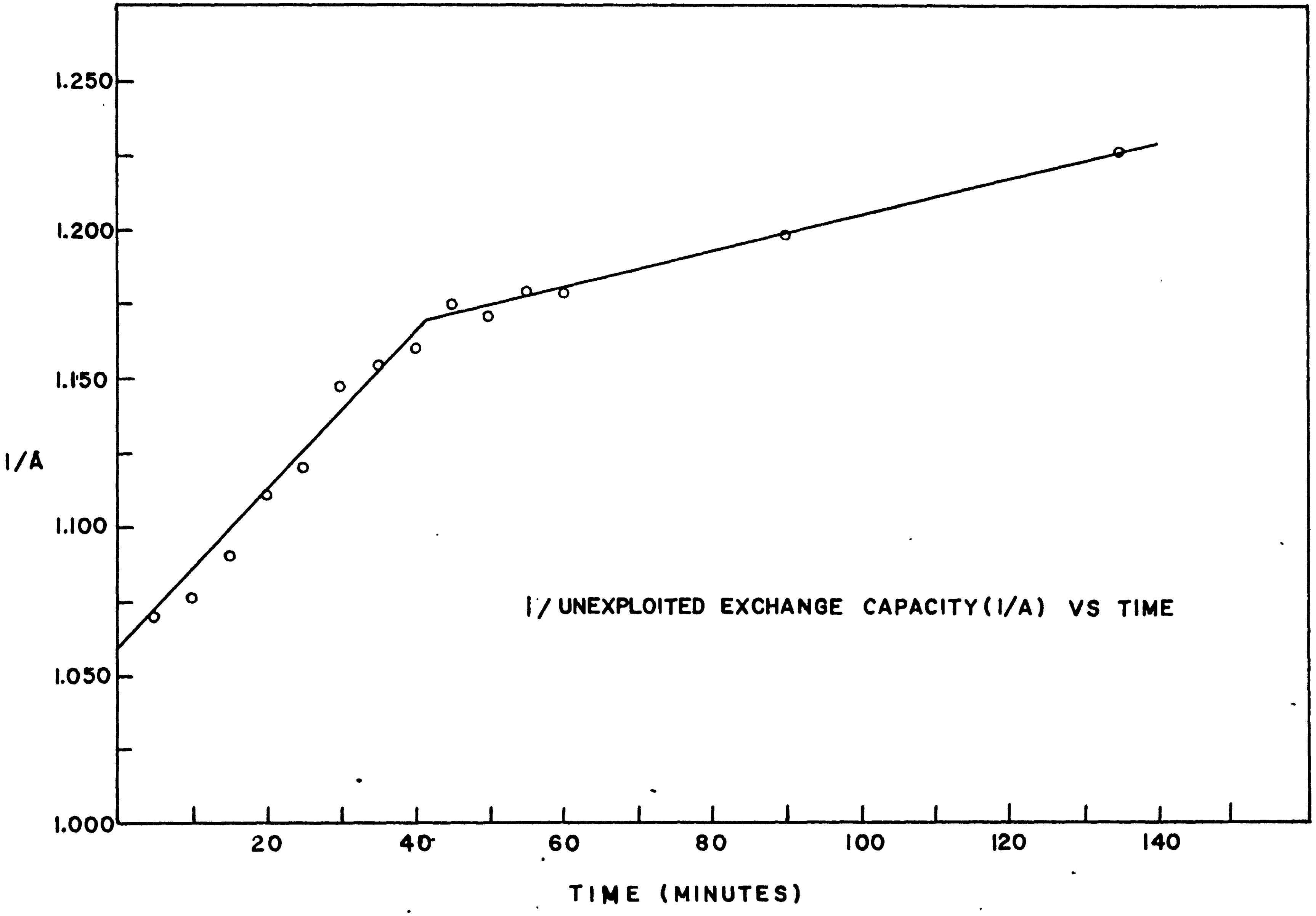
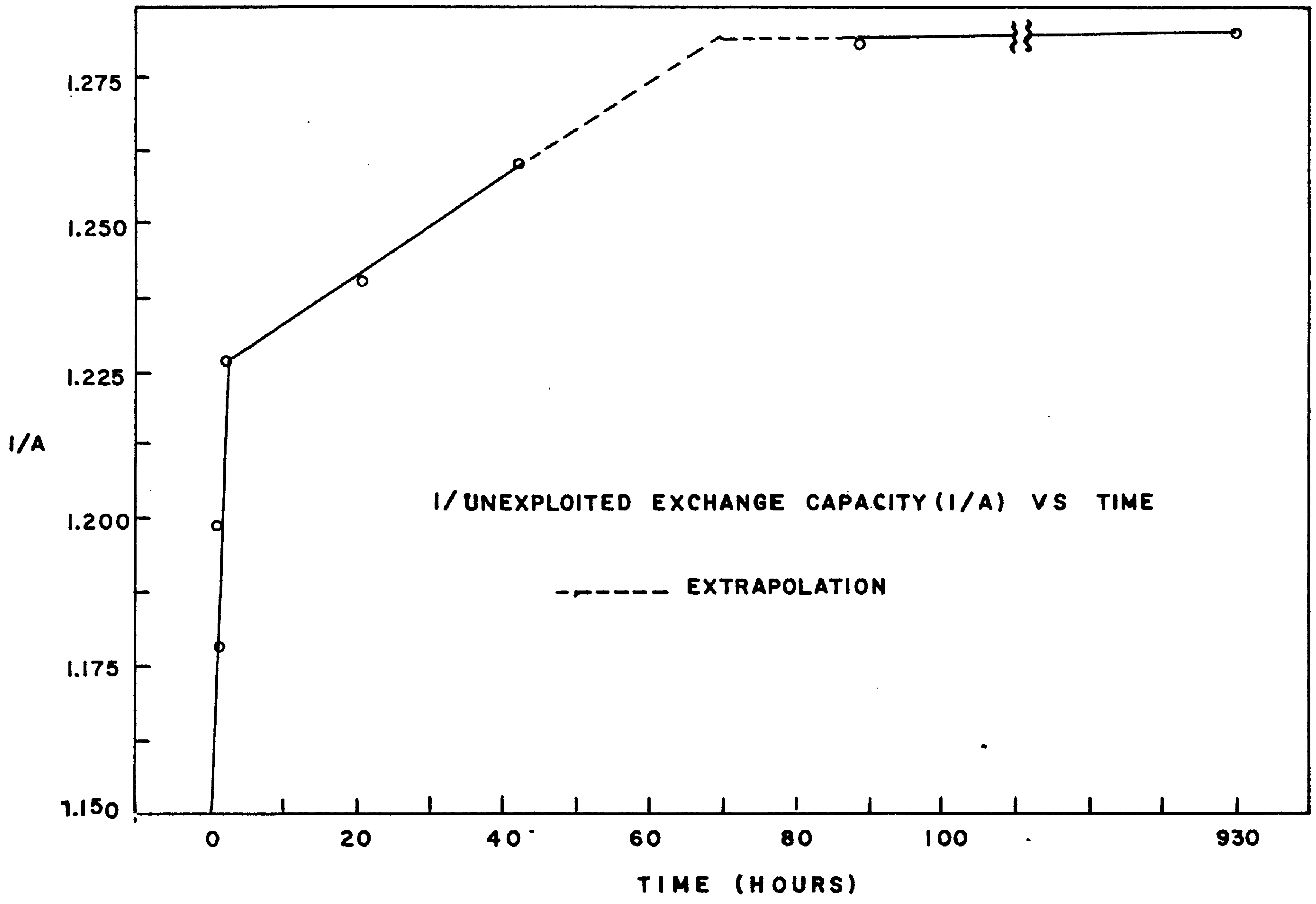

1.250
1.200
1.150
1.100
1.050
1.000
1/A
20
40
60
80
100
120
140
TIME (MINUTES)
1/UNEXPLOITED EXCHANGE CAPACITY (1/A) VS TIME

FIGURE 3.


1/UNEXPLOITED EXCHANGE CAPACITY (1/A) VS TIME
------ EXTRAPOLATION
1/A
1.275
1.250
1.225
1.200
1.175
1.150
0
20
40
60
80
100
930
TIME (HOURS)

"unexploited exchange capacity" is the total exchange capacity minus the meq. cesium exchanged per 100 grams. What proved to be particularly interesting was that after one minute 25 meq. cesium per 100 grams of vermiculite were exchanged. The effect of mass action was shown by the fact that even though this particular sample has an exchange capacity of 120 meq. per 100 grams only 42 meq. per 100 grams were utilized. Less than 50% of the cesium available was exchanged.

Table 18

Time Study of Cesium Saturation

Saturation Time	Meq. Cesium Exchanged/100 g	100/Residual Exchange Capacity Meq./100 ($\frac{1}{A}$)*
5 minutes	26.60	1.071
10 "	27.15	1.077
15 "	28.40	1.092
20 "	30.10	1.112
25 "	30.90	1.122
30 "	32.90	1.148
35 "	33.40	1.155
40 "	33.85	1.161
45 "	34.90	1.175
50 "	34.70	1.172
55 "	35.20	1.179
60 "	35.10	1.178
90 "	36.50	1.198
135 "	38.50	1.227
21 hours	39.45	1.241
43 hours	40.70	1.261
89 "	41.95	1.281
161 "	42.05	1.283
257 "	42.15	1.284
425 "	42.05	1.283
929 "	42.05	1.283

$$* \frac{1}{A} = \frac{1}{\text{Total Exchange Capacity} - \text{Meq. Cesium Exchanged/100 g}}$$

and the total exchange capacity for this sample was found to be 120 meq./100 g.

IV. SUMMARY

A modified procedure was developed for determining the cation exchange capacity of vermiculites: 100 mesh vermiculite is saturated with 5 N NaCl at 70 to 80° C. for approximately three weeks. After washing off the unexchanged ions with absolute methanol the sodium saturated sample is leached with 2 N $NH_4C_2H_3O_2$ for about six hours; the desorbed sodium is determined. This procedure is applicable to a wide variety of vermiculites, especially to those which with previous procedures gave low exchange capacity values. The cation exchange capacities of eight vermiculites were determined by the procedure described; their capacities ranged from 120 to 172 milliequivalents per 100 grams.

Experiments were made with cesium using cesium^{137} as a tracer. It was found that vermiculite adsorbs cesium firmly in the pH range of 3 and above but that this exchange reaction can be reversed by hydrogen ions at pH values of 1 and less. The interference which aluminum exerts on the cesium exchange with natural vermiculite can be largely removed by using a sodium saturated vermiculite at pH 12.6.

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