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REMOVAL OF RADIOISOTOPES FROM SOLUTION
BY EARTH MATERIALS FROM EASTERN IDAHO

by

M. W. Wilding and D. W. Rhodes

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M. W. Wilding and D. W. Rhodes

PHILLIPS PETROLEUM COMPANY
Atomic Energy Division
Idaho Falls, Idaho

Abstract

Naturally occurring earth materials from Idaho, primarily from localities near the National Reactor Testing Station (NRTS), were used in laboratory tests for the removal of radioisotopes from aqueous solutions. These earth materials included lignitic deposits, clay-like materials, and specific minerals; ion exchange resins were also considered for a specific application. The aqueous solutions were low-level radioactive cooling water or synthetic solutions made up to represent low-level radioactive wastes at the NRTS.

Cation exchange capacities and other properties which affect the removal of radioisotopes from solution were determined. The cation exchange capacities varied from 0.006 to 1.0 meq/g of solid. Earth materials with cation exchange capacities greater than 0.3 meq/g, in general, had distribution coefficients in excess of 1000. The highest distribution coefficients for cesium and strontium occurred in the pH range from 6.0 to 9.0.

The possible use of these materials for decontaminating low-level radioactive waste at the NRTS is discussed. The result of laboratory studies using these materials and an organic ion exchange resin for decontaminating a specific NRTS waste are given. A material high in clinoptilolite from a location near the NRTS was considered to be the most promising material for use in large beds or ion exchange-type columns.

Introduction

One of the consequences of the use of atomic energy has been the need to dispose of large volumes of low-level radioactive waste solutions. Examples of such wastes at the NRTS are cooling water and steam condensate, usually with contamination on the order of 10^{-5} $\mu\text{c/ml}$ or less of gross fission products. Such low-level wastes have often been disposed of by direct and economical means such as returning them to the environs (ground, sea, or rivers) with little or no pre-treatment, relying on dilution or adsorption on earth materials to reduce the concentration of radionuclides to acceptable levels. Long-lived radioisotopes, however, present a potential biological threat as long as they are free to move in the environs.

The purpose of this study was to gain a better understanding of what happens to radioactive nuclides when they come in contact with specific earth materials that are available for possible use in large ion exchange beds at the NRTS. From the results of this study, it should be possible to select those earth materials which can best be used to remove economically the long-lived radioisotopes from waste streams originating at the NRTS, possibly by use of large beds or ion exchange-type columns.

A lignite, a clay-bearing material, and a natural mineral, were selected from forty-two earth materials as being representative of the three general classes that were studied. The lignite was selected from the materials with a high content of organic matter, the clay represented typical clay-bearing materials, and clinoptilolite was chosen as a naturally occurring mineral. The results of laboratory tests for these three earth materials are described.

Earth Material Characterization

The forty-two earth materials used in the laboratory studies were obtained from natural deposits in Idaho. These materials were in the form of peat, low grade coal deposits, tailings from phosphate mines, volcanic deposits, core drillings, and alluvial and mineral deposits.

The percent ash, percent carbonate, aluminum-to-silicon mole ratios and cation exchange capacities were determined for each material. Table 1 shows the results of these determinations for the three representative earth materials.

Table 1

PROPERTIES OF THREE TYPICAL EARTH MATERIALS

<u>Materials</u>	<u>Ash Content (% by wt.)</u>	<u>Carbonate Content (% by wt.)</u>	<u>Aluminum-to-Silicon Mole Ratio of Ash</u>	<u>Cation Exchange Capacity meq/g</u>
Lignite	14.6	0.20	1.00	1.08
Clay	92.9	0.23	0.25	0.67
Clinoptilolite	88.9	1.37	0.35	0.35

The ash of those earth materials that contained large quantities of volatile organics (lignites) had a high aluminum-to-silicon mole ratio. This ratio is considerably higher than would be expected for clay minerals of the montmorillonite structure, suggesting that the inorganic fraction contains primarily kaolinitic type minerals with little of the expanding layer lattice (high ion exchange) type.

One of the most important properties of an earth material from the standpoint of use as a waste treatment medium, is its cation exchange capacity. The cation exchange capacity is defined as the number of chemical equivalents of cations that can be held on the exchange sites of a unit weight of material. The method used to determine the cation exchange capacity of the materials in Table 1 was the manganous ion replacement method⁽¹⁾. These cation exchange capacities should be considered as apparent capacities for several reasons. First, the manganous ion replacement method is based essentially on the uptake of manganous ions by the solid followed by replacement of the manganous ions with potassium ions through mass action forces. If the solid contained some constituent which precipitated or "fixed" the manganous ions, the result would be an apparent low exchange capacity. Secondly, the exchange capacity will vary with pH. The pH of the manganous chloride solution used for the laboratory measurement was on the acidic side (pH 4.1); however, since this is near the pH of many of the low-level radioactive waste solutions at the NRTS, measurement of the cation exchange capacity at this pH should be meaningful. Finally, the capacity for specific ions will vary somewhat from the value determined with manganous ions. Although the manganous method is adequate for comparing the exchange capacities of various materials, the exchange properties need to be determined for each specific ion.

The exchange capacities of the forty-two earth materials studied ranged from 0.006 meq/g for a basalt core drilling from the NRTS to 1.08 meq/g for a lignite from eastern Idaho.

In general, the clay-bearing materials from the NRTS, as well as those from other areas, had exchange capacities in the range 0.3 to 0.8 meq/g, a range expected for a bentonite-type clay material. However, these clays dispersed relatively easily in solution, especially in the alkaline pH range, forming colloidal particles that made columns impervious to water flow. The presence of appreciable amounts of organic matter (lignites) nearly always indicated an exchange capacity in the range 0.4 to 1.0 meq/g. However, these lignites, when wetted, tended to swell and decrease the flow rates through fixed bed columns.

Equilibrium-Type Cation Adsorption Experiments with Earth Materials

Batch equilibrium-type experiments were run to study the removal of radioisotopes from solution by ion exchange reactions with the earth materials. The effect of time of contact on the adsorption of cesium and strontium by lignites and clinoptilolite indicate that after four hours, equilibrium (greater than 99 percent adsorption) for all practical purposes had been reached.

In general, the highest adsorption of cesium and strontium by the various earth materials occurred in the pH range from 6.0 to 9.0, although there were some exceptions to this generalization. Many earth materials had distribution coefficients (K_d) above 1000 for cesium-137, strontium-90, cobalt-60, cerium-144, chromium-51, and ruthenium-106 in the pH range from 6.0 to 9.0. Clinoptilolite had a K_d greater than 1000 for cesium and strontium over the pH range from 2 to 10. Because of this wide range and its favorable physical properties, clinoptilolite appeared to be a likely candidate for the removal of radioisotopes from acidic waste.

Adsorption of Cesium and Strontium on Organic Ion Exchange Resins

During the course of this study, a need arose to develop a method for the decontamination of a specific waste at the NRTS. This waste consisted of fuel storage basin water from the Idaho Chemical Processing Plant (ICPP). Although considerable data had been accumulated on the probable performance of several earth materials, it was decided to include the use of ion exchange resins as a possible decontamination method because of their known creditable performance in similar applications. Consequently, several brands of organic ion exchange resins were equilibrated with solutions of fuel storage basin

water that was "spiked" with cesium and strontium to compare the adsorption of these radioisotopes on earth materials with the adsorption on organic ion exchange resins. The results are shown in Table 2.

Table 2

EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR CESIUM
AND STRONTIUM IN STORAGE BASIN EFFLUENT

Temperature: 23°C		
Water Hardness: Total hardness as CaCO ₃ , 190-200 ppm		
Ion Exchange Material	Equilibrium Distribution Coefficient, (K _d)	
	Cesium	Strontium
Nalco HDR-W	3,140	7,240
Duolite C-3	2,060	2,840
Amberlite-200	1,240	2,800
Amberlite-122	787	8,130
Dowex 50W-X8	762	15,500
Lignite	7,700	360
Clay	3,000	240
Clinoptilolite	4,200	1,300

Dowex 50W-X8 and clinoptilolite were selected for column testing with low-level radioactive waste in view of their superior performance in the removal of strontium-90 as shown in Table 2. However, Dowex 50W-X8 was considerably less effective for cesium than any of the other ion exchange materials in Table 2.

Ion Exchange Column Experiments with Low-Level Radioactive Waste

Columns using the organic ion exchange resin in both the hydrogen and sodium forms were run at a flow rate of about 20 ml/(cm²)(min). The Dowex resin, "as received", was in the sodium form but it was converted to the hydrogen form by washing repeatedly with 1.0N nitric acid, then washing with water. With the resin in the hydrogen form, the column capacity was approximately one-hundred column volumes of effluent more than with the resin in the sodium form.

The results of the ion exchange resin column experiments, which are shown in Figure 1, indicate that cesium-137 is the limiting radioisotope.

Fig. 1 Breakthrough curves for cesium, strontium, and total hardness from storage basin water in a DOWEX 50W-X8 hydrogen form resin column

In fact, as hardness breakthrough approaches, the calcium and magnesium in the water apparently have the effect of eluting the sorbed cesium sufficiently to cause the cesium concentration in the effluent to reach a maximum exceeding the cesium concentration in the influent by approximately a factor of 10. At the point of total hardness breakthrough, however, the elution of cesium is essentially complete and the ratio of cesium in the effluent to cesium in the influent becomes approximately 1.0.

Strontium adsorption is apparently extremely good even after total hardness breakthrough occurs, especially for the hydrogen form of the resin.

A clinoptilolite column containing particles 0.35 to 1.0 mm diameter was operated at a flow rate of about $4 \text{ ml}/(\text{cm}^2)(\text{min})$. This column had four sampling ports at intervals of one foot throughout the length of the column; thus, samples were actually collected from four clinoptilolite columns of different lengths. The results of several column experiments with clinoptilolite are shown in Figure 2 with C/C_0 (concentration in the effluent/concentration in the influent) plotted against column length with column volumes used as a parameter. By extrapolating the curves in Figure 2, it is possible to estimate the column length required to achieve a given C/C_0 value for a known number of column volumes of effluent passing through the column.

Additional column tests using a flow rate of $0.8 \text{ ml}/(\text{cm}^2)(\text{min})$ through a clinoptilolite column indicated that the decreased flow rate favored strontium adsorption from solution. Approximately 1000 column volumes of effluent passed through the column before C/C_0 for strontium reached a value of 0.001 in this case.

Breakthrough of cesium was achieved only in the top fourth of the four-section column. The breakthrough curve for cesium in this top (one foot) section is shown in Figure 3. The breakthrough curve for strontium in the same column and in the four-foot column are also shown for comparison. This more efficient removal of cesium reflects the specificity of the mineral clinoptilolite for cesium. According to Mercer⁽²⁾, cesium adsorption is not noticeably affected by the flow rate of the solution within the ranges of flow rate and particle size used in this work. From the data obtained in the column experiments, the limiting radioisotope for the clinoptilolite column with ICPP storage basin water appears to be strontium-90 with a capacity of about 600 column volumes. Using the ion exchange resin in the

Fig. 2 Strontium breakthrough in clinoptilolite columns

Fig. 3 Cesium and strontium breakthrough from fuel storage basin water in clinoptilolite columns

hydrogen form, cesium appears to be the limiting radioisotope with a capacity of about 500 column volumes.

The resin, of course, has the disadvantage of relatively high initial cost. In addition, regenerating equipment is required to avoid additional material cost, and the eluate from the regeneration step must be stored. Presumably, the exhausted clinoptilolite column could be sent to permanent burial pits.

Summary and Conclusions

The results of the laboratory experiments indicated that cesium, strontium, cobalt, cerium, ruthenium, and chromium all were adsorbed on locally available earth materials under favorable conditions. The basalt, which occurs in the subterranean of the NRTS, had the lowest exchange capacity (0.006 meq/g) of the materials tested. The lignite had the highest exchange capacity (1.08 meq/g) and the clay an exchange capacity intermediate between the basalt and the lignite. However, both the clay and the lignite had undesirable physical properties which interfered with the movement of water through the soil.

The organic ion exchange resin Dowex 50W-X8 can be used to remove both cesium and strontium from low-level radioactive waste at the NRTS, but the hardness of the water limits the capacity of the resin by eluting cesium. In addition, the resin must be regenerated and reused many times to avoid excessive material costs. The spent regenerating solution must then be stored in tanks, which is expensive.

The mineral clinoptilolite had good physical characteristics and good ion exchange characteristics over a wide pH range and was easily prepared in any desired particle size. Clinoptilolite is very selective for cesium, and has a fairly good capacity for strontium as well as most of the other cations studied. In addition, the low cost of the material permits it to be used on a "once through" basis. This type of material, which has been studied extensively at other sites, seems to be the best possibility for decontaminating low-level radioactive waste streams of the type considered in this study.

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