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A study of the adsorption of radioactive zirconium, niobium, cesium, and barium on alumina, silica gels and clays

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A STUDY OF THE ADSORPTION

OF RADIOACTIVE ZIRCONIUM, NIOBIUM, CESIUM AND BARIUM

ON ALUMINA, SILICA GEL AND CLAYS

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BY

DALE WESLEY HARRIS, 1936

A

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

The rapid development of the nuclear reactor with the accompanying
waste fission products has produced the problem of disposing of the
fission products without injury to the inhabitants of the surrounding
area. The fission products are radioactive, giving off beta and gamma
radiations which can cause ionization in the cells of the human body.
This ionization can lead to the following general types of injury:
(1) x-ray dermatitis, (2) induction of tumors, (3) leukopenia,
(4) leukemia, (5) anemia, (6) bone necrosis, (7) glandular dys-
function, and (8) fetal injury.

Irradiated reactor fuels are chemically processed to reclaim the
unburned nuclear fuel and to recover the transmutation products, such
as uranium-233 and plutonium-239, from the fission products and inert
components of the fuel. At the present time, these are separated by
solvent extraction. While the dissolution techniques vary with the type
of fuel being processed and the plant performing the operation, the
basic principles are the same. The solid fuels are stored 90 to 120
days following removal from the reactor to permit decay of the short-
lived fission product activities. These fuels are then dissolved in
nitric acid and the solution is fed to an extraction system where the
process of separation is completed.

The Redox and Purex processes are in current use for processing
irradiated fuels. The Purex process utilizes tributyl phosphate (TBP)
in hydrocarbon as the solvent and nitric acid as a salting agent to

separate natural uranium and plutonium from the fission products. Natural uranium and plutonium are separated from the fission products in the Redox process by using methyl isobutyl ketone (hexone) as the solvent and aluminum nitrate as the salting agent. Approximately 1000 gallons of untreated high-activity waste is produced per metric ton of uranium in each process.

Three types of irradiated fuels are currently being processed: (1) natural uranium, where plutonium and uranium are separated from fission products and from each other, (2) uranium-235-aluminum alloys where uranium-235 is recovered and separated from fission products, and (3) thorium, where uranium-233 and thorium are separated from fission products and each other. The waste from the liquid-liquid extraction of these fuels contain trace amounts of iron, nickel and chromium, present as products of corrosion of the stainless steel process equipment. Purex-type wastes are mainly fission products in approximately one molar nitric acid solution. Redox-type wastes contain significant amounts of aluminum with some sodium, which is added in adjusting the feed solution to an acid deficient condition, and some dichromate, which is used to oxidize the plutonium to an extractable oxidation state. In addition to the inert chemicals, all wastes contain fission products and lesser amounts of uranium, plutonium, and other heavy elements.

Many methods of disposing of the fission products have been proposed but only a few are in use today. The methods used are: (1) storage in underground tanks, (2) direct disposal of low level products to the ground or rivers, (3) fixing the fission products in siliceous materials for burial, and (4) packaging the fission products in concrete for burial at sea.

Storage of the fission products is the method most utilized and the most expensive method. A large number of tanks is required and each tank must be provided with a continuous monitoring system to detect leaks, heat exchange equipment to remove the heat generated during decay of the fission products, and continuous maintainance. The cost of maintaining this storage system is approximately 300 million dollars per year.

Disposal of the low level products to the ground or rivers can lead to the contamination of ground water or pollution of streams. In all cases, the amount of waste disposed of in this way must be kept below tolerance levels.

Fixing of the fission products in siliceous materials for burial is not used extensively. This method consists of fixing the fission products on the material by base exchange, surface adsorption or interstitial precipitation.

Packaging the fission products in concrete for burial at sea is used extensively in Great Britian because of the small land mass available. This method is effective for the present time but after a period of time the concrete will become weakened due to errosion and the pressure exerted by the water.

The growth of nuclear power will involve a large increase in production of radioactive wastes. It is imposible to predict either the rate and magnitude of such an increase or the characteristics of the wastes to be encountered. However, from an economic viewpoint, an increase in the production of radioactive wastes will prohibit the use of present disposal methods.

The purpose of this investigation was: (1) search the literature and review various methods investigated for the safe storage of radioactive waste products, (2) study the possible methods for the recovery of useful radioactive isotopes by selective adsorption, (3) perform laboratory tests to determine the capacity of various adsorbents for radioactive isotopes, (4) evaluate the data and correlate it with the findings reported in the literature, (5) make recommendations of the feasibility of using these adsorbents for removal or storage of the radioactive products, and (6) make recommendations for further investigations. The adsorption of radioactive zirconium, niobium, cesium and barium on alumina, silica gel, and clays was investigated. The adsorbents were contacted with aqueous solutions of the pure isotopes for two hours. Tests at pH values from one through seven were made for each adsorbent. The activities before and after adsorption were determined and from these data the activities removed were calculated. The data from the tests were tabulated so that a comparison of the activity removed by each adsorbent could be made. The data from the tests also enabled comparisons of the effect of pH on each adsorbent to be made.

The batch method using agitation was employed rather than a fixed bed in a column, because it was believed that this method would give more thorough mixing and result in a better determination of adsorption capacity.

II. LITERATURE REVIEW

This review is presented in two parts: (1) the long-term aspect of fission product disposal, and (2) a discussion of the methods under study for the disposal of fission products.

Long-Term Aspect of Disposal

Radioactive wastes [36] may be in liquid, gaseous, solid states, or in some intermediate form. The kind and intensity of radioactive wastes are not detectable by human senses. This characteristic makes radioactive wastes especially dangerous because they could be released to the soil the air, or to the surface waterways without detection.

Important from the waste disposal point of view are the long half-lives and known damaging properties to human tissues of certain of the isotopes. Regardless of the chemical treatment or what use is made of a radioisotope, it will continue to give off radiation at its natural decay rate.

Glueckauf [12] estimates that after one year, 99 per cent of the beta and gamma radiation emitted by the fission products is due to eight of the original 35 elements produced. He further states that if the fission products of over one year of age would be accumulated in one place where they would continue to decay and every year the waste from 1000 tons of burned material would be added, the activity would increase until an equilibrium condition is reached. The equilibrium level of energy dissipated in Mev curies is shown in Figure 1. The quantities

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All references are in bibliography.
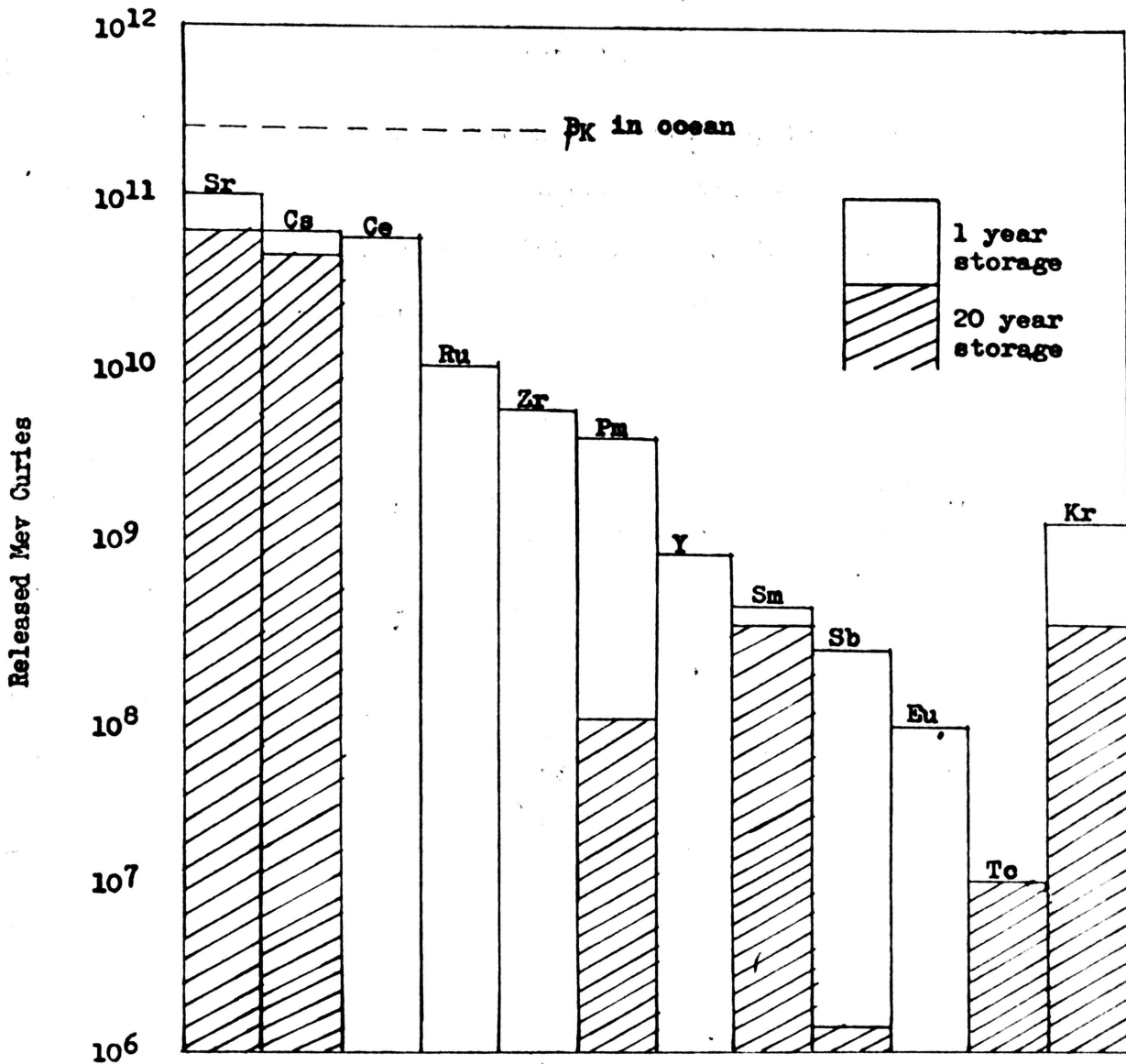
Figure 1. Equilibrium Activities of Fission Products Built
Up by the Annual Use of 1000 Tons of Fissile Material.

Glueckauf, E.: Long-Term Aspect of Fission Product Disposal, Vol. 9, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, pp. 3-8, United Nations, New York, N.Y. (1956).

are large by all known standards, but compared with the radiation from potassium-40 in the oceans, it is seen that the total activity will not exceed the activity of the potassium-40 if an annual production of 1000 tons is not exceeded.

After twenty years storage, the fission products of one year or less half-life will decay to an insignificant activity level. The equilibrium activity distribution which would result is indicated by the shaded portions of Figure 1. The activity from strontium-90 and cesium-137 now completely dominate.

The quantitative removal of these two species would decrease the activity of the bulk solutions by a factor of 1000. Figure 2 shows the decay of biologically weighted activity for a solution batch without and with the removal of cesium and strontium. It shows clearly that the solution remains at a high level of toxicity for a very long time when strontium and cesium are present, while after the removal of cesium and strontium, there is a rapid and continuing decrease of activity. This is an important feature of fission product disposal.

Composition and Quantity of Fission Product Solutions. The composition [12] of the fission products resulting from one ton of uranium-235 depends on the rate of burn-up and the time elapsed since their removal from the reactor. An example is represented in Table I in which the principle elements are ordered according to their position in the periodic table.

The fission products are extracted in a recycling process and are, therefore, mixed with a large quantity of chemicals which are derived
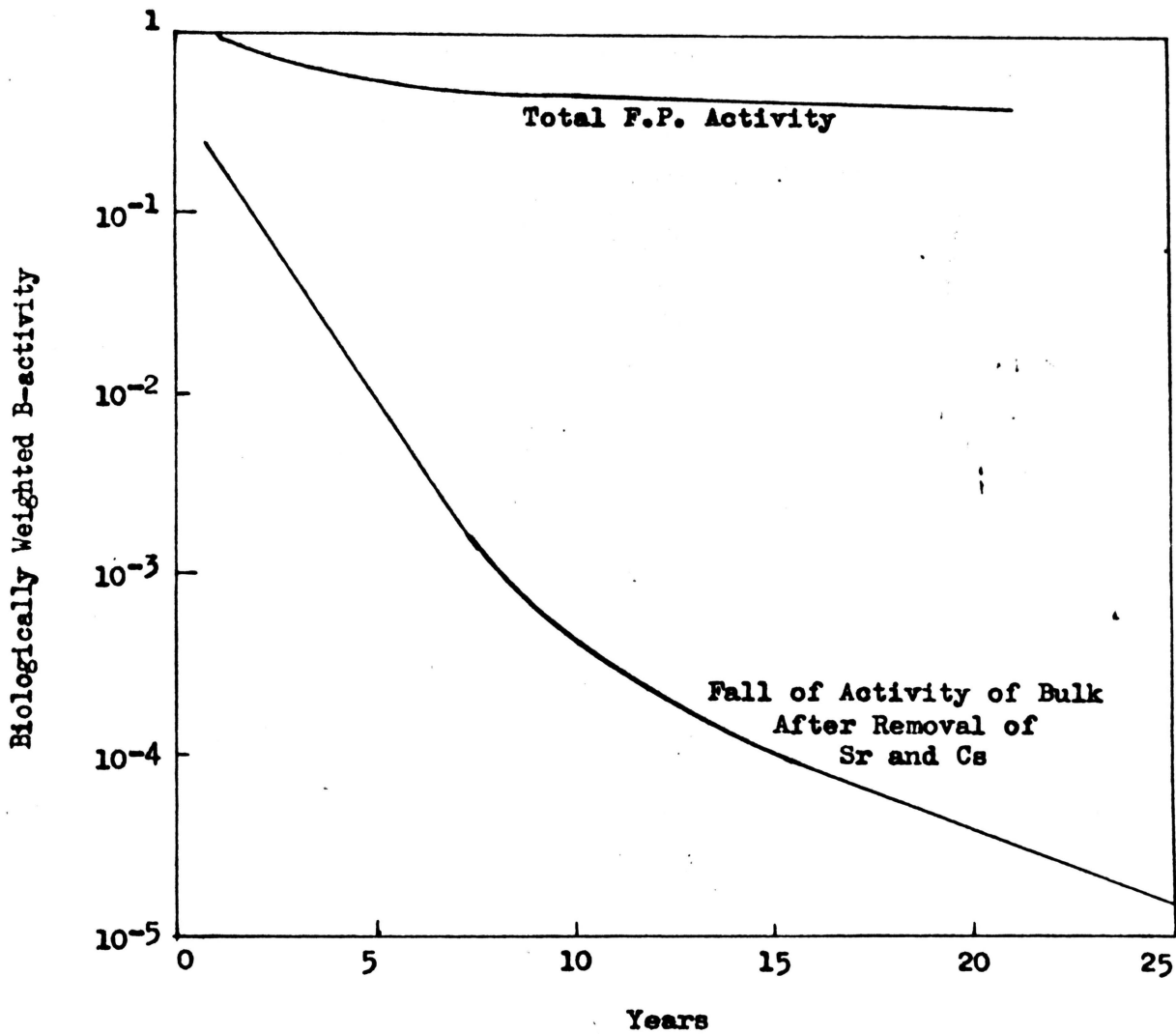
Figure 2. The Decay of "Biological" β-activity in a Batch of Mixed Fission Products.

Glueckauf, E.: Long-Term Aspect of Fission Product Disposal, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 9, pp. 3-8, United Nations, New York, N.Y. (1956).

TABLE I

Quantities of Fission Products Derived from One Ton of U^{235} (150 days irradiation, 30 days cooling)

Group	Element	kg
0	Kr + Xe	128
1	Rb	15
	Cs	118
2	Sr	42
	Ba	43
3	Rare earths + Y	317
4	Zr	125
5	Nb	5
6	Mo	92
	Te	16
7	Tc	29
	I	7
8	Ru, Rh, Pd	61

Glueckauf, E.: Long-Term Aspects of Fission Product Disposal, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 9, pp. 3-8, United Nations, New York, N.Y. 1956.

from (1) impurities of the reactor fuel, (2) products of the interaction of neutrons with the reactor fuel, (3) incompletely separated reactor fuel, (4) incompletely removed canning or alloying material, (5) chemicals added during separation, and (6) corrosion products from plant and storage vessels. The quantities of these will vary greatly according to the reactor materials and to the extraction process employed.

An example of the type of fission products produced in a graphite-moderated reactor using slightly enriched uranium as fuel is shown in Table II. Nitric acid has been used as a salting-out agent in the solvent extraction process.

Disposal at Sea. The complete and uniform dissipation of all fission products in the sea would eventually reach the activity level of potassium-40, and the high toxicity of strontium-90 would result in a higher toxicity than is normally present due to potassium-40.

After removal [1] of strontium-90 and cesium-137, an immediate and uniform dissipation of the remaining fission products in the oceans could be considered safe. However, uniform dissipation cannot be achieved and storage of the remaining fission products for 13 years would be required before disposal in the oceans.

Disposal on Land. The fission product solutions will remain active for 1000 years and will require completely deserted and inaccessible areas for disposal, or else it will be necessary to turn the radioactive materials into solid products from which the fission products cannot be leached, e.g., as glasses [10] or ignited clays [14].

Disposal of Strontium and Cesium. Strontium and cesium need not be disposed of until their activities have considerably decayed. These

TABLE II

Quantities of Solutions Arising from the

Solvent Extraction of One Ton of U^{235}

Constituent	Before Concentration Tons	After Concentration Tons
Total Volume of Solution	5-10,000 m^3	25 m^3
HNO_3	1300	10.5
$Fe(NO_3)_3$		6.8
$Cr(NO_3)_3$		1.5
$Al(NO_3)_3$		0.6
$Ni(NO_3)_2$		0.5
$UO_2(NO_3)_2$		1.3
Mixed Fission Products		1.8

Glueckauf, E.: Long-Term Aspect of Fission Product Disposal, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy. Vol. 9, pp. 3-8, United Nations, New York, N.Y. 1956.

two materials can be of great value as sources of radiation especially in the case of the gamma radiating cesium.

When the specific activity of these elements becomes too low for economical use, disposal may be considered. The quantities for disposal would be small and adsorption in silica bonded clays [6] or in the montmorillonite greensands [4] followed by baking at 1000 degrees could be employed. These greensands have the advantage that they are suitable for column packing without special treatment. For this type of disposal, it is not necessary to have expensive heat treatment equipment. The heat generated by the decay of strontium and cesium raises the temperature above 1000 degrees centigrade. Perring [23] has calculated the diameters of the boreholes required for obtaining such temperatures. The diameter depends on the exchange capacity of the adsorbing material and the specific activity of the final product.

<u>Decontamination of Low-Level Liquid Wastes.</u> [33] Conventional water treatment processes that have been investigated for the removal of radioactive materials include: (1) coagulation, (2) sedimentation, (3) filtration, (4) lime-soda ash softening, and (5) ion exchange.

Coagulation involves the formation of chemical flocs that adsorb, entrap, or otherwise bring together suspended matter. The addition of coagulating chemicals will result in the precipitation of some of the soluble constituents in the waste as metal hydroxides.

Coagulation with settling has been studied extensively at the Oak Ridge National Laboratory. [33] The results of these studies show that with the exception of most cations of valence three, four or five, coagulation is not very effective for the removal of radioactive materials

from water. Coagulation will be helpful in the removal of radioactive material attached to or adsorbed on the natural turbidity in surface waters. Since coagulation will remove much of the turbidity, the activity attached will also be taken out.

Sand filtrations [33] have not been effective for the removal of radioactive materials. Their major function is to remove the radio-activity previously incorporated in floc particles. Removals vary, depending on the nature of the materials.

Softening with lime and soda ash has been studied, and under proper conditions, effective removals of strontium, barium, cadmium, yttrium, scandium, and zirconium-niobium were obtained. Removals of 95 to 99 per cent or better are possible. For the most satisfactory removal of strontium, increased amounts of both lime and soda ash were required. [17]

Removal of radioactive materials by ion exchange is feasible, and for most effective removal, mixed resins in series is recommended. [33] The results show that 99 per cent of the radioelements can be removed if mixed resins are utilized. The initial and operating costs may pro-hibit wide spread usage until suitable regeneration techniques are developed.

Methods Under Study for the Disposal of Fission Products

The methods under study for the disposal of fission products include: (1) adsorption on solids, (2) packaging in ceramic bodies, and (3) calcination of solvent extraction wastes.

Lacy[19] reports that Conasauga shale will remove certain radio-nuclides from effluent wastes by base exchange, surface adsorption, and interstitial precipitation.

Clay, shale, and soil materials, when moist, are charged electro-negatively. What accounts for the exchange capacity in shale are: (1) broken bonds at the edges of the silica-alumina units, (2) substitution within the lattice structure of a trivalent for quadrivalent ions resulting in unbalanced charges within the shale unit, and (3) replacement of the hydrogen of exposed hydroxyl groups by a cation.

The outside faces, edges and corners of the shale crystal[19] have associated with them various cations. When the surface atoms are ionized, the shale particle carries a negative ionic charge. The positive ions are contained in the ionic layer adjacent to this negative charge. Therefore, the surface of a shale or clay particle could adsorb a molecular layer of the radioactive material.

Lacy[19] also reports that precipitation of certain ions will take place between the shale particles if the solubility product is exceeded. Removal of ions from the liquid phase and their replacement with milli-equivalent amounts from the solid phase can cause local precipitation.

Grover[14] has reported that a process for the bonding of mont-morillonite clay by mixing with hydrolysed ethyl silicate has been developed for the preparation of granules in the size range 10 to 30 B.S. mesh. The breakthrough capacity was determined to be 15 to 20 milliequivalents per 100 grams and the ultimate capacity was determined as 25 to 30 milliequivalents per 100 grams.

Amphlett[2] reports that radionuclides in waste solutions may be fixed by mixing with suitable siliceous materials and firing to high temperatures to produce a ceramic. Solutions containing cesium-137, cerium-144, strontium-90, and synthetic mixed fission products were contacted with montmorillonite. This clay was chosen because of its high exchange capacity. Adsorption of the activity followed by firing at 1000 C for eight hours leads to fixation of the species cesium, strontium, yttrium, cerium, barium, and mixed fission products. It was reported that approximately 99 per cent retention is obtained with this method.

Leaching tests[2] were made with sea water, distilled water, and five normal nitric acid. Sea water and distilled water leaching had almost no effect on the per cent retention. Nitric acid leached small amounts of the activity from the fired material.

Cook and Wilkinson[9] have studied the removal of mixed fission products by adsorption on inert substances and adsorption on precipitates. The adsorption was studied both by batch and column techniques. An activity of 3000 counts/minute/ milliliter was used in dilute acid solution. The columns consisted of glass tubes 13 centimeters long and $2\frac{1}{2}$ centimeters in diameter. The adsorbing media were mixed with glass helices to increase the flow rate. In the batch experiments, approximately 5 grams of adsorbent was stirred with 50 milliliters of effluent for one hour. The results of these experiments are given in Table III.

The adsorption of fission products from three normal nitric acid solutions using the batch technique was also employed. The adsorbent

TABLE III

Adsorption of Fission Products by Various Adsorbents

Adsorbent	Column Activity Removed, %	Batch Activity Removed, %
Fullers Earth	97	82
China Clay	98	74
Calcined Al_2O_3	99	80
Harwell Soil	99-80	85-95
Charcoal		25
Barium Sulfate		51

Cook, G.B. and J. Wilkinson: The Sorption of Fission Product
Mixtures in Relation to Effluent Disposal, Atomic Energy Re-
search Establishment, Harwell, England, A.E.R.E. C/R-340, 1957.

was added to the acid solution and stirred for one hour. Parallel experiments were also performed on the solutions first made alkaline with caustic soda. These results are given in Table IV. The only satisfactory adsorbent is calcium phosphate in alkaline solution. This may be attributed to the fact that a large number of elements form phosphates insoluble in alkaline solution and are thus readily adsorbed.

The effect of flocculent precipitates on the adsorption of fission products was also investigated by Cook and Wilkinson.[9] Solutions such as ferric chloride and aluminum sulphate were added with continuous stirring to the effluent previously made alkaline with caustic soda. Ferric hydroxide was the best settling precipitate removing 98 per cent of the activity present. Experiments were performed to determine the effect of pH on the adsorption capacity of the precipitate. The results show that as high a pH as possible is advisable.

White and Lahaie[35] have investigated the adsorption properties of bentonite, stoneware clay, and white art china clay. Experiments were based upon the typical wastes expected from the TBP solvent extraction process. For preliminary work, an inactive synthetic waste solution was prepared. This solution was called S-1 and has the analysis shown in Table V.

The clays were mixed by hand with solution S-1 and then were shaped into balls 2 inches in diameter. The balls were dried at $100^{\circ}C$ for 12 hours and then fired at $1250^{\circ}C$ for 6 hours. After firing the clays had a brick-like texture, were mechanically stable, but very porous.

Lower melting components such as a soft glass, a glaze, and nepheline syenite were added to the clays to increase the density of the final

TABLE IV

Adsorption of Fission Products

from Acid and Alkaline Solution

Adsorbent	Activity Removed from 3 N/HNO$_3$ Solution, %	Activity Removed from Effluent Made Alkaline with NaOH, %
Al$_2$O$_3$	2	78
China Clay	8	81
Fullers Earth	3	86
Calcium Phosphate	Soluble	99
Harwell Soil	27	87

Cook, G.B. and J. Wilkinson: The Sorption of Fission Product Mixtures
   in Relation to Effluent Disposal, Atomic Energy Research Establishment,
   A.E.R.E. C/R-340, 1957.

TABLE V

Synthetic Waste Solution Concentrate-S-1

Element	Parts Per Million
Aluminum	100
Calcium	100
Copper	100
Iron	200
Magnesium	100
Lead	200
Silica	250
Strontium	100
Sodium	200
Total	1350
Nitric Acid	7N

White, J.M. and G. Lahaie: Ultimate Fission Product
   Disposal-The Disposal of Curie Quantities of Fission
   Products in Siliceous Materials, Chalk River, Ontario,
   CRCE-591, 1955.

product and decrease the firing temperature. The addition of the flux
reduced the fusion temperature by several hundred degrees, but was not
large enough to consider using this method for final disposal.

Nepheline syenite[35] has been investigated using S-1 solution
taged with various isotopes contained in the effluent waste. The ratio
of liquid to solid was chosen as 1:1 since gelation and volume change
on fusion were both satisfactory. The range of acidity over which
satisfactory gelling occured was very broad. The gel time varied from
30 minutes with 3 normal acid to less than one minute at 7 normal.

Thirty milliliters of solution were mixed with 30 grams of
nepheline syenite and allowed to gel. When gelation was completed,
the samples were heated and the vapors collected and condensed. Two
series of tests were conducted. One at 525°C and the other at 1225°C,
the fusion point of nepheline syenite. The results are given in Table
VI. The results indicate the feasibility of combining fission products
with nepheline syenite to form a glass. The only isotope which vaporized
to any extent was ruthenium. The addition of 12 per cent boron oxide
as a flux reduced the fusion point to 1000°C.

The relative capacity[25] of 8 preformed adsorbents for ruthenium
and zirconium have been determined by batch wise experiments over the
pH range 1 to 11. The capacities of the adsorbents are nearly constant
over the pH range 3.5 to 10. The results of these experiments are
listed in Table VII. An initial activity of 1.9 x 10^6 counts/minute/
milliliter of ruthenium at a pH of 8.9 and 1.3 x 10^6 counts/minute/
milliliter of zirconium at a pH of 6.1 was used. The experiment was
of the batch type using 0.17 grams/milliliter and a contact time of 20

TABLE VI

Activity in Distillates

Solution	525°C			1225°C		
	Total Count in 1 ml of Origional Solution	Total Count in 1 ml of Distillate	% Activity in Distillate	Total Count in 1 ml of Origional Solution	Total Count in 1 ml of Distillate	% Activity in Distillate
Sr^{90}	3.3×10^6	8	0.001	3.3×10^6	None	0.001
Cs^{137}	1.5×10^6	232	0.02	1.5×10^6	None	0.001
Ce^{144}	4.4×10^6	14	0.001	4.4×10^6	None	0.001
Ru^{106}	4.5×10^3	1.3×10^3	28	-	-	-
Mixed F.P.	1.9×10^7	7.4×10^4	0.4	1.9×10^7	4.5×10^5	2.4

White, J.M. and G. Lahaie: Ultimate Fission Product Disposal-The Disposal of Curie Quantities of Fission Products in Siliceous Materials, Chalk River, Ontario, CRCE-591, 1955.

TABLE VII

Relative Sorbing Capacities of Adsorbers

for Ruthenium-106 and Zirconium-95

Adsorber	% Remaining Ruthenium-106	% Remaining Zirconium-95
Silica Gel	6.2	1.9
Activated Carbon	0.2	0.2
Aotivated Alumina	1.7	0.9
Manganese Dioxide	0.04	0.04
Super Filtrol FO	1.4	0.07
Attapultus Clay	1.9	0.05
Titanium Dioxide	0.3	0.4
Zirconium Dioxide	-	0.8

Quarterly Report For Liquid Waste Disposal Research, Mound
Laboratories, AECD-4148 (1950).

hours. The per cent activity remaining is inversely proportional to the relative capacity of the adsorbent for each element.

Additional investigations were made with Nuchar 000 to determine the capacities as a function of the concentration of radioactive material and the amount of adsorbent used. The procedure used was to shake the desired amount of adsorbent with a solution of pure isotope for 20 hours. The maximum per cent removal of cesium was found to be 70 per cent at a concentration of 1000 parts per million. One hundred per cent removal of zirconium and cerium can be obtained by using 4000 and 5000 parts per million respectively. In the presence of hydrogen sulfide, the activity remaining can be reduced to zero.

A number of tests [30] have been conducted on Hanford type soils to characterize the effect of various parameters on the adsorption of isotopes. The adsorption by soil of the studied isotopes from solutions whose concentrations varied from 10^{-3} to 10^{-8} moles/liter is attributed to ionic exchange because: (1) the cations so adsorbed are quantitatively recoverable by exchange with other added cations, (2) the concentrations involved are in many cases less than the solubility product, (3) electrophoresis tests have failed to show the presence of radiocolloids, and (4) the adsorption on soils is non linear with increasing concentration in solution of the cation being removed. The equilibrium adsorption of radioisotopes from solutions is in the decreasing order: plutonium, cerium, yttrium, cesium, and strontium.

Many radioactive waste solutions [30] which are disposed to the ground contain total salt concentrations up to four molar, and such

concentrations of salts have a depressive effect on the ion exchange
at equilibrium.

Hamner and Haydon[15] report that radioisotopes can be fixed in
ceramic bodies by sintering at a temperature below that at which a
glass is formed. They have found that the addition of limestone,
sodium carbonate, and shale to a solution of effluent wastes forms
a stiff gel. Firing of this gel to temperatures from 850 to 1750 C
fixes the radioisotopes in the gel. After leaching for 90 days, the
activity in the leach water was slightly radioactive.

Incorporation of fission products into glass has been studied at
Chalk River.[10, 29] Feldspars and nepheline syenite which produce
durable glasses when fused are available at low cost. The mineral
nepheline, present in nepheline syenite, has the property of forming
a silica gel when mixed with acid. This material when mixed in a 1:1
weight/volume ratio with fission product solution containing at least
two normal acid forms a firm gel which can be dried without appreciable
loss of fission products other than ruthenium. When the dried gel is
heated to 1300°C it fuses to an extremely viscous melt which on cooling
produces a durable glass.

Experiments[10] have shown that practically all the ruthenium
distills from the nitric acid containing gel during drying. This
will necessitate pretreatment of the solutions to remove ruthenium,
followed by a separate disposal. If nitric acid is not present,
ruthenium will not distill.

As a means of removing nitric acid, electrodialysis[10] of fission
products has been investigated. This produces a precipitate which

could be mixed with a siliceous material and fused to a glass. Another advantage is that the long-lived strontium and cesium can be separated from the remainder of the fission products.

Ion exchange of waste fission products on clays and subsequent fixation by firing has promising aspects for permanent disposal. However, wastes from aluminum and zirconium clad and alloyed fuels contain large amounts of the multivalent ions of aluminum and zirconium which are preferentially absorbed by the clay. These ions must be separated from the fission products and this is done by calcination [1, 13] of the waste solution and separation of the leachable fission products from the insoluble aluminum and zirconium oxides.

Abriss, Reilly, and Tuthill [1] have investigated the calcination of aluminum and zirconium wastes for the subsequent recovery of cesium and strontium. Calcination of the waste solutions was accomplished by heating to $350^\circ C$ in a low temperature kiln to decompose the nitrates and then heating to $550^\circ C$ in a high temperature kiln where complete conversion to the oxides was effected. The solid oxides are discharged to a leaching tank.

Several types of leaching techniques were used: (1) non-continuous agitated system, (2) continuous non-agitated system, and (3) continuous system with mixing. All leachings were carried out at room temperature. The choice of leaching solutions is restricted by the solubility of aluminum oxide and zirconium oxide. The optimum leaching solutions were determined to be nitric acid at a pH of 3 for aluminum oxide and nitric acid at a pH of 1 for zirconium oxide. A combination of the continuous non-agitation and non-continuous agitated

systems was found to be most suitable for the removal of strontium and cesium oxides. The continuous non-agitated system was employed for 10 days and then changed to the non-continuous agitated system for 60 days. Eighty-five per cent of the cesium and strontium oxides were removed. A calciner pilot plant [16] has been developed at the Brookhaven National Laboratory for carring out this process.

The methods [2, 4, 6, 14, 19, 21, 35] for disposal of highly active wastes in natural siliceous materials requires, in all cases, the firing of the finished material at temperatures of 1000°C or higher, so that negligible activity is removed on leaching. The fired material can then be stored in boreholes, underground tunnels or caverns, or beneath water. Whatever form of storage is adopted, the solid wastes will tend to heat up due to radioactive disintegration.

Amphlett and Warren [3] have studied the effect of heating a large clay block at its center to determine the feasibility of self-fixation of the fission products on the clay. A furnace was placed in the center of the block by means of a borehole. Thermocouples were placed at varying distances from the central axis to determine the radial temperature distribution. Heating was begun with an input of 182 watts and continued until an input of 618 watts was obtained. The temperature rise at 182 watts was small at first until the bulk of the moisture was driven off. The temperature then rose rapidly from 80 to 230°C in one day. Temperature increases in the outer thermocouples followed a more gradual course, but the same result was noted. Considerable fissuring occured extending from the furnace zone toward the outside of the block. The clay changed from a blue-gray appearance to a dull brown, hard

brick on baking to 1000°C. The temperature along the center plane falls to one-half the furnace temperature within two inches of the edge of the heated zone. It is necessary to ensure that heating is achieved in less time than that required for the activity to diffuse through this distance.

III. EXPERIMENTAL

Purpose of Investigation

The purpose of this investigation was to determine the adsorption capacity of alumina, silica gel, and clays for zirconium, niobium, cesium and barium at varying pH values.

Plan of Experimental

The experimental work consisted of the following steps: (1) preparation of aqueous solutions of the radioisotopes, (2) adjustment of the pH of the solutions, (3) sampling the solution to determine the activity, (4) weighing the required amount of solid adsorbent, (5) mixing the adsorbent and solution, (6) contacting the adsorbent with solution by agitation, (7) filtration or centrifugation as required, (8) sampling the filtrate to determine the activity, (9) recording the data, and (10) calculation of the activity removed.

Materials

The materials used in this investigation, their specifications or composition, the manufacturer or supplier, and the use of the material are listed.

Aluminum Oxide (Acid). Activity grade 1; pH, 4; extractible salts, less than 0.4%; filtration speed, 0.2 ml/min; specific gravity,

0.9. Manufactured by M. Woelm-Eschwege, West Germany. Distributed by Alupharm Chemicals, New Orleans, La. Used as an adsorbent for radio-nuclides.

Aluminum Oxide (Basic). Activity grade 1; pH, 10; extractable salts, less than 0.2%; filtration time, 0.2 ml/min; specific gravity, 0.9. Manufactured by M. Woelm-Eschwege, West Germany. Distributed by Alupharm Chemicals, New Orleans, La. Used as an adsorbent for radionuclides.

Aluminum Oxide (Neutral). Activity grade 1; pH, 7.5; extractable salts, less than 0.2%; filtration time, 0.2 ml/min; specific gravity, 0.9. Manufactured by M. Woelm-Eschwege, West Germany. Distributed by Alupharm Chemicals, New Orleans, La. Used as an adsorbent for radionuclides.

Ammonium Hydroxide. U.S.P. Aqua Ammonia 26° Baume. Manufactured and distributed by E.I. Du Pont De Nemours and Co., Inc., Wilmington, Del. Used to adjust pH of aqueous solutions.

Buffer Solution. Part No. 103-1-0-2, Leeds and Northrup Co., Philadelphia, Penn. Used to standardize pH meter.

Clay, Burnt Refractory. Bureau of Standards sample No. 78, powder form. Composition: Aluminum oxide (Al_2O_3), 69.97%; silicon oxide (SiO_2), 20.78%; titanium oxide (TiO_2), 3.34%; potassium oxide (K_2O), 2.9%; magnesium oxide (MgO), 0.52%; calcium oxide (CaO), 0.32%; sodium oxide (Na_2O), 0.26%; zirconium oxide (ZrO_2), 0.12%; lithium oxide (Li_2O), 0.03%. Obtained from the United States Bureau of Standards, Washington, D.C. Used as a solid adsorbent.

Clay, Feldspar. Sample No. 14, powder form. Composition:
silicon oxide (SiO_2), 69.99%; aluminum oxide (Al_2O_3), 18.19%; iron
oxide (Fe_2O_3), 1.0%; potassium oxide (K_2O), 0.85%; magnesium oxide
(MgO), 0.76%; calcium oxide (CaO), 0.51%; sodium oxide (Na_2O), 0.45%.
Supplied by William S. Murray, Inc., Utica, N.Y. Used as an adsorbent
for radionuclides.

Clay, Kaolin. Washed powder, lot No. 10241, chemical formula,
$Al_2O_3-2SiO_2-2H_2O$. Obtained from J.T. Baker Chemical Co., Phillipsburg,
N.J. Used as an adsorbent for radionuclides.

Clay, Soda-Feldspar. Bureau of Standards sample No. 99, Powder
form. Composition: silicon oxide, 68.65%; aluminum oxide, 19.06%;
sodium oxide, 10.73%; potassium oxide, 0.41%; calcium oxide, 0.36%;
iron oxide, 0.067%; magnesium oxide, 0.053%. Obtained from the United
States Bureau of Standards, Washington, D.C. Used as an adsorbent for
radionuclides.

Clay, Sodium-Bentonite (Wyoming). Powder form, chemical formula,
$5Al_2O_3-2MgO-24SiO_2-6H_2O-(Na_2O, CaO)$. Manufactured by C. Volday Corp.
Distributed by International Minerals and Chemicals Corp., Skokie, Ill.
Used as an adsorbent for radionuclides.

Good-rite (Microsil). Finely divided particles, high silica
content. Com. No. 5450-0090, surface area, 162 m^2/gm. Manufactured
by B.F. Goodrich Co., Avon Lake, Ohio. Used as an adsorbent for
radionuclides.

Isotope (Zirconium and Niobium). Zr-Nb, 95-P processed, carrier
free, batch No. 43; chemical form, oxalate; concentration, 7.80 mc/ml;

normality, 0.3 acid. Obtained from the United States Atomic Energy Commission, Oak Ridge, Tenn. Used to prepare aqueous solutions of the radionuclides.

Isotope (Cesium and Barium). Cs-Ba-P processed, carrier free, batch No. 49; chemical form, CsCl in hydrochloric acid; concentration, 6.94 mc/ml; radiochemical purity, greater than 99%. Obtained from the United States Atomic Energy Commission, Oak Ridge, Tenn. Used to prepare aqueous solutions of the radionuclides.

Nitric Acid. Meets ACS specifications, lot No. 90231; assay 69.0 to 71.0% HNO_3; specific gravity at 60/60°F, 1.416 to 1.424; residue after ignition, 0.0004%; chloride (Cl), 0.00005%; sulfate (SO_4), 0.0001%; arsenic (As), 0.000001%; heavy metals (as Pb), 0.00002%; iron (Fe), 0.00002%; copper (Cu), 0.00005%; nickel (Ni), 0.00005%. Manufactured and distributed by J.T. Baker Chemical Co., Phillipsburg, N.J. Used to acidify and adjust pH of aqueous solutions.

Silica Gel. Laboratory product. Prepared by a method similar to the procedure outlined by Bartell and Fu.[5] Used as an adsorbent for radionuclides.

Silicon Tetrachloride ($SiCl_4$). Technical grade, 90 to 92%; formula weight, 169.92; catalogue No. S-165. Manufactured by Fisher Scientific Co., New York, N.Y. Used to prepare silica gel.

Water, Distilled. Obtained from distilled water tap, Quantitative Analysis Laboratory, Room 306, Chemical Engineering Building, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used to prepare silica gel and aqueous solutions of radionuclides.

Apparatus

The apparatus used in this investigation, the specifications for use, the manufacturer or supplier, and the use of the apparatus are given.

Balance. Analytical, MSM property No. 13191, weighing range 0 to 100 grams, to nearest 0.1 mg. Manufactured by William Ainsworth and Sons, Inc., Denver, Colorado. Used to weigh solid adsorbents.

Counter. Geiger-Muller radiation, type 100 NB, No. 29162, 900 v, dc, 3.5 mg/cm^2 mica window. Manufactured by NRD Instrument Co., St. Louis, Mo. Used to count radiation from zirconium and niobium.

Counter. Well scintillation, MSM property No. 21643, model CS-600, tube No. 2-7-825, NaI and anthracene crystals. Manufactured by NRD Instrument Co., St. Louis, Mo. Used to count radiation from cesium and barium.

Counting Dishes. Stainless steel, 1 inch diameter, 5/8 inch deep. Manufactured by Radiation Counter Laboratories, Skokie, Ill. Used to contain samples to be counted.

Dosimeters. Type 362. Manufactured by Victoreen Instrument Co., Cleveland, Ohio. Used to detect radiation dosage received by author.

Filter Paper. Blue ribbon, No. 589, 11 cm. Manufactured by Schleicher and Schuell Co., Inc., New York, N.Y. Used to filter slurry of adsorbent and radioactive solution.

Glassware. An assortment of glassware was used which included; 50 ml shaking bottles, filter funnels, stirring rods, Erlenmeyer flasks, and pipettes. Obtained from stock room, Chemical Engineering Building, Missouri School of Mines and Metallurgy, Rolla, Missouri.

<u>Heat Lamp</u>. Infrared, type 7A-N, 110 v, ac-dc, 2 amp. Manufactured by Prometheus Electric Corp., New York, N.Y. Used to dry liquid samples.

<u>Micro Centrifuge</u>. MSM property No. 13866, model 496 E, 110 v, dc, 60 cy. Manufactured by International Equipment Co., Boston, Mass. Used to centrifuge slurry of adsorbent and radioactive solution.

<u>Minometer</u>. MSM property No. 22566, serial No. 287-3145, 100 to 125 v, 60 cy. Manufactured by Victoreen Instrument Co., Cleveland, Ohio. Used to read Victoreen dosimeters.

<u>Oven</u>. Drying, model No. 255, temperature range 0 to 100°C, 220 v, dc. Distributed by Eimer and Amend Laboratory Furnishers, New York, N.Y. Used for drying silica gel.

<u>Oven</u>. Drying, model No. 1255, temperature range 0 to 200°C, 220 v, 60 cy, single phase, 800 watts. Manufactured by Precision Scientific Co., Chicago, Ill. Used to dry solid adsorbents.

<u>pH Meter</u>. Cat. No. 7664, 115 v, ac, 60 cy. Manufactured by Leeds and Northrup Co., Philadelphia, Penn. Used to indicate pH of aqueous solutions.

<u>Scaler</u>. MSM property No. 21630, Model B-1800R, 105 to 125 v, 50 to 60 cy, 206 watts. Manufactured by NRD Instrument Co., St. Louis, Mo. Used to record activity of samples.

<u>Scaler</u>. MSM property No. 21631, model B-1602, 105 to 125 v, 50 to 60 cy, 100 watts. Manufactured by NRD Instrument Co., St. Louis, Mo. Used to record activity of samples.

<u>Scaler</u>. MSM property No. 21640, model B-1601, 105 to 135 v, 50 to 60 cy, 100 watts. Manufactured by NRD Instrument Co., St. Louis, Mo. Used to record activity of samples.

Shaker. Burton clinical modified, Model No. 1450, 110 v, ac, 60 cy. Manufactured by Burton Manufacturing Co., Los Angeles, Calif. Used to agitate samples.

Shield. Lead counter, MSM property No. 21642. Manufactured by NRD Instrument Co., St. Louis, Mo. Used to shield samples from atmospheric radiation.

Vials. Shell, 15 x 45 mm, short style. Manufactured by Kimble Glass Co., Toledo, Ohio. Used to contain liquid samples for well counter.

Method of Procedure

The method of procedure for this investigation has been divided into nine parts. They are: (1) determining the efficiency of the counter, (2) preparation of the aqueous solution of radioisotopes, (3) adjustment of the pH of the solutions, (4) sampling the solution before adsorption, (5) weighing the solid adsorbent, (6) contacting the adsorbent with solution, (7) filtration or centrifugation (8) sampling the filtrate after adsorption, and (9) counting the samples. Unless otherwise specified, the steps of the procedure are applicable for each of the four radioisotopes investigated.

Efficiency of Counter. The efficiency of the counters were determined by counting standard sources for one hour. The Geiger-Muller counters and beta scintillation counters were standardized against N.B.S. radium D & E standard No. 3537. The gamma scintillation counter was standardized against a 0.1 mc radium source. The efficiencies of the counters were calculated and recorded.

Preparation of Aqueous Solution. The solution containing zirconium and niobium was prepared in a different manner than the solution containing cesium and barium. Therefore, they will be discussed separately.

Zirconium-Niobium Solution. Two milliliters of the pure isotope solution was transferred to a beaker by means of a pipette. Ten milliliters of distilled water and a small amount of nitric acid were added. The resulting solution was boiled to destroy the oxalate. The solution was then transferred to a two liter reagent bottle and diluted to approximately one liter with distilled water.

In aqueous solution, zirconium becomes colloidal at approximately a pH of 2 and adheres to the walls of the container. For this reason, sufficient nitric acid was added to the solution to obtain a pH of one.

Cesium-Barium Solution. One-half milliliter of the pure isotope solution was pipetted into a one liter reagent bottle. Distilled water was added until a volume of approximately one liter was obtained.

Adjustment of pH. The reagent bottle containing the solution of isotopes, was shaken by hand to ensure an even distribution of the solution. Approximately 50 milliliters of the solution was transferred from the reagent bottle to a beaker. The electrodes of the pH meter were immersed in the solution and nitric acid or ammonium hydroxide, depending on the pH value desired, was added slowly with continuous stirring until the desired pH was obtained.

Sampling the Solution Before Adsorption. The procedure for removing samples of the zirconium-niobium solution for counting differed from the procedure used for the cesium-barium solution and will be discussed separately.

Zirconium-Niobium Solution. After adjustment of the pH, one milliliter of the solution was pipetted into a counting dish and dried by a heat lamp. The counting dishes were then cooled and stored in a dry atmosphere.

Cesium-Barium Solution. After adjustment of the pH, one-half milliliter of the solution was pipetted into a counting dish and dried by a heat lamp. A second one-half milliliter sample was pipetted into a glass vial and counted immediately in the well scintillation counter.

Weighing the Solid Adsorbent. The required amount of adsorbent was weighed on an analytical balance and transferred to a 50 milliliter shaking bottle. The amount of solid used depended on the physical nature of the adsorbent and the particular test under investigation.

Contacting the Adsorbent and Solution. Twenty-five milliliters of the aqueous solution was transferred from the beaker to the shaking bottle containing the adsorbent. The shaking bottles were placed in the holder on the clinical shaker and secured with wire. The shaker was started and allowed to run for two hours. The shaker was then stopped and the bottles removed from the holder.

Filtration. The solution containing the adsorbent was filtered using blue ribbon filter paper and standard filtration funnels. In

some cases the adsorbent was suspended in the solution and it was necessary to centrifuge the slurry to separate the adsorbent from the solution.

Sampling the Filtrate After Adsorption. The procedure for sampling the filtrate was identical to the procedure for sampling the solution before adsorption.

Counting the Samples. The procedure for counting the zirconium-niobium samples differed from the procedure used for cesium and barium and each will be discussed separately.

Zirconium-Niobium. Because of the short half-lives of zirconium and niobium, it was necessary to count the samples taken before and after adsorption at the same time. A Geiger-Muller radiation counter was used to count the beta radiation from the samples.

A background count was made before counting the samples. The counting dishes were placed in the lead shields on the second shelf. The same geometry was used for each sample counted. The scalers were then turned on and the samples counted for one hour. The number of counts was recorded and the dishes removed from the lead shields.

Cesium. A scintillation counter with an anthracene crystal was used to count the beta radiation from cesium. A background count was made before counting the samples.

The counting dish was placed on the second shelf of the lead shield and the scaler started. After counting for one hour, the scaler was turned off and the sample removed from the lead shield. The number of counts obtained was then recorded.

Barium. A scintillation well counter with a sodium iodide crystal was used to count the gamma radiation from barium. A background count was made before counting the samples.

The glass vial containing the sample solution, was placed in the well. The scaler was started and allowed to run for one hour. At the end of the hour, the number of counts was recorded. The glass vial was then removed from the well.

It was necessary to use a count rate meter to count part of the cesium and barium samples. The procedure was similar to the procedure given above except the samples were not counted for one hour. Sufficient time was allowed for the meter to reach equilibrium before a reading was made. The activity of the sample was obtained directly from the meter expressed in counts per second.

All data were corrected for background and counting efficiency. Since the samples were almost weightless and the activities were compared with reference samples, no corrections were made for back-scattering and self-adsorption.

Data and Results

The data and results obtained by this investigation for the different adsorbents have been grouped according to the radioisotopes under investigation.

The results of the adsorption tests are presented in Figures 3 to 12. These graphs were obtained by plotting the data from the adsorption tests. The figures are presented in groups according to the

adsorbent used. The curves show the per cent removal of activity at varying pH values. For better comparison of results, the curves for the per cent removal of zirconium-niobium, cesium and barium, for each adsorbent, are shown on the same figure.

The average deviation for the tests are shown by the symbols used in Figures 3 to 12. In a few cases, the deviations were too large to represent graphically. In all cases, the deviations are shown in Tables VII to XXVI.

The standard deviation of the scalers was determined by counting a sample for one hour 10 times. The data is presented in Table XXVII. The count rate meter had a standard error of 2 per cent.

TABLE VIII

Removal of Zirconium and Niobium by Alumina (Acid)

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity cps	Per Cent Removed	Average Deviation
0.04	1.7	3.9	817.59	98.7	
	3.0	4.5	672.85	94.6	0.2
	3.0	4.5	715.39	94.9	
	4.1	4.9	397.93	90.2	0.3
	4.1	4.8	390.30	89.6	
	5.4	4.8	101.11	85.1	0.9
	5.4	4.7	92.80	83.4	
0.02	1.5	1.8	1892.66	90.4	1.2
	1.5	1.9	1824.99	92.8	
	2.8	4.0	1619.28	98.5	0.2
	2.8	4.1	1183.84	98.8	
	4.1	4.5	888.05	94.3	1.2
	4.1	4.5	882.57	92.0	
	5.5	4.5	1112.77	93.9	1.7
	5.5	4.3	1150.11	90.6	

TABLE IX

Removal of Zirconium and Niobium by Alumina (Basic)

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity cps	Per Cent Removed	Average Deviation
0.04	1.6	3.9	1562.54	99.6	0.2
	1.6	3.9	1574.76	99.9	
	5.3	6.9	1612.39	99.6	0.1
	5.3	6.9	1492.37	99.4	
0.02	1.6	2.4	863.06	98.3	0.9
	1.6	2.5	846.57	96.5	
	5.3	7.3	824.96	98.1	0.2
	5.3	7.3	781.53	98.5	

TABLE X

Removal of Zirconium and Niobium by Alumina (Neutral)

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity cps	Per Cent Removal	Average Deviation
0.04	1.6	4.2	1446.42	99.7	0.0
	1.6	4.2	1411.71	99.7	
	5.6	7.1	1440.66	99.9	0.0
	5.6	7.1	1334.93	99.9	
0.02	1.6	2.4	908.62	98.1	0.2
	1.6	2.6	861.92	97.8	
	5.8	7.2	828.88	99.7	0.1
	5.8	7.4	874.81	99.8	

TABLE XI

Removal of Zirconium and Niobium by Silica Gel

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity cps	Per Cent Removal	Average Deviation
0.04	0.28	-	10,495.30	98.2	0.3
	0.28	-	10,843.93	98.8	
	1.1	1.0	741.31	89.4	1.2
	1.1	0.9	728.84	87.8	
	5.5	4.0	7,463.47	98.1	0.2
	5.5	4.2	7,551.52	97.7	

TABLE XII

Removal of Zirconium and Niobium by Microsil

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity cps	Per Cent Removal	Average Deviation
0.01	1.7	1.6	2003.19	97.3	1.3
	1.7	1.8	1963.68	94.8	
	2.7	3.1	1354.23	98.6	0.4
	2.7	3.1	1498.51	99.3	
	4.3	3.9	2266.40	77.2	2.0
	4.3	3.9	2276.02	73.2	
	5.7	4.3	1224.14	63.0	3.4
	5.7	4.2	1377.07	69.8	

TABLE XIII

Removal of Zirconium and Niobium by Bentonite

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity cps	Per Cent Removal	Average Deviation
0.04	1.6	1.8	2176.24	97.6	0.1
	1.6	1.8	2324.85	97.5	
	2.8	6.5	2211.38	99.2	0.0
	2.8	6.9	2198.21	99.2	
	4.2	7.2	2270.25	99.1	0.2
	4.2	7.2	2123.45	98.7	
	5.6	7.1	2133.00	99.3	0.1
	5.6	7.1	2170.56	99.4	

TABLE XIV

Removal of Zirconium and Niobium by Burnt Refractory

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity ops	Per Cent Removal	Average Deviation
0.04	1.7	2.1	2205.94	93.8	
	1.7	2.0	2214.32	94.1	0.2
	2.8	6.4	2288.63	99.3	
	2.8	6.4	2320.49	99.3	0.0
	4.4	6.9	1402.84	99.0	
	4.4	6.9	1233.89	99.0	0.0
	5.9	6.9	1714.80	99.5	
	5.9	7.0	2223.20	99.6	0.1

TABLE XV

Removal of Zirconium and Niobium by Feldspar

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity cps	Per Cent Removal	Average Deviation
0.04	1.6	1.8	2663.89	73.2	1.8
	1.6	1.8	2759.66	76.7	
	2.8	4.8	2112.45	95.6	0.0
	2.8	4.8	2117.32	95.6	
	4.4	5.0	2060.45	96.1	0.4
	4.4	5.3	1826.24	96.9	
	5.8	5.3	2097.67	99.4	0.0
	5.8	5.3	1849.48	99.4	

TABLE XVI

Removal of Zirconium and Niobium by Kaolin

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity cps	Per Cent Removal	Average Deviation
0.04	1.8	2.0	2091.81	94.5	0.2
	1.8	2.0	2082.95	95.2	
	2.8	2.9	1961.85	99.0	0.1
	2.8	3.0	2175.01	98.8	
	4.5	3.6	2483.04	99.7	0.1
	4.5	3.6	2282.17	99.8	
	5.8	4.6	2488.46	99.7	0.1
	5.8	5.0	2338.63	99.9	
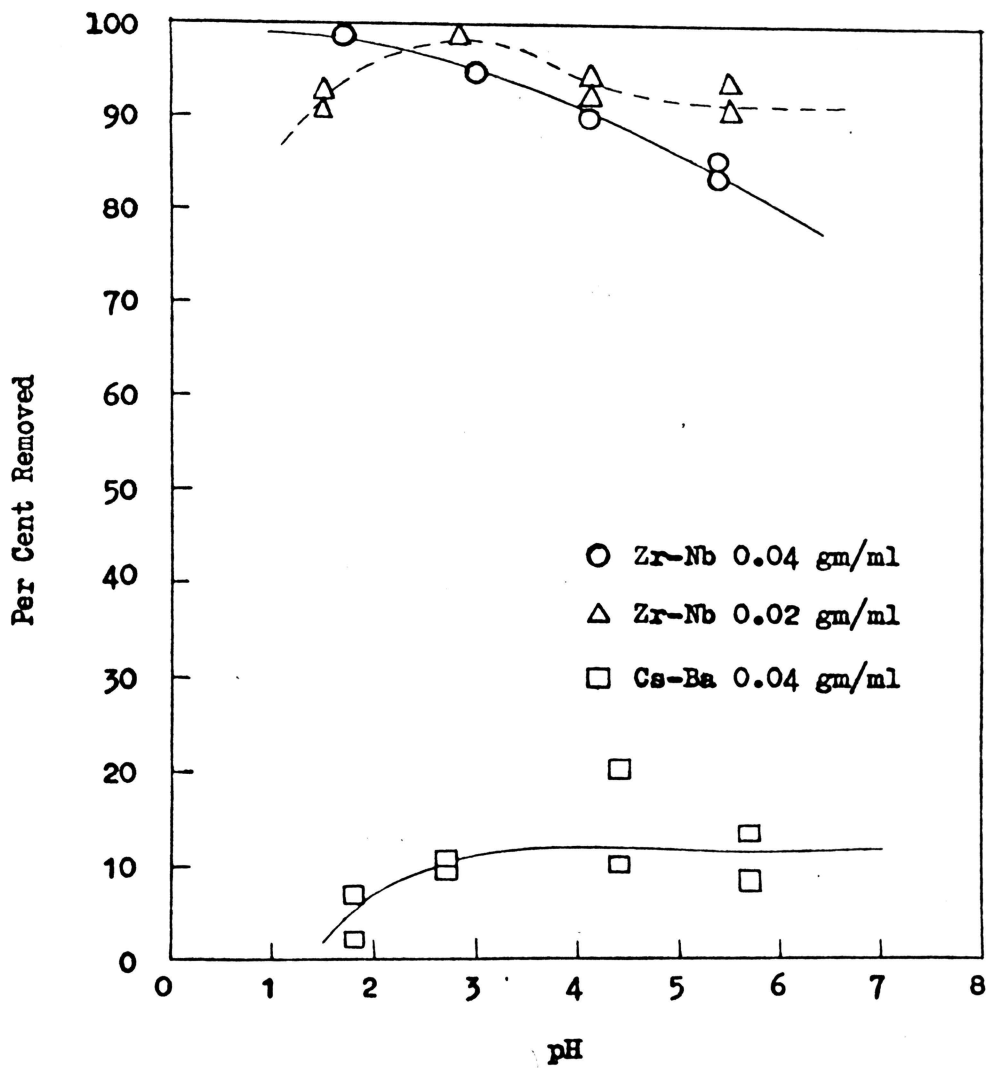
Figure 3. Removal of Activity by Alumina (Acid).
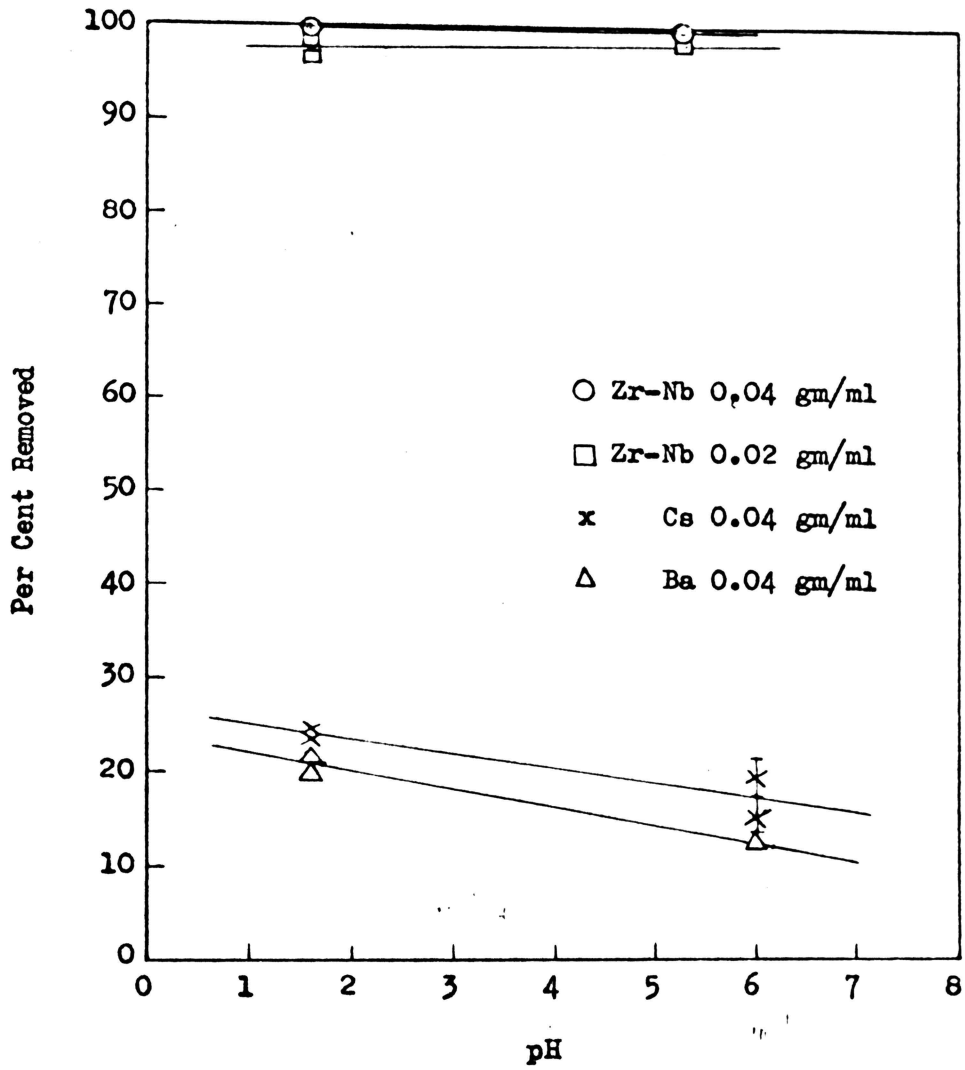
Figure 4. Removal of Activity by Alumina (Basic).
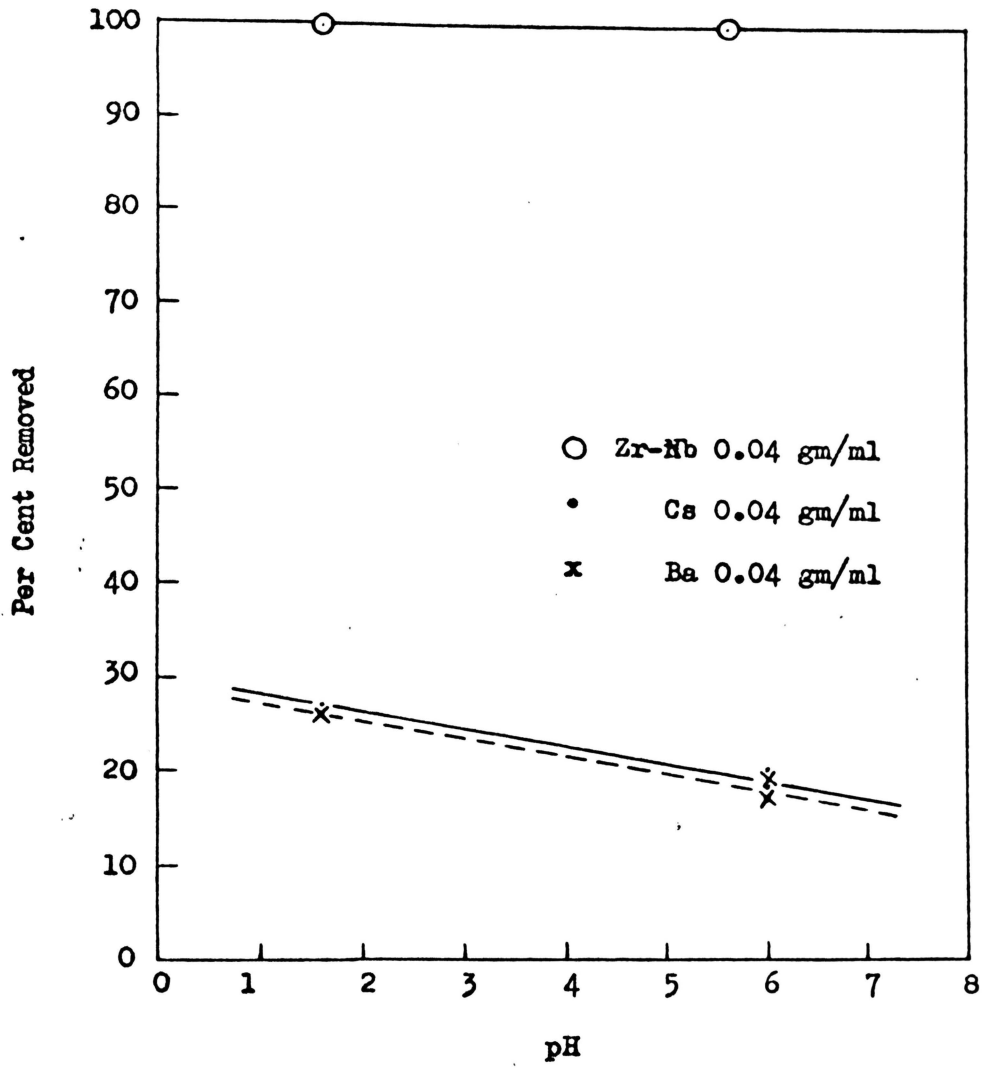
Figure 5. Removal of Activity by Alumina (Neutral).
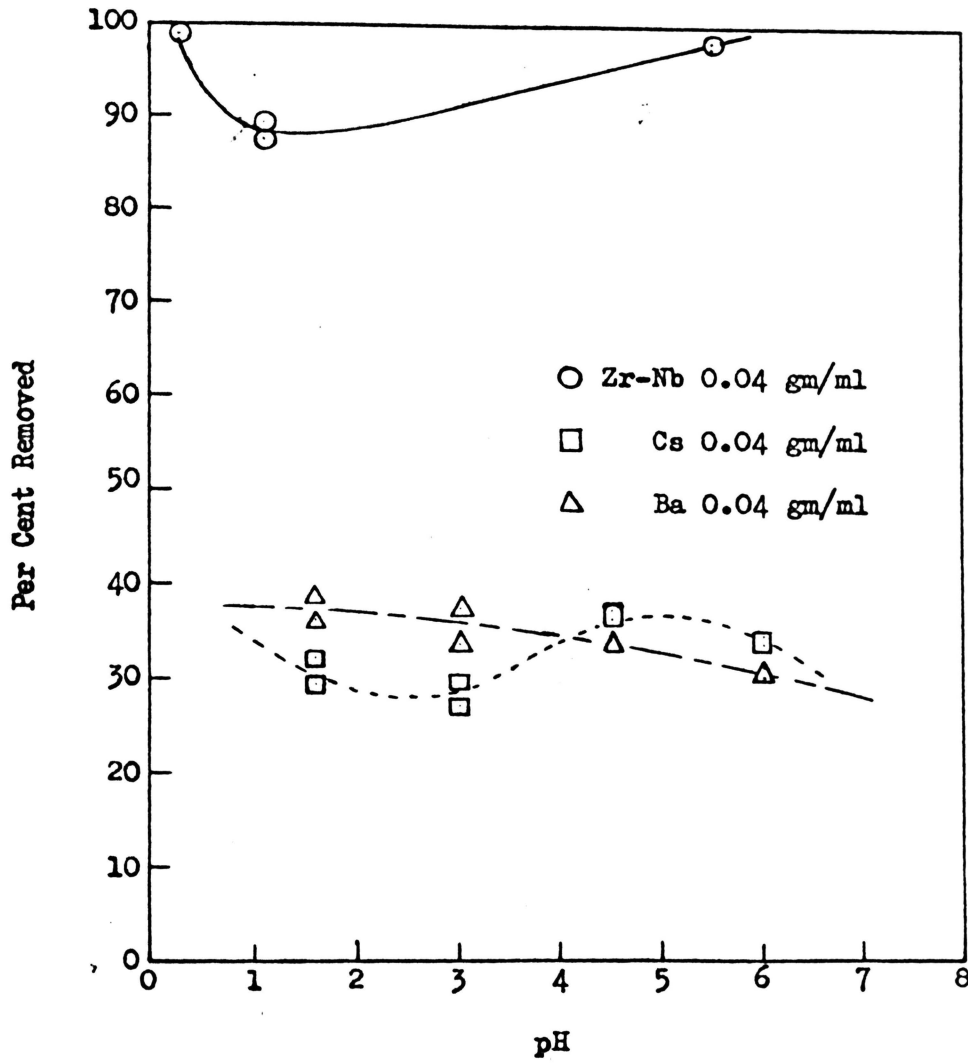
Figure 6. Removal of Activity by Silica Gel.
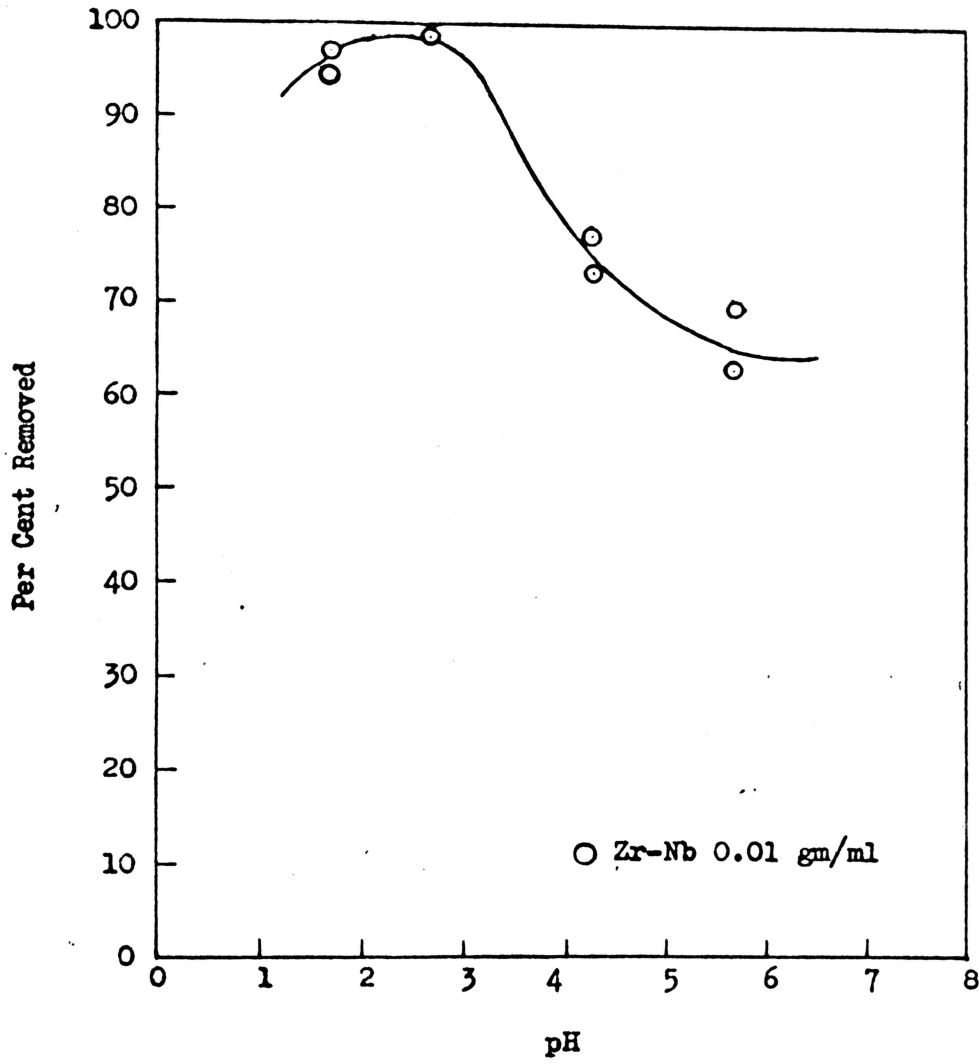
Figure 7. Removal of Activity by Microsil.
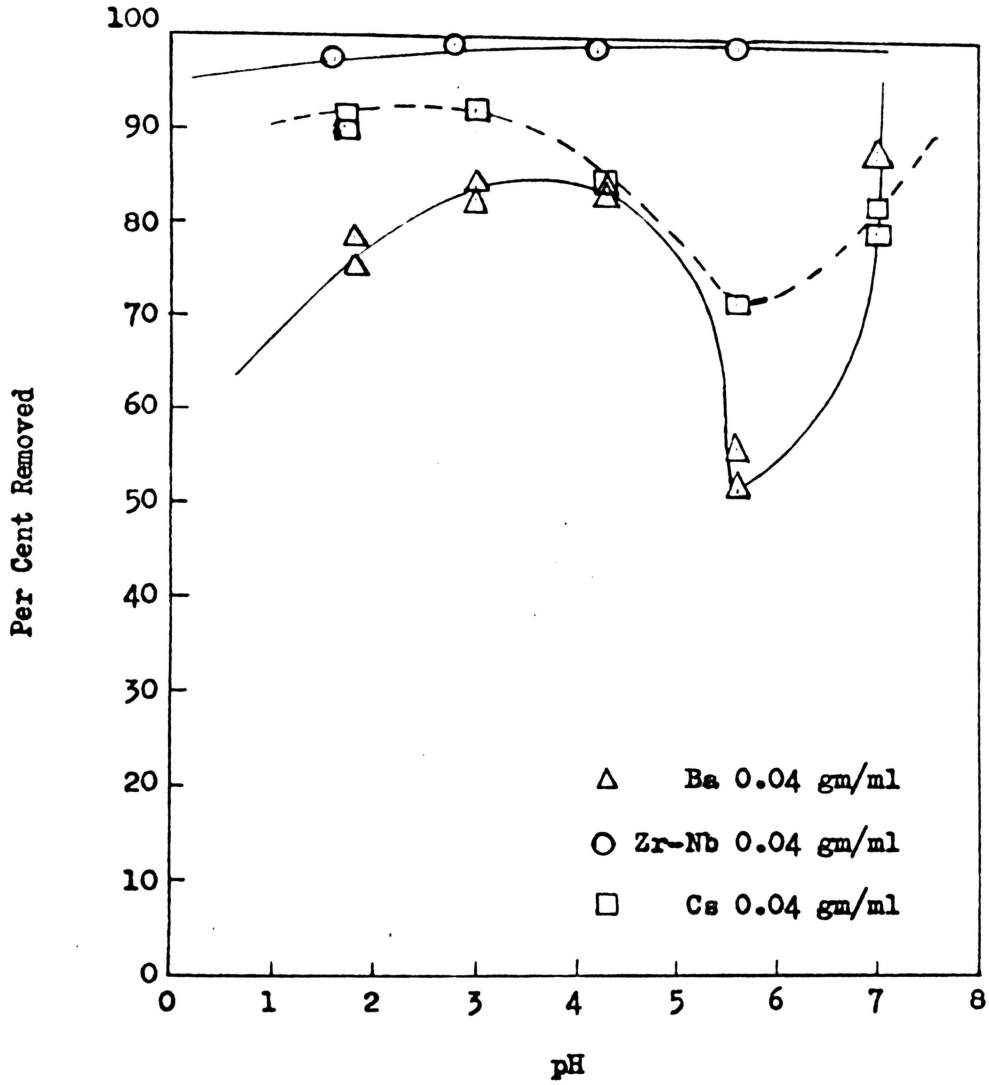
Figure 8. Removal of Activity by a Wyoming Sodium-Bentonite.
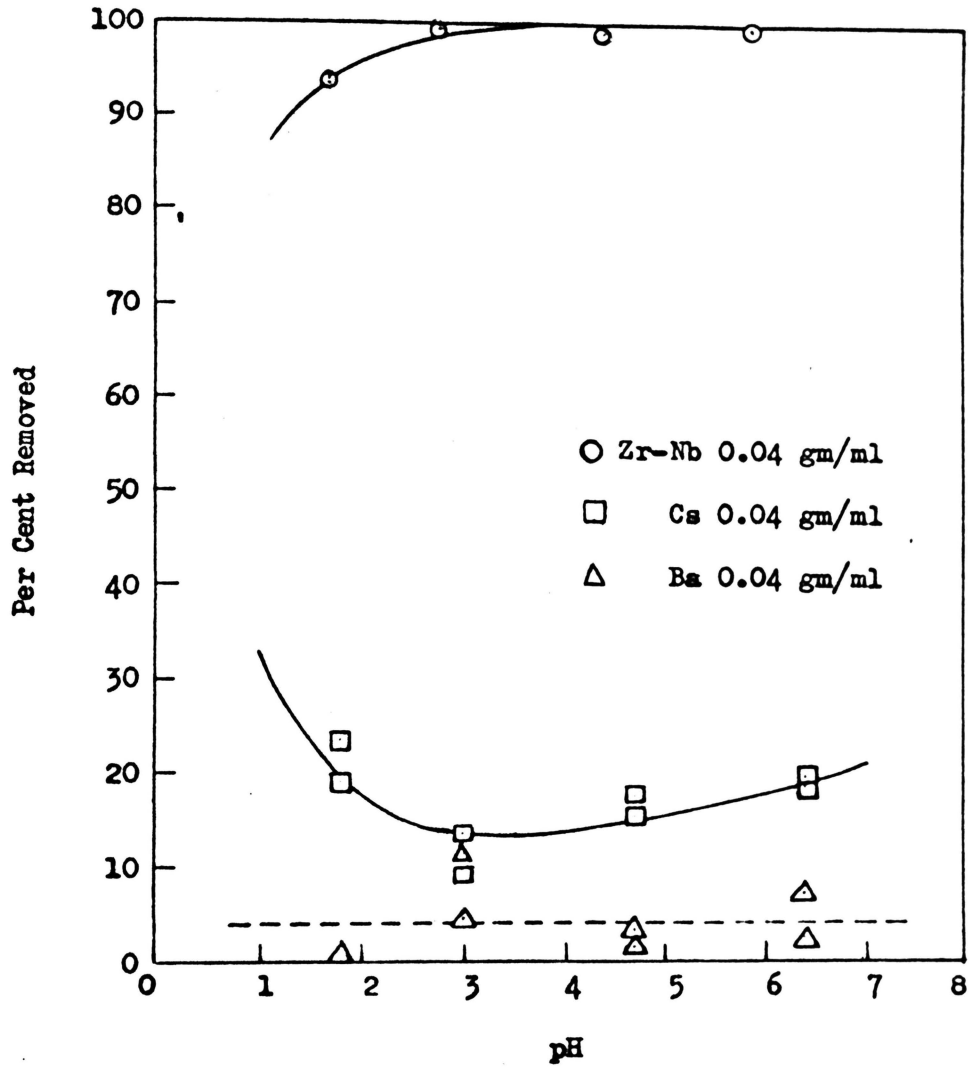
Figure 9. Removal of Activity by Burnt Refractory.
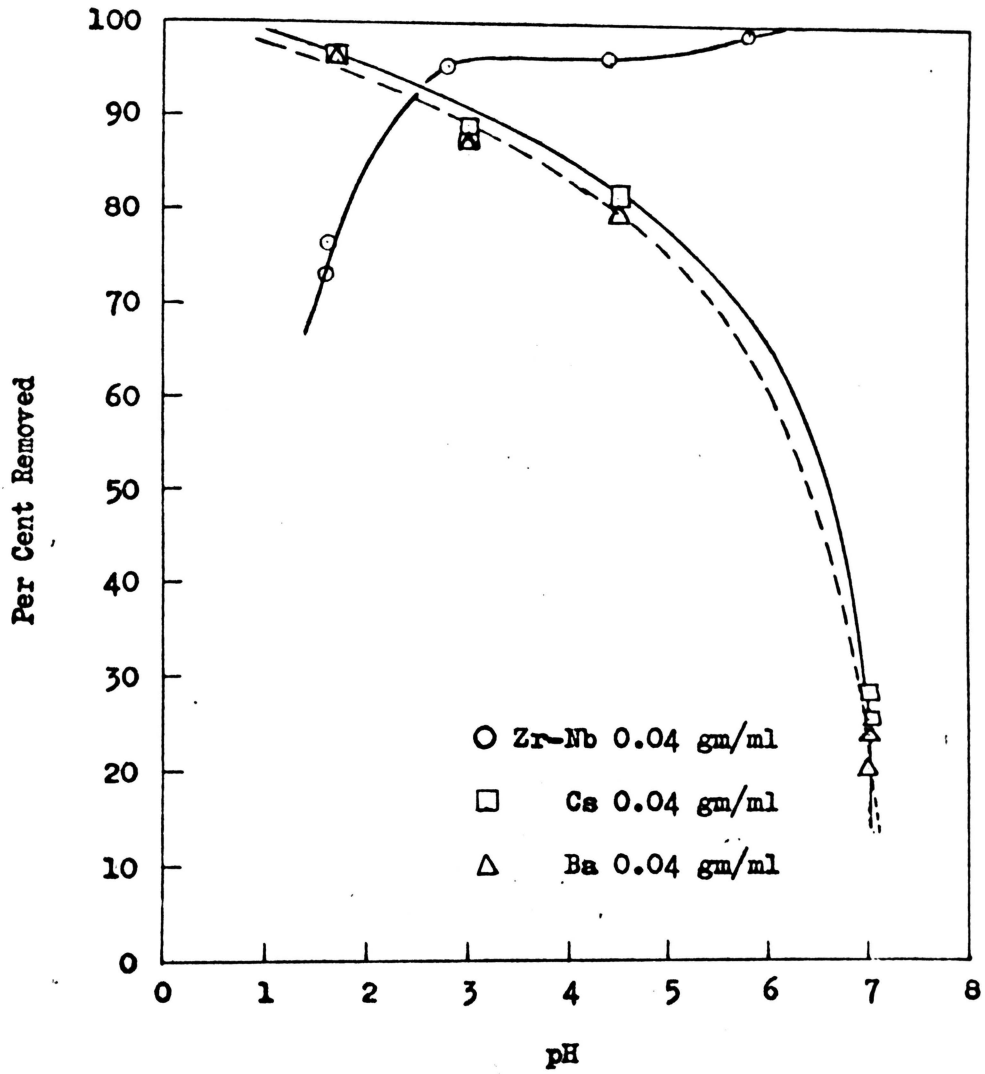
Figure 10. Removal of Activity by Feldspar
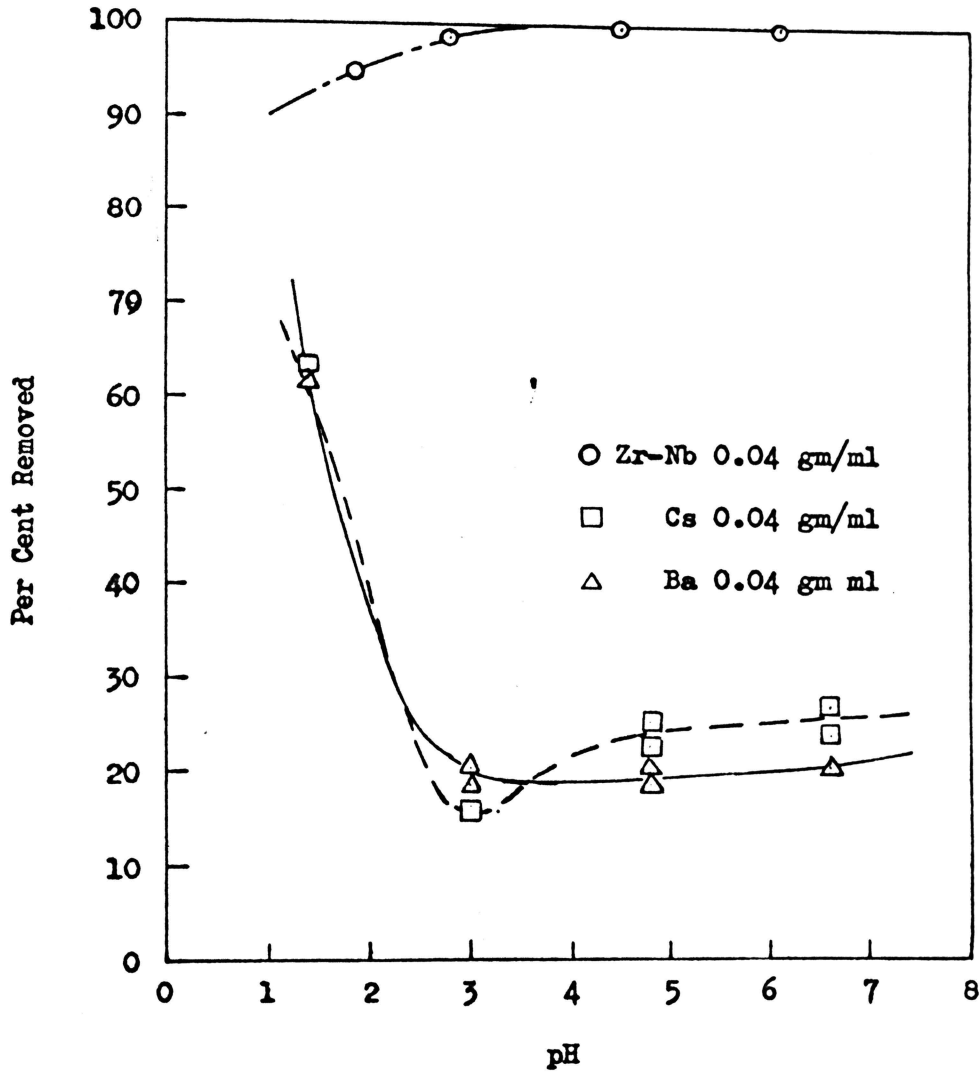
Figure 11. Removal of Activity by Kaolin.
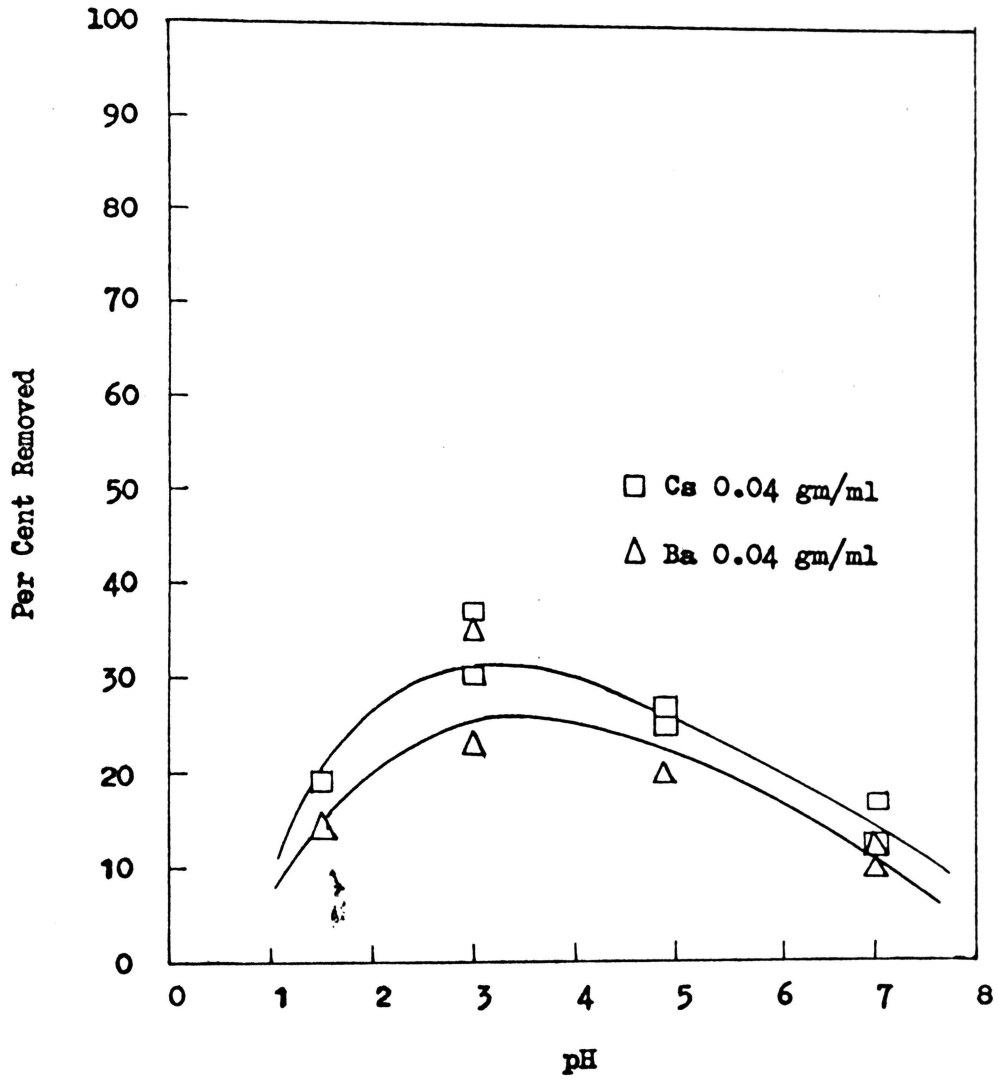
Figure 12. Removal of Activity by Soda-Feldspar.

TABLE XVII

Removal of Cesium and Barium by Alumina (Acid)

Concentration of Adsorbent gm/ml	Initial pH	Final pH	Initial Activity ops	Per Cent Removal	Average Deviation
0.04	1.8	3.7	1633.36	2.2	2.5
	1.8	3.7	"	7.1	
	2.7	4.2	"	10.9	0.8
	2.7	4.2	"	9.3	
	4.4	4.7	"	20.3	5.0
	4.4	4.8	"	10.3	
	5.7	5.0	"	8.8	2.6
	5.7	5.1	"	13.9	

TABLE XVIII

Removal of Cesium and Barium by Alumina (Basic)

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.6	2.8	973	23.7		1386	19.9	
1.6	2.8	"	24.6	0.5	"	21.3	0.7
6.0	7.7	"	15.3		"	12.4	
6.0	7.7	"	19.5	2.1	"	15.7	1.7

TABLE XIX

Removal of Cesium and Barium by Alumina (Neutral)

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.6	3.7	973	27.1	0.0	1386	26.7	0.5
1.6	3.7	"	27.1		"	27.6	
6.0	7.6	"	18.7	0.9	"	17.3	1.1
6.0	7.6	"	20.4		"	19.4	

TABLE XX

Removal of Cesium and Barium by Silica Gel

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.6	1.8	973	29.7		1386	36.3	
1.6	1.8	"	32.2	1.3	"	38.6	1.2
3.0	3.4	"	27.1		"	33.9	
3.0	3.4	"	29.7	1.3	"	37.5	1.8
4.5	5.0	"	36.5		"	34.6	
4.5	4.8	"	37.3	0.4	"	34.2	0.2
6.0	5.4	"	33.9		"	31.1	
6.0	5.4	"	34.7	0.4	"	30.2	0.5

TABLE XXI

Removal of Cesium and Barium by Microsil

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.7	1.8	1227.28	0.0		1741.15	4.2	
				0.0			2.1
1.7	1.8	"	0.0		"	0.0	
3.0	3.1	"	0.0		"	6.3	
				0.0			3.2
3.0	3.1	"	0.0		"	0.0	

TABLE XXII

Removal of Cesium and Barium by Bentonite

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.7	2.1	1973.71	91.6	0.6	1931.63	75.3	1.7
1.7	2.1	"	90.4		"	78.6	
3.0	5.2	"	92.4	0.2	"	82.8	0.6
3.0	5.8	"	92.0		"	84.0	
4.3	7.0	"	62.2	11.4	1741.16	84.8	0.5
4.3	7.1	"	84.9		"	83.8	
5.6	6.8	"	71.7	0.3	"	56.0	2.1
5.6	6.8	"	72.2		"	51.9	
7.0	6.5	866.00	79.8	1.3	1370.00	88.2	0.2
7.0	6.5	"	82.3		"	87.9	

TABLE XXIII

Removal of Cesium and Barium by Burnt Refractory

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.8	1.9	1973.71	23.6		2626.19	1.3	
1.8	1.9	"	19.1	2.3	"	0.5	0.9
3.0	7.2	"	13.7		"	4.6	
3.0	7.5	"	9.5	2.1	"	11.3	3.4
4.7	6.9	"	17.6		"	3.1	
4.7	6.6	"	15.4	1.1	"	1.5	0.8
6.4	7.2	"	19.7		"	2.5	
6.4	7.3	"	18.9	0.4	"	7.1	2.3

TABLE XXIV

Removal of Cesium and Barium by Feldspar

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.7	2.1	1973.71	96.8	0.1	2626.19	96.2	0.1
1.7	2.1	"	96.9		"	96.3	
3.0	5.8	"	87.7	0.7	"	86.6	0.5
3.0	5.8	"	89.1		"	87.7	
4.5	6.5	"	81.5	0.3	"	80.0	0.9
4.5	6.5	"	82.1		"	81.7	
7.0	6.9	"	28.6	1.5	"	24.0	2.0
7.0	6.9	"	25.6		"	20.1	

TABLE XXV

Removal of Cesium and Barium by Kaolin

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.4	1.7	1376	63.4		1903	62.1	
1.4	1.7	"	62.9	0.3	"	59.9	1.1
3.0	3.0	"	15.6		"	20.3	
3.0	3.5	"	16.1	0.3	"	18.6	0.9
4.8	5.5	"	22.8		"	18.8	
4.8	5.4	"	25.1	1.2	"	20.2	0.7
6.6	6.3	"	26.9		"	20.9	
6.6	6.3	"	23.9	1.5	"	20.5	0.2

TABLE XXVI

Removal of Cesium and Barium by Soda-Feldspar

Initial pH	Final pH	Cesium			Barium		
		Initial Activity cps	Per Cent Removed	Average Deviation	Initial Activity cps	Per Cent Removed	Average Deviation
1.5	1.6	1336	19.8		1987.45	14.1	
1.5	1.6	"	18.8	0.5	"	15.0	0.5
3.0	6.5	"	37.7		"	35.7	
3.0	6.5	"	30.9	3.4	"	23.1	6.3
4.9	6.7	"	25.3		2354.49	20.2	
4.9	6.7	"	27.2	1.0	"	24.3	2.1
7.0	7.0	"	17.3		"	12.8	
7.0	6.8	"	13.6	1.9	"	10.3	1.3

TABLE XXVII

Data for Standard Deviation

Tect	Activity cps	Algebraic Deviation, (X)	x^2
1	241.29	-3.13	9.7969
2	242.00	-2.42	5.8264
3	246.19	+1.77	3.1329
4	244.76	+0.34	0.1156
5	244.90	+0.48	0.2304
6	244.70	+0.28	0.0784
7	245.17	+0.75	0.5625
8	244.86	+0.44	0.1936
9	245.34	+0.92	0.8464
10	244.86	+0.53	0.2809
Total	2444.16	11.06	21.0940

Sample Calculations

Calculation of Efficiency of Counters. The efficiency of the ounters was calculated in the following manner.

$$\text{Efficiency} = \frac{\text{Measured activity} - \text{Background count}}{\text{Correct activity}} \times 100$$

N.B.S. RaD & E source No. 3537 = 594 cps

$$\text{Efficiency} = \frac{52.58 - 0.22}{594} \times 100$$

$$= 8.81\%$$

Calculation of the Activity Removed. The activity removed by each adsorbent was calculated in the following manner.

$$\text{Per cent activity remaining} = \frac{\text{Activity after adsorption}}{\text{Activity before adsorption}} \times 100$$

$$= \frac{12.76}{1562.54} \times 100$$

$$= 0.1\%$$

$$\text{Per cent activity removed} = 100 - \text{per cent activity remaining}$$

$$= 100 - 0.1$$

$$= 99.9\%$$

Calculation of the Average Deviation. The average deviation of the results was calculated for each adsorbent. All calculations were made in the following manner.

$$\text{Average} = \frac{\text{Activity removed, test 1} + \text{activity removed, test 2}}{2}$$

$$= \frac{85.1 + 83.4}{2}$$

$$= 84.25$$

Deviation from average = Average - Activity removed

$$= 84.25 - 83.4$$

$$= 0.85 \text{ (test 1)}$$

$$= 84.25 - 85.1$$

$$= -0.35 \text{ (test 2)}$$

Average deviation = $\dfrac{\text{Deviation from average (test 1 + test 2)}}{2}$

$$= \dfrac{0.85 + 0.85}{2}$$

$$= 0.85$$

$$= 0.9 \text{ (rounded to nearest significant figure)}$$

Calculation of Standard Deviation of Scalers. The data used for this calculation was taken from Table XXVII.

$$\text{Standard deviation} = \sqrt{\frac{X^2}{n - 1}}$$

where, X^2 is the square of the algebraic deviation from the mean.

n is the number of readings.

$$\text{Standard deviation} = \sqrt{\frac{21.094}{9}}$$

$$= 1.53 \text{ cps}$$

IV. DISCUSSION

The discussion is presented in three sections; (1) discussion of results, (2) recommendations, and (3) limitations.

Discussion of Results

The results are discussed in the same order as the data and results were presented in the preceeding section.

Alumina (Acid). Figure 3 shows the per cent removal of activity at varying pH values. A concentration of 0.04 gm/ml adsorbs 99 per cent of the activity from zirconium and niobium at an initial pH of 1.7. The equilibrium pH value of the solid-solution mixture was 3.9.

An initial pH of 2.8 was required for 99 per cent removal of activity using a concentration of 0.02 gm/ml. An observation of Table VIII shows an equilibrium pH value of 4.0. Therefore, it appears that the removal of this amount of activity depends upon the equilibrium pH value and not on the concentration of adsorbent or the initial pH value.

Figure 3 also shows that removal of the cesium and barium activity is not feasible. The maximum removal was approximately 10 per cent at a pH of 4.4 and levels off at this value with increasing pH.

Alumina (Basic). Observation of Figure 4 shows that a concentration of 0.04 gm/ml removes 99 per cent of the activity from zirconium and niobium solutions. The initial and final pH seems to have no effect on the adsorption capacity of the basic alumina.

A concentration of 0.02 gm/ml removes approximately 98 per cent of the activity. The per cent removal was almost constant over the entire pH range investigated and seems to indicate that the pH of the solution has little or no effect on the adsorption within this range.

As in the case of acid alumina, removal of cesium and barium was too low for commercial application. The maximum removal was approximately 25 per cent at a pH of 1.6 and decreased with increasing pH values.

Alumina (Neutral). The removal of zirconium and niobium by adsorption on neutral alumina was constant at approximately 100 per cent over the entire pH range investigated. Observation of Figure 5 and Table X show that the initial and final pH at a concentration of 0.04 gm/ml had no effect on the per cent removal. Table X indicates that the final pH affects the removal when a concentration of 0.02 gm/ml was used; the removal increased with increasing pH values.

Removal of cesium and barium from solution decreased with increasing pH values. The maximum removal obtained was approximately 27 per cent at a pH of 1.6.

Silica Gel. Figure 6 shows that 99 per cent of the zirconium and niobium was removed at a pH of 0.3. The per cent removal then passes through a minimum of 88 per cent at a pH of 1.1 and increases to 98 per cent as the pH increases to 5.5.

The maximum removal of barium was 37 per cent. A pH of 1.6 or lower was necessary to obtain this removal. As the pH increases, the per cent removal decreases.

At the low end of the pH range, the per cent removal of cesium was 30 per cent. As the pH increases, the per cent removal increases to a maximum of 37 per cent at a pH of 5.0.

Microsil. Observation of Figure 7 indicates that microsil removes 99 per cent of the zirconium and niobium at an initial pH of 2.7. Above a pH of 3.0 the per cent removal decreases with increasing pH values. The most effective removal occurs in the pH range 2.5 to 3.0.

Table XXI indicates that essentially none of the cesium or barium was adsorbed by the solid. There was very little difference in the initial and final pH of the solutions and this may be the reason for the low removal.

Bentonite. Figure 8 indicates that above a pH of 2.8, 99 per cent of the zirconium and niobium was removed from solution. Observation of Table XIII shows that the final pH of the solutions was approximately 7.0. It has been reported that at this pH, the ion exchange properties of the clay are a maximum. The results seem to be in agreement with this information.

The maximum removal of cesium was 92 per cent at an initial pH of 3.0. Table XXII indicates that more cesium than barium was adsorbed by the clay at this pH. Selection rules for ion exchange of clays predict just the opposite result. The test at a pH of 7.0 shows that more barium than cesium was adsorbed but only at this pH did this occur. The maximum removal of barium from solution was 88 per cent at a pH of 7.0.

Doubling the concentration of solid increased the per cent removal by 10 per cent at initial pH values of 3.0 and 4.3.

The only difficulty encountered during the tests was the filtration speed of the clay. Bentonite becomes suspended in the solution and was very difficult to filter.

Burnt Refractory. The results in Table XIV and Figure 9 indicate that zirconium and niobium were effectively removed from solution at a pH of 3.0 or higher. The final pH of the solutions was near 7.0, where the ion exchange properties are the greatest.

The removal of cesium and barium was fairly constant over the pH range investigated. Cesium has a minimum of approximately 10 per cent at a pH of 3.0 as indicated in Figure 9.

Feldspar. The results of the tests are shown in Figure 10 and Tables XV and XXIV. The per cent removal of zirconium and niobium increases from 76 per cent at a pH of 1.6 to 99 per cent at a pH of 5.8.

Observation of Figure 10 shows that the removal of cesium and barium was approximately the same over the entire pH range. The maximum removal occurs at a pH of 1.7 and decreases as the pH increases.

Kaolin. Figure 11 indicates that 99 per cent of the zirconium and niobium were removed from solution above a pH of 2.8. The change in the initial pH was small. This seems to indicate that the removal was accomplished by surface adsorption rather than ion exchange.

Table XXV and Figure 11 show the results of the tests with cesium and barium. The maximum removal occurs at a pH of 1.4 and decreases

to a minimum at a pH of 3.0, where the removal then levels off and remains fairly constant over the remainder of the pH range. Here, also, the change in the initial pH was small and indicated that most of the removal was accomplished by surface adsorption.

Soda-Feldspar. The results are indicated in Figure 12 and Table XXVI. The removal of cesium and barium was quite low. A maximum removal of 35 and 30 per cent was obtained at a pH of 3.0 for cesium and barium respectively. The results indicate that the removal was accomplished by surface adsorption rather than ion exchange because more cesium than barium was removed from the solution.

Recommendations

There are several ways in which this investigation could be extended. The first way would be to carry out leaching tests on the solids after adsorption to determine how strongly the radioisotopes are bound to the solids. If leaching removes appreciable amounts of the activity, an investigation should be made to determine methods of permanent fixation.

Another possible extension would be to study the adsorption of other radioisotopes such as cerium and strontium, to determine the feasibility of using clays for permanent disposal.

A third extension would be to study the adsorption of cesium and barium on clays other than the ones used in this investigation.

It would also be of interest to extend the pH range further than the range covered in this investigation.

Limitations

There are three limitations in this investigation that could have an important effect on the results. They are as follows:

Constant Activity of Zirconium-Niobium Stock Solution. To obtain accurate comparisons of results, the activity of the stock solution should be fairly constant. The activity of the zirconium-niobium stock solution decreased with time due to adsorption on the walls of the container and could not be kept constant. However, the activity of the stock solution was determined for each experiment.

Sampling the Solutions. Samples taken for purposes of counting the activity were removed by pipetting from the container to the counting dish. The same procedure was followed each time but accurate reproduction of the volumes taken for samples was subject to error.

Drying the Samples. The liquid samples were dried using a heat lamp. Uniform layers were impossible to obtain. This could change the results considerably since no correction for self-adsorption or backscattering was made.

V. CONCLUSIONS

Investigation of the adsorption capacity of alumina, silica gel, and clays for zirconium, niobium, cesium and barium has led to the following conclusions:

A. Alumina (Acid).

   1. Zirconium and niobium.

      a. A concentration of at least 0.04 gm/ml of the alumina was necessary for effective removal of the zirconium-niobium concentration studied.

      b. The pH of the solution should not be greater than 1.7.

   2. Cesium and barium.

      a. Cesium and barium were not effectively removed from the solution.

B. Alumina (Basic).

   1. Zirconium and niobium.

      a. The pH of the solution had no effect on the per cent removal.

      b. A concentration of 0.04 gm/ml was necessary to remove the activity investigated.

   2. Cesium and barium.

      a. The maximum removal occured at low pH values.

      b. The commercial application of this method would not be feasible, using this amount of alumina.

C. Alumina (Neutral).

    1. Zirconium and niobium.

        a. The pH of the solution did not effect the removal when a concentration of 0.04 gm/ml of alumina was used.

        b. pH values in the range 5.0 to 6.0 were necessary for good removal when a concentration of 0.02 gm/ml of alumina was employed.

    2. Cesium and barium.

        a. Cesium and barium were not effectively removed from solution.

D. Silica Gel.

    1. Zirconium and niobium.

        a. The pH of the solution affects the removal.

        b. Maximum removal of activity occured at pH values of 0.3 and 5.5.

    2. Cesium and barium.

        a. The removal of cesium and barium was nearly constant over the pH range investigated. The maximum removal was 37 per cent.

E. Microsil.

    1. Zirconium and niobium.

        a. Effective removal occured in the pH range 2.5 to 3.0.

        b. A low concentration of adsorbent was necessary because of the large surface area of the solid.

    2. Cesium and barium.

        a. Cesium and barium were not effectively removed from solution.

F. Bentonite.

   1. Zirconium and niobium.

      a. A pH of 2.8 or greater was necessary for the effective removal of the activity.

      b. The solid was practically impermeable when filtration was attempted.

      c. Removal was a maximum when the final pH of the solution was near 7.0.

   2. Cesium.

      a. The maximum removal occured at a pH of 3.0. At this pH, H^+ ions are preferred for ion exchange. Therefore, the removal must have been accomplished by surface adsorption.

   3. Barium.

      a. The results indicate that the removal was accomplished by ion exchange because the maximum removal occured at a pH of 7.0. At this pH, the ion exchange capacity of bentonite is a maximum.

G. Burnt Refractory.

   1. Zirconium and niobium.

      a. A pH of 2.8 or higher was necessary for the effective removal of zirconium and niobium.

      b. No definite conclusions can be made as to the mechanism of adsorption.

2. Cesium.

    a. The maximum removal occured at a pH of 1.8. As in the case of bentonite, this indicates that the removal was accomplished by surface adsorption.

3. Barium.

    a. Barium was not effectively removed from solution.

H. Feldspar.

    1. Zirconium and niobium.

        a. A pH of 5.8 or higher was necessary for the removal of zirconium and niobium.

        b. The results indicate that removal was accomplished by surface adsorption because below a pH of 7.0, H^+ ions are preferred for ion exchange.

    2. Cesium and barium.

        a. A pH of 1.7 was necessary for the maximum removal of cesium and barium. As in the case of zirconium and niobium, this indicates that the mechanism of removal was surface adsorption.

I. Kaolin.

    1. Zirconium and niobium.

        a. A pH of at least 2.8 was necessary for the effective removal of zirconium and barium.

        b. The mechanism of removal, as indicated by the low pH value, was surface adsorption.

2. Cesium and barium.

 a. The maximum removal occured at a pH of 1.4 and decreased with increasing pH values.

 b. The low pH value required for effective removal indicates that removal was accomplished by surface adsorption.

J. Soda-Feldspar.

 1. Cesium and barium.

  a. The maximum removal occured at a pH of 3.0.

  b. The final pH was near 7.0 indicating ion exchange as the mechanism of removal.

Three general conclusions may be drawn from the preceding itemized conclusions. They are as follows:

A. Zirconium and niobium were effectively removed from solution by all the adsorbents as long as the pH was 2.8 or higher.

B. Cesium and barium were effectively removed from solution by feldspar and to a less extent by bentonite at low pH values. The low pH value required for removal indicates that removal was accomplished by surface adsorption.

C. The only safe means of using alumina, silica gel and clay for removal and storage of cesium and barium is to use very large quantities of adsorbent. This may not always be practical.

VI. <u>SUMMARY</u>

The purpose of this investigation was to determine the adsorption capacity of alumina, silica gel and clays for zirconium, niobium, cesium and barium at varying pH values.

The solution of radioisotopes and the solid adsorbent were agitated for two hours by means of a clinical shaker. Preliminary tests showed that the solutions reached equilibrium after two hours of contact time. Samples of the radioactive solution were taken before and after adsorption to determine the activity. From this data the per cent removal was calculated. The results of the tests were tabulated so that comparisons could be made.

The investigation led to the following conclusions:

1. Feldspar was the only adsorbent that effectively removed cesium and barium from solution.

2. Zirconium and niobium were effectively removed from solution by all the adsorbents tested at pH values of 2.8 or higher.

3. The pH of the solutions affects the removal of activity by the adsorbents.

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VIII. <u>ACKNOWLEDGMENTS</u>

IX. VITA

Dale Wesley Harris was born September 19, 1936, in Hannibal, Missouri.

He attended public school at Hannibal, Missouri, and graduated from high school in May, 1954.

He enrolled at the Missouri School of Mines and Metallurgy in September, 1954, and received the degree of Bachelor of Science in Chemical Engineering in June, 1958.

In September, 1958, he entered the Graduate School at the Missouri School of Mines and Metallurgy, where he began a course of study in Nuclear Engineering under a one-year fellowship granted by the United States Atomic Energy Commission. Upon completion of the requirements for this degree, he will go to Cincinnati, Ohio, where he has accepted a position with the Aircraft Nuclear Propulsion Division of the General Electric Company.

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