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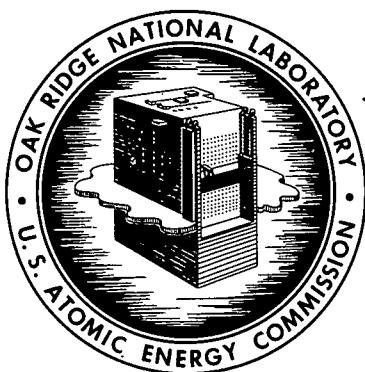
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REMOVAL OF  $\text{Cs}^{137}$ ,  $\text{Sr}^{90}$ , AND  $\text{Ru}^{106}$  FROM  
ORNL PLANT WASTES BY SORPTION ON  
VARIOUS MINERALS

S. J. Rimshaw  
D. C. Winkley



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ON VARIOUS MINERALS

S. J. Rimshaw

D. C. Winkley

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Oak Ridge National Laboratory  
Oak Ridge, Tennessee  
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REMOVAL OF Cs<sup>137</sup>, Sr<sup>90</sup>, AND Ru<sup>106</sup> FROM ORNL PLANT WASTES BY SORPTION  
ON VARIOUS MINERALS

S. J. Rimshaw

D. C. Winkley

ABSTRACT

A series of minerals (120) were tested as to their efficiency in removing cesium, strontium and ruthenium from dilute alkaline wastes prior to ground disposal. Strontium-90 exchanges rapidly with calcium in Florida pebble phosphate. The best results were obtained with Tennessee phosphate heated to 600°C for one hour, but part of the increase in sorption of strontium is due to ion exchange. Heating Tennessee phosphate resulted in a material with excellent hydraulic properties that sorbs Cs<sup>137</sup> and Sr<sup>90</sup> from dilute alkaline solutions. Other calcium minerals such as calcite or dolomite can be activated to adsorb Sr<sup>90</sup> by heating or by treating with caustic or phosphate solutions.

Cesium-137 in dilute alkaline solutions exchanges preferentially with the potassium present in a number of mica schists and mica minerals that possess a layer lattice type of structure. The high selectivity for cesium of Tennessee phosphate heated to 600°C for one hour is ascribed to the presence of bentonitic impurities present in this material.

The kinetics and adsorption of Ru<sup>106</sup> are known to be complex and slow due to the large number of chemical forms and complexes of ruthenium that can exist under varying conditions. Copper in conglomerate, various sulfide minerals containing copper, cuprite (cuprous oxide) and descloizite (basic zinc lead vanadate) remove 90% of the ruthenium under reducing conditions at a pH of 7 when heated at 60°C for 16 hours. At lower temperatures (25°C) the removal of ruthenium from aged solutions takes days or even weeks.

INTRODUCTION

The concept of a soil column envisions the placement of a number of readily available ores or commercial products in a sealed pit. The removal of various fission products from alkaline intermediate-level waste would be effected by

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percolating the solution through this pit. The behavior of  $\text{Cs}^{137}$ ,  $\text{Sr}^{90}$  and  $\text{Ru}^{106}$  in such a soil column is of special interest. The dispersion of these long-lived nuclides to the environment must be accurately known and controlled within narrowly prescribed limits. The position and relative movement of these radionuclides through the soil column can be evaluated and controlled. The effluent from the column can be monitored and treated further, if necessary. Thus a controlled operation of this type can be of value in meeting certain specific requirements of a particular waste disposal problem. This report discusses the results obtained in testing and evaluating a number of materials that could be used in such a soil column.

#### MATERIALS AND METHODS

The minerals used in the experiments were obtained from Ward's National Science Establishment, Rochester, New York, and are typical of those found in nature. The minerals were ground and sized to 50-100 mesh for use in these experiments.

The seepage from the waste pits at Oak Ridge National Laboratory was found to contain only  $\text{Ru}^{106}$  activity. Before using the solution in the experiments it was made 0.1  $\text{N}$  in  $\text{NaOH}$  and filtered in order to remove (as magnesium hydroxide) the magnesium picked up from the ground. The amount of ruthenium carried on this magnesium hydroxide was less than 5%.

The filtrate from the  $\text{Mg}(\text{OH})_2$  precipitation was diluted by a factor of 5 and adjusted to be 0.25  $\text{N}$  in  $\text{NaNO}_3$ . Additions of reducing agents or oxidizing agents were made to this diluted seepage solution.

Solution from the waste pit was used undiluted in some of the experiments. Ruthenium-106 and Cs<sup>137</sup> were present in nearly equal concentrations in the pit waste, according to gamma-ray spectrometry.

The Cs<sup>137</sup> and Sr<sup>89</sup> tracers used in the experiments met the catalog specifications of the isotopes sold by Oak Ridge National Laboratory. In these single-tracer experiments Cs<sup>137</sup> was determined by counting gross gamma on a gamma scintillation counter. Strontium-89 was determined by counting bremsstrahlung radiation on the same instrument, and also by gross beta counting.

In the equilibrium experiments a known quantity of mineral was weighed and equilibrated with a certain volume of aqueous solution containing the tracer. The solutions were shaken several times and the total time of contact was noted. Distribution coefficients were calculated as follows for cesium and strontium:

$$K_D = \frac{i - f}{f} \times \frac{ml}{g},$$

where

i = initial count rate in the solution,

f = final count rate in the solution,

ml = milliliters of solution,

g = grams of mineral.

A percentage removal was calculated for ruthenium. This figure was determined by dividing the final count rate by the initial count rate and subtracting the resulting number from 100.

## STRONTIUM EXCHANGE

### Introduction

Interest in the exchange of strontium with various minerals has been growing in recent years.

Bagretsov (1) could not detect any exchange of strontium tracer from aqueous solution with dolomite,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ . However, on heating at  $700^\circ\text{C}$  for two hours,  $\text{CaCO}_3 \cdot \text{MgO}$  is formed, and this fired dolomite exchanges rapidly with strontium tracer. Heating at  $700^\circ\text{C}$  disrupts the crystal lattice and activates the dolomite. If  $\text{Na}_2\text{CO}_3$  (2.0 g/l) or  $\text{Na}_3\text{PO}_4$  (0.5 g/l) is added to the solutions containing strontium tracer, strontium exchange with the calcium in dolomite (activated by heating) is increased from 70 to 95% respectively.

V. I. Spitsyn et al., (2) have shown that the ion exchange sorption of strontium by montmorillonite is subject to the law of mass action. The sorption of cesium, ruthenium and strontium on various other minerals was also investigated. Ames and others (3) noted that the presence of phosphate in solution in small quantities ( $5 \times 10^{-4}$  M) activated the sorption of strontium by carbonates of the calcite type of lattice structure (i.e.,  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ) and of the aragonite type of lattice structure (i.e.,  $\text{BaCO}_3$ ). X-ray diffraction patterns of calcite that had been in contact with phosphate ions in solution showed a poorly crystalline apatite in the process of replacing the calcite.

Gitelman and Neuman show (4) that the interchange of lead with synthetic hydroxy apatite crystals proceeds via a complicated mechanism.

Lieser and Hild (5) investigated the exchange of strontium with  $\text{CaSO}_4$  and  $\text{BaSO}_4$ . They note that as a result of mixed crystal formation,  $\text{Sr}^{90}$  in tracer amounts can be removed from solution by  $\text{BaSO}_4$ . However, the sorption of strontium by  $\text{CaSO}_4$  is a surface effect. Undoubtedly there are a number of other isomorphous salts of calcium and barium that would be effective in removing strontium from aqueous solutions.

#### Experimental

Several insoluble calcium minerals were tested for their ability to exchange the strontium in solution with the calcium in the mineral. A synthetic solution (0.25 N  $\text{NaNO}_3$ , 0.1 N  $\text{NaOH}$ , and  $\text{Sr}^{89}$  tracer) was used in these experiments. In Table 1 the distribution coefficients of strontium are listed for marble chips, Florida pebble phosphate, and Tennessee phosphate (which had been heated to  $600^\circ\text{C}$  for 1 hr.).

Table 1. Removal of Strontium by Several Materials

Material	$K_D$ Contact Time of 0.5 hr.
Marble chips	13.1
Florida pebble phosphate	55.0
Tennessee phosphate (heated to $600^\circ\text{C}$ )	1475

Part of the exchange of strontium with heated Tennessee phosphate is due to ion exchange.

Unheated Tennessee phosphate is merely dispersed when contacted with water. Heating to 600°C gives a crystalline material with good hydraulic properties. It can be seen (Table 1) that the exchange of strontium with calcium is more rapid and complete with Tennessee phosphate than it is with Florida pebble phosphate. The phosphate content of Tennessee phosphate is only half that of Florida pebble phosphate (16 vs 32% P<sub>2</sub>O<sub>5</sub>). However, the heat treatment of Tennessee phosphate results in a more finely divided crystalline apatite in a silicate matrix, which promotes the exchange of strontium with calcium. As can be seen from Appendix 4, the K<sub>D</sub> of heated Tennessee phosphate decreases from 3190 in 0.1 N NaOH to 188 in 4.0 N NaNO<sub>3</sub>-0.1 NaOH. Thus, part of the exchange is due to ion exchange.

The exchange of strontium from aqueous solution with calcium can be promoted or retarded by changes in crystalline structure which result from heating. This effect was investigated as a function of the temperature used in heating the mineral for marble chips, Florida pebble phosphate, and dolomite. The results are presented in Table 2.

As is evident, CaCO<sub>3</sub> (marble chips) is rather stable to heat treatment up to 700°C. The rate of exchange of strontium with calcium is slow and increases with time, as strontium tends to replace the calcium in the crystal lattice. The rate of exchange of strontium with calcium is more rapid with Florida pebble phosphate than with marble chips. The formation of condensed phosphates (P-O-P) bonds is appreciable at 500-700°C, but these polyphosphates hydrolyze with time so that exchange of strontium with

mineral	phosphate content	600°C K <sub>D</sub>	600°C K <sub>D</sub>
CaCO <sub>3</sub> (marble chips)	16%	3190	188
Florida pebble phosphate	32%	188	188

calcium increases with time. Heating has a deleterious effect on the exchange of strontium with calcium. Dolomite was only slightly activated by heating.

Table 2. Effect of the Temperature of Heat Treatment of Various Minerals on the Exchange of Strontium with Calcium

Material	Temperature (°C)	K <sub>D</sub> , Contact Time of 1 hr	K <sub>D</sub> , Contact Time of 18 hr	K <sub>D</sub> , Contact Time of 6 Days
Marble chips	250	1.97	1.94	4.09
Marble chips	500	0.324	0.324	3.15
Marble chips	700	0.961	0.961	2.41
Florida pebble phosphate	250	144	336	1875
Florida pebble phosphate	500	98.4	210	1662
Florida pebble phosphate	700	13.8	17.5	381
Dolomite	700	1.07	2.54	2.65

The distribution coefficient of strontium for Florida pebble phosphate as a function of pH is presented in Table 3.

Thus, the sorption of strontium by Florida pebble phosphate is highest when the solution is at pH = 13. In this case, lowering the pH to 5 results in a sixfold reduction in the distribution coefficient of strontium.

The time of equilibration is also an important variable. This is

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evident from the results presented in Tables 2 and 3. Although the distribution coefficient of strontium for Florida pebble phosphate is only 55 after one-half hour, this value rises to 1544 at the end of two days. Again it may be noted that strontium has a definite tendency to replace calcium in the crystal lattice.

Table 3. Effect of pH on the Removal of Strontium by Florida  
Pebble Phosphate

pH	$K_D$ Contact Time of One Day	$K_D$ Contact Time of Two Days
5	30.7	37
7	128	245
9	159	468
11	483	
13	341	1544

Column experiments were run by using the synthetic solution with strontium tracer. Five milliliters of mineral was used, and the columns were operated at a flow rate of one column volume per hour. The results of column experiments with Florida pebble phosphate, marble chips and dolomite appear in Table 4.

Table 4. Strontium Breakthrough for Several Types of Column Materials

Basis: Breakthrough is calculated as a percentage of the Sr in the feed solution.

Number of Column Volumes	Amount of Strontium in Effluent (%)
Florida Pebble Phosphate Column	
10	0.03
20	0.05
50	2.5
100	1.98
200	0.82
Marble-Chip Column	
3	11.3
6	9.6
10	4.0
15	2.2
30	0.9
50	2.0
100	2.9
200	0.85
Dolomite Column	
2	21.8
5	25
20	28
60	5.3
100	3.2

### Conclusions

Florida pebble phosphate was very effective in removing strontium up to 200 column volumes of solution or possibly more. The interesting feature about the operation of the columns of marble chips and dolomite is that the percentage of strontium breakthrough decreased with the number of successive column volumes. Bagretsov (1) and Ames (2) have both noted that dolomite and marble chips can be activated to exchange strontium with calcium by carbonate or phosphate ion in solution. The whole field of chemical activation in insoluble calcium minerals opens up interesting possibilities. It is evident that phosphate, whether in solution or in the mineral, promotes rapid exchange of strontium with calcium. It would be worthwhile to investigate the effect of phosphate in activating dolomite and limestone. In this case it seems that chemical activation of marble chips and dolomite was being effected by caustic or by carbonate.

### CESIUM EXCHANGE

#### Introduction

Tamura and Jacobs (6) showed that the layer-lattice clays, such as the micas, montmorillonite and illite show a high preference for cesium over sodium. The evidence indicates that the affinity for cesium is increased when the interlayer spacing is reduced from 14 to 10 A. They point out that illite contains a high percentage of potassium and that these potassium ions are accommodated between the aluminosilicate sheets.

When potassium is used as the saturating cation, collapse of the interlayer spacing occurs, with an increase in affinity for cesium. However, it should be stressed that the rate of cesium sorption decreases, and ample time must be allowed to attain equilibrium. Lewis (7) finds that the sorption of cesium from 0.45 N  $\text{NaNO}_3$  by Decalso is complete in 64 hr, while in 4.0 N  $\text{NaNO}_3$  solutions equilibrium is reached in 1 hr. Lewis also points out that the affinity of most minerals for cesium is an inverse function of the sodium ion concentration raised to the 1.7 power. Therefore, dilution of the feed solution, which reduces the sodium ion concentration, will raise the  $K_D$ , while the rate at which cesium enters the lattice structure decreases.

#### Experimental

Three series of minerals were tested for their ability to remove cesium. A synthetic solution with 0.25 N  $\text{NaNO}_3$ , 0.1 N  $\text{NaOH}$  ( $\text{pH} > 13$ ) and  $\text{Cs}^{137}$  tracer was used. In the first series, 1 g of mineral was contacted with 20 ml of solution. The distribution coefficient of cesium was determined, and the results are presented in Appendix 1. Ten of the minerals exhibiting the highest distribution coefficients are listed in Table 5.

In the second series the same synthetic solution was adjusted to pH 7, and 10 ml of solution was contacted with 0.2 g of mineral. The distribution coefficients for all minerals in this series are presented in Appendix 3. Ten of the minerals showing the highest distribution coefficients are listed in Table 6.

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Table 5. The Ten Minerals Exhibiting the Highest Distribution Coefficient for Cesium in Their Order of Relative Effectiveness

Mineral	$K_D$ Contact Time of 22 hr
Lepidomelane	830
Fuchsite	468
Glauconite	279
Collinsite	184
Rutile	157
Florida pebble phosphate	108
Muscovite	105
Cuprite	67.4
Dufrenite	71.1
Limonite	57.2

Table 6. Ten Minerals Exhibiting the Highest Distribution Coefficient for Cesium in Their Order of Relative Effectiveness

Mineral	$K_D$ Contact Time of 3 Days
Mica, augite periodite	1146
Biotite	719
Graphite mica schist	482
Oil shale (Tasmanite)	415
Dacite	402
Crumpled mica schist	360
Allophane	342
Green slate	312
Biotite gneiss	227
Mica periodite	218

Several other materials of interest were tested. The distribution coefficients were determined by using 10 ml of the standard synthetic solution (pH > 13) and 0.2 g of material, and the results are shown in Table 7.

Table 7. Distribution Coefficients for Cesium

Material	Contact Time (hr)	K <sub>D</sub>
Vermiculite	0.5	830
Tennessee phosphate (heated to 600°C)	0.5	3400
Duolite C3	0.5	1635
Florida phosphate	0.5	2.5
Attapulgus clay (heated to 600°C)	2	20
Decalso	24	73.8

#### Conclusion

The results show that the highest distribution coefficients were exhibited by the minerals having an interlayer-lattice type of structure. Various micas, such as lepidomelane, fuchsite, biotite, mica augite periodite, graphite mica schist and vermiculite have distribution coefficients of 400 or greater. Several minerals, such as glauconite, oil shale (tasmanite), and Tennessee pebble phosphate, which all contain

various clay minerals as impurities, also show high distribution coefficient for cesium. The distribution coefficient for heated Tennessee phosphate is outstanding.

Florida pebble phosphate has a  $K_D$  of 2.5 for cesium when the time of contact is only 0.5 hr (Table 6), but the  $K_D$  for cesium rises to 108 at the end of 22 hr. Tennessee phosphate, pretreated by heating to  $600^{\circ}\text{C}$  for approximately 1 hr, exhibits a very high  $K_D$  (3400) at the end of 0.5 hr.

Tamura and Jacobs (8) point out that when montmorillonites (Wyoming bentonite) are heated to elevated temperatures, irreversible collapse of the lattice (from  $14 \text{ \AA}$  to  $10 \text{ \AA}$ ) will result. This pretreatment of montmorillonites will increase their affinity for cesium. Cesium sorption by Wyoming bentonite is not affected by pretreating the bentonite to temperatures less than  $600^{\circ}\text{C}$ . Above  $800^{\circ}\text{C}$  the layer-lattice structure of Wyoming bentonite is destroyed, which results in a loss in its affinity for cesium. At  $700^{\circ}\text{C}$  an irreversible collapse of the lattice takes place with an increase in the affinity for cesium. He notes that the maximum sorption of cesium by calcium montmorillonite takes place after heating to  $600^{\circ}\text{C}$ . Thus, it was fortuitous that the sample of Tennessee phosphate was heated to  $600^{\circ}\text{C}$ , a temperature which favors irreversible collapse of the lattice of bentonite impurities in Tennessee phosphate. Tennessee phosphate that was not heated was highly dispersed when contacted with water. This behavior is characteristic of the bentonites. However, by heating at  $600^{\circ}\text{C}$

for 2 hr, a crystalline aggregate is formed which is stable in water or dilute alkaline solutions. A column of this material showed good hydraulic characteristics. In addition, the data show that Tennessee phosphate (heated to 600°C for 2 hr) is superior to Florida pebble phosphate for sorption of strontium. Thus, it must be concluded that this mineral shows good promise for sorption of strontium and cesium from dilute alkaline solutions.

Two synthetic ion exchange materials, Duolite C3 and Decalso have distribution coefficients for cesium of 1635 and 73.8, respectively, at the end of 30 min. Duolite C3 is an organic phenolsulfonic type of ion exchange resin. This type of resin was shown by Miller and Kline (9) to have a greater selectivity for cesium than the sulfonic type of ion exchange resins have. The phenolsulfonic organic resin is more resistant to high radiation fields because of the presence of methylene bridges. However, it is rapidly degraded by mild reagents, such as dilute nitric acid, which results in the formation of gases. Decalso is an inorganic synthetic ion exchanger manufactured by the Permutite Company. It is made by heating  $Al_2O_3$  and sodium silicate at high temperatures.

The effect of pH and time of contact were studied by contacting the standard synthetic solution with vermiculite (a natural mica) and Decalso. The data appears in Table 8.

The pH of the solution has little effect on the sorption of cesium by vermiculite, while the distribution coefficient for Decalso rises from

273 at pH 13 to 1494 at pH 7. The effect of pH and rate of absorption of cesium on the mineral must be known in order to predict the best material for use in a known situation.

Table 8. Effect of pH on the Absorption of Cesium by Vermiculite and Decalso

Material	pH	$K_D$ Contact Time of 1 hr	$K_D$ Contact Time of 2 hr
Vermiculite	5	49.0	90.2
	7	67.1	108
	9	74.1	114
	11	60.3	94
	13	54.9	116
Decalso	5	291	1494
	7	213	511
	9	155	444
	11	114	295
	13	73.8	273

The standard synthetic solution with  $Cs^{137}$  tracer was passed through a 5-ml column of vermiculite at a flow rate of one column volume per hour. The amount of cesium in the effluent, as a function of the number of column volumes of solution passed through the column, is presented in Table 9.

Other minerals which have high  $K_D$ 's for cesium are being investigated under column conditions.

Table 9. Cesium Breakthrough on a Vermiculite Column

Number of Column Volumes	Amount of Cesium in Effluent (%)
10	0.5
20	0.07
33	0.17
55	33.2
94	66.6

#### RUTHENIUM REMOVAL

##### Introduction

The chemistry of ruthenium is complex. For instance, Il'enko, Nikol'skii and Trofimov (10) infer on the basis of many investigations that ruthenium can exist in aqueous solution in numerous forms. Various hydration processes can result in complex shifts of equilibria. Figure 1 shows an idealized scheme which encompasses 18 forms of ruthenium originating in this way. These authors investigated the adsorption of ruthenium on strong, average, and weakly basic anion exchangers and also on sulfonic and carboxylic cation exchangers as a function of pH. They found that at room temperature it may take as long as 200 days to attain equilibrium (95% ruthenium removed), while after one day they were far from equilibrium (less than 10% ruthenium removed). Maintaining the temperature of the solution at 60°C gave equilibrium results at the end of 16 to 24 hr.

Consequently, in many of the experiments described herein the solutions were heated at 60°C for 16 hr.

Zvyagintsev and Starostin (11) prepared a number of unusually strong ruthenium complexes which did not react with thiourea, which normally gives a characteristic reaction with ruthenium. The precipitation of the strongly complexed ruthenium by reducing agents was slow and difficult.

Pshenitsyn and Ginzburg (12) note the formation of an intermediate product in the reduction of Ru(IV) to Ru(III) which impedes the reaction in some obscure fashion. Silverman and Levy (13) studied the upper valence states of ruthenium in alkaline solutions. They noted that the decomposition of ruthenate and perruthenate to ruthenium dioxide is a complicated disproportionation reaction. The rate of decomposition is rapid at pH 8 or lower and decreases with increasing pH.

Starik and Kositsyn, (14) as well as Pushkarev, (15) report that greater than 90% of the ruthenium is carried by ferric hydroxide at pH 7. Experience at the Fission Products Pilot Plant at ORNL showed that ruthenium was found to carry well (greater than 90%) at pH 7 on most hydrous precipitates (such as those of aluminum, iron and the rare earths). It should be emphasized at this point that in the above experiments ruthenium was present in acid solutions in a form that precipitates readily on neutralization of the acid. However, in aged alkaline wastes ruthenium is present as an oxy-aquo complex which is not readily precipitated on a hydrous carrier.

Fletcher and Martin (16) stress that the general properties of the nitrosyl-ruthenium complexes are quite different from those of Ru(IV) and that formation of an insoluble nitrosylruthenium hydroxide does not take place when ruthenium complexes of this type are neutralized with alkali. Preliminary experiments with alkaline waste (pH > 13) containing ruthenium from pit 3 at ORNL and from seepage water (pH 8) from the pits showed that less than 1% of the ruthenium is carried on 0.1 g/liter of iron at pH 7. The yield could be increased to 20 to 30% by heating at 60°C for 4 hr. The addition of a reducing agent (0.02 M  $\text{Na}_2\text{SO}_3$ ) raised the yield to 50 to 60%. Because of this great difference in the behavior of ruthenium, all experiments were performed by using the alkaline waste from the pits (pH > 13) or with seepage water from the pits (pH 8). No activities other than  $\text{Ru}^{106}$  could be detected in the seepage water. Therefore, it was possible to follow the ruthenium by gross gamma counting.

Removal of ruthenium from aqueous solutions was investigated under oxidizing and reducing conditions. The use of oxidizing conditions at high pH converts the ruthenium to the ruthenate or even perruthenate (13). The possibility of exchange of ruthenium as ruthenate or perruthenate with other anions such as sulfate, phosphate, chromate or molybdate was studied.

Ruthenium forms an insoluble sulfide or hydrated oxide under reducing conditions at pH 7. This reaction is relatively fast and complete at pH 7 but is slow and incomplete at a pH greater than 11.

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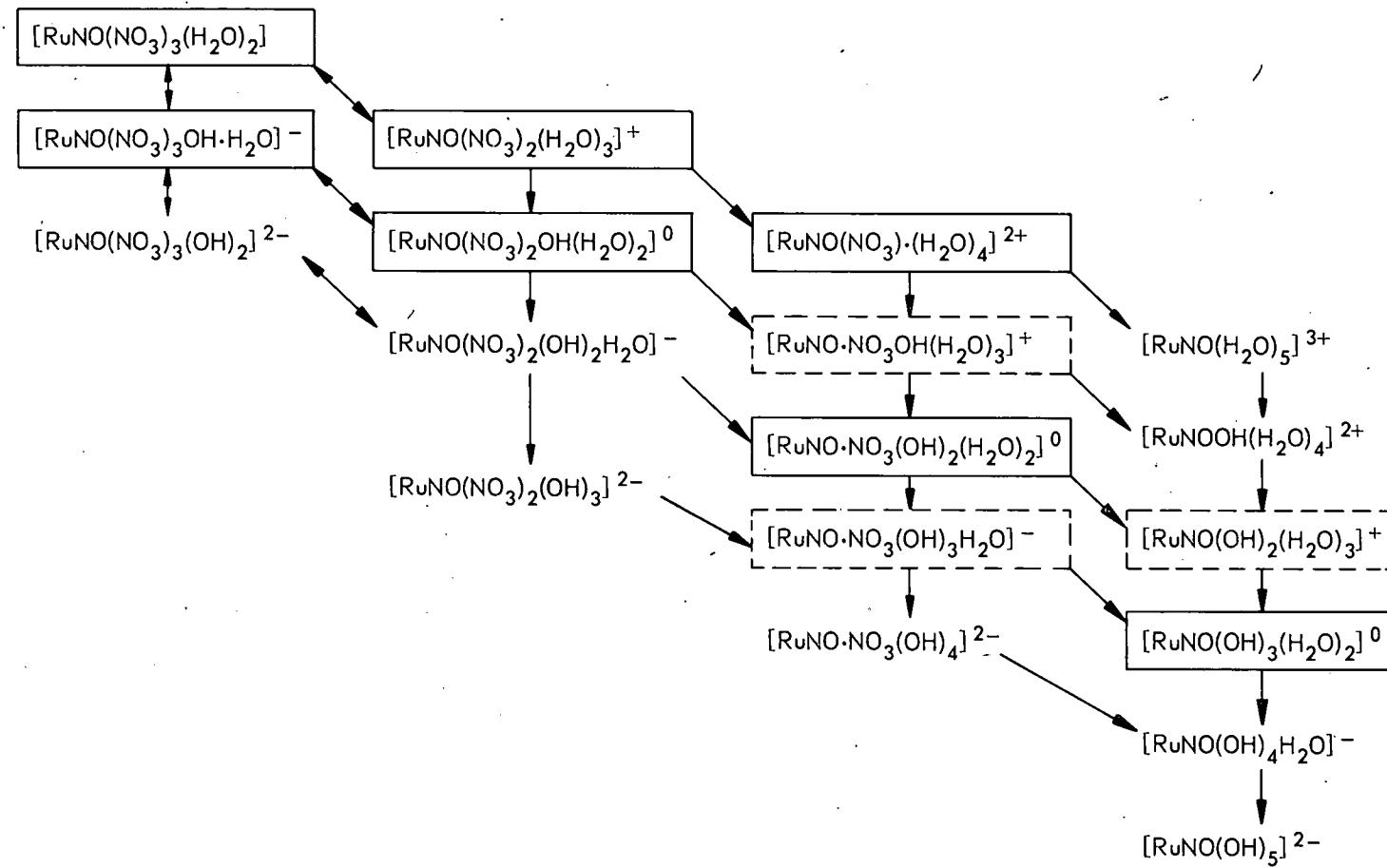


Fig. 1. Formation of Nitroso-Nitrate Complexes of Ruthenium.

Seepage solution from the pits containing Ru<sup>106</sup> was treated as previously described. The pH of the solution was adjusted to 7 for the experiments under reducing conditions (0.02 M sodium hydrosulfite).

Under oxidizing conditions, the ruthenium is stabilized as ruthenate or perruthenate at high pH. Hence, a pH greater than 13 was used for oxidizing conditions (0.02 M sodium persulfate).

In both sets of experiments 10 ml of solution was contacted with 0.2 g of mineral. Due to the presence of the many forms of ruthenium in solution, calculation of a distribution coefficient was not possible. Thus, the results are expressed as a percentage of ruthenium removed from solution. These results are presented in Appendix 2. The results for ten of the minerals showing the highest percentage removal of ruthenium under reducing and oxidizing conditions, respectively, are presented in Table 10. In this table, kinetic data showing the slow approach to equilibrium under reducing conditions are also included.

It can be seen that no appreciable exchange of ruthenium as the ruthenate takes place, as the percentage removal of ruthenium under oxidizing conditions is much lower than it is under reducing conditions. Removal of ruthenium is slow, even under reducing conditions at a pH of 7. However, heating accelerates the rate at which ruthenium is removed.

Table 10. Minerals Exhibiting the Highest Percentage of Removal  
of Ruthenium in Their Order of Relative Effectiveness

Mineral	Amount Removed (%) pH 7, Contact Time, 1 day	Four Days	Four Days, Plus 16 hr at 60°C
Reducing Condition, pH 7			
Copper in conglomerate	53.7	73.7	92.7
Descloizite	46.3	72.3	91.5
Copper	45.9	72.8	91.1
Fuchsite	72.2	80.7	89.7
Zirconium phosphate	57.0	79.0	87.0
Cuprite	56.2	78.6	85.7
Chalcocite	29.3	48.3	82.2
Barium chromate	49.7	78.6	81.0
Smaltite	31.3	62.4	77.8
Glauconite	30.1	61.1	76.6
Oxidizing Condition, pH > 13			
Rammelsbergite		44.4	
Chalcocite		26.1	
Diginite in pyrite		25.2	
Copper in conglomerate		25.2	
Fuchsite		24.7	
Limonite		21.5	
Realgar		21.0	
Copper (native)		19.2	
Psilomelane		18.8	
Sphalerite		17.4	

Another series of minerals was also tested to find those minerals that would remove ruthenium from solution. Since none of the minerals in the previous series were effective in removing ruthenium at pH 13 under oxidizing conditions, this series of minerals was tested at pH 13 with no oxidizing agent present. It was presumed that ruthenium would be present predominantly as the ruthenate. These minerals were also tested for their ability to remove ruthenium under reducing conditions (0.02 M sodium hydrosulfite) at pH 7. The other experimental conditions remained the same. The results are presented in Appendix 3. The ten minerals which were most effective in removing ruthenium are listed in Table 11.

The results show that ruthenium is removed more completely under reducing conditions than it is when the solution is not reduced.

The removal of ruthenium from solution as a function of pH was investigated. Four minerals, which were found to be effective in removing ruthenium from solution under reducing conditions at a pH of 7, were selected for further study to find the optimum pH for ruthenium removal. The minerals tested were digenite in pyrite, pyrrhotite, chalcocite and copper in conglomerate. The experimental conditions were the same as previously described, except that acid or base was added to adjust the pH and that the solution from pit 3 was used. The results are presented in Table 12.

Minerals	Reduction	Oxidation
Digenite in pyrite	7.0	13.0
Pyrrhotite	7.0	13.0
Chalcocite	7.0	13.0
Copper in conglomerate	7.0	13.0

Reduction

Table 11. The Ten Minerals Exhibiting the Highest Percent Removal of Ruthenium, in Their Order of Relative Effectiveness

Mineral	Ruthenium Removed (%)
pH 13, Contact Time of Four Days	
Mica Peridotite	28.3
Oil Shale, Tasmania	25.2
Anglesite	22.5
Oil Shale, Colorado	18.3
Oil Shale, Tasmanite	16.8
Serpentine, Crysotile	14.4
Peat	12.5
Periodite changing to serpentine	12.3
Dacite	11.4
Serpentine, Maryland	10.2
pH 7, Reducing Conditions, Contact Time of Two Days	
Allophane	85.0
Halloysite	74.1
Dacite	67.2
Cerussite	65.9
Dumortierite	65.8
Oligoclase	64.4
Oil shale, Tasmanite	63.0
Vintahite	62.8
Beryl	62.1
Biotite	61.1

Table 12. Effect of pH on the Removal of Ruthenium by Several Minerals

pH	Percent Ruthenium Removed Contact Time of Two Days	
	Ruthenium	Cesium
Digenite in Pyrite		
5	42	19
7	27	16
9	12	12
11	15	12
13	24	12
0.1 <u>N</u> NaOH	19	10
Pyrrhotite		
5	54	25
7	54	21
9	15	16
11	10	12
13	19	16
0.1 <u>N</u> NaOH	27	16
Chalcocite		
5	4	21
7	57	25
9	20	16
11	25	21
13	19	14
0.1 <u>N</u> NaOH	20	16
Copper in Conglomerate		
5	62	28
7	79	32
9	50	35
11	54	23
13	45	21
0.1 <u>N</u> NaOH	27	21

The percentage removal of ruthenium increases as the pH of the solution is decreased. Since these solutions (Table 12) were not heated at 60°C for 16 hr, the percentage removal of ruthenium from these solutions is moderately low. However, the data show that the optimum removal of ruthenium takes place at a pH of 5 to 7.

A column containing 20 ml of copper in conglomerate ore was prepared to test the removal of ruthenium under column conditions. Waste from pit 3 was adjusted to pH 7, and 0.02 M sodium hydrosulfite was added as a reducing agent. The column was electrically heated to 85°C by wrapping heating tape around the outside. The flow rate was about one column volume of solution every 2 hr. About 95% of the ruthenium was removed from the first few column volumes of solution. Eighty percent of the ruthenium removed after 50 column volumes of solution had been passed through the column. This experiment is still in progress at the time of writing.

A number of conditions favoring the removal of ruthenium from solution were employed in this experiment, such as a high temperature (85°C), slow flow rate (one column volume every 2 hr), a pH of 7, and reducing conditions (0.02 M sodium hydrosulfite). These factors have been previously shown to be important in the removal of ruthenium.

#### CONCLUSIONS

It has been shown in this report that the concept of a soil column is feasible. A combination of a number of minerals described in this report can be utilized to remove strontium, cesium, and ruthenium from dilute intermediate-level alkaline fission product wastes. This column will operate satisfactorily, within limits. To remove ruthenium, in particular, a number of critical operating conditions must be met. The over-all performance of the column would be materially simplified and improved if the removal of ruthenium could be effected at a higher pH.

The authors are indebted to T. Tamura and D. G. Jacobs of the Health Physics Division at Oak Ridge National Laboratory for valuable discussions and advice, and to R. R. Richard of the Analytical Chemistry Division for timely assistance. The active interest of A. F. Rupp in this work is acknowledged with pleasure. We are indebted to G. F. Malling for the results in Appendix 4.

APPENDIX 1

Distribution Coefficients for Cesium with Various Minerals

Mineral	Chemical Formula	K <sub>D</sub> After 2 hr	K <sub>D</sub> After 48 hr
Alunite	KAl <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>	0.146	0.20
Arsenopyrite	FeAsS	1.81	3.26
Baddeleyite	ZrO <sub>2</sub>	3.29	10.4
Cassiterite	SnO <sub>2</sub>	6.04	15.1
Celestite	SrSO <sub>4</sub>	0.0	0.24
Chalcocite	Cu <sub>2</sub> S	5.71	35.6
Chromite	Ferrous Mg Metachromite	4.32	15.0
Collinsite	Hydrous Ca, Mg, Iron Phosphate	27.9	184
Copper	Cu	5.56	27.2
Copper	Cu in Conglomerate	2.03	5.54
Descloizite	Basic Pb, Zn, Vandate	3.43	7.04
Dufrenite	Hydrous Iron Phosphate	20.9	71.1
Franklinite	Zn, Mg, Metaferrite	0.46	0.64
Galena	PbS	0.28	0.43
Griphite	Complex, Fe, Mg, Ca, Al Phosphate	2.10	6.02
Ilmenite	Ferrous Metatitanate	4.32	7.45
Langbeinite	K, Mg Sulfate	0.11	0.04
Lepidolite	Li, K, Al Fluosilicate	5.60	19.4
Leucite	K Aluminum Metasilicate	14.9	44.5

Mineral	Chemical Formula	$K_D$ After 2 hr	$K_D$ After 48 hr
Limonite	Ferric Hydroxide	13.2	57.2
Magnetite	Ferrous Metaferrite	1.13	1.90
Molybdenite	Mo Sulfide	3.75	13.4
Pentlandite	Iron and Nickel Sulfide	1.32	5.94
Psilomelane	Impure Hydrous $MnO_2$	5.16	11.3
Pyrite	Iron Disulfide	0.91	2.60
Pyrolusite	$MnO_2$	0.26	0.53
Pyrrhotite	Ferrous Sulfide	1.72	6.16
Rammelsbergite	Nickel Diarsenite	0.23	0.95
Realgar	Arsenic Disulfide	5.66	34.2
Rhodachrosite	$MnCO_3$	1.61	4.72
Rhodonite	Mn Metasilicate	0.26	0.61
Rutile	$TiO_2$	21.6	157
Scorodite	Hydrous Ferrous Arsenate	1.49	2.90
Smaltite	Cobalt Diarsenide	3.39	14.8
Sphalerite	Zn Sulfide	1.91	6.49
Spodumene	Li Aluminum Metasilicate	0.60	1.51
Wavellite	Hydrous Basic Al Phosphate	10.7	25.7
Marcasite	Iron Disulfide	0.16	0.65
Cinnabar	HgS	5.04	34.5

Mineral	Chemical Formula	K <sub>D</sub> After 2 hr	K <sub>D</sub> After 48 hr
Cobaltite	Cobalt Sulfarsenide	0.81	2.44
Columbite	Fe and Mn Metaniobate and Tantalate	6.18	37.7
Wolfomite	Fe, Mn Tungstate	<0.01	0.35
Cuprite	Cuprous Oxide	13.7	67.4
Digenite in Pyrite	Cuprous Sulfide	0.42	1.44
Glauconite	Hydrous K Ferric Silicate	103	279
Kalinite	Hydrous K Aluminum Sulfate	0.20	0.03
Lepidomelane	Acid K, Mg, Fe, Aluminum Orthosilicate	258	830
Microcline	K Aluminum Trisilicate	1.09	2.17
Muscovite	Acid K Aluminum Orthosilicate	116.4	468.0
Niccolite	Nickel Arsenide	0.47	0.59
Stibnite	Antimony Sulfide	3.20	7.10
Pollucite	Hydrous Cesium Aluminum Silicate	1.51	2.42
Florida Pebble Phosphate	Ca Phosphate	46.6	108
Dowex 50 WX 12		16.7	25.6
Dowex 1 NO <sub>3</sub> <sup>-</sup> Form		<0.01	<0.01

APPENDIX 2

Percentage Removal of Ruthenium with Various Minerals

Mineral	Reducing Conditions, pH 7		Oxidizing Condition, pH >13		
	Percent Removed, Contact = 1 day	Percent Removed, Contact = 4 days	Percent Removed Four Days Plus 16 hr at 60°C	Percent Removed 1 Day	Percent Removed 4 Days
Alunite	31.2	25.3	22.2	7.2	< 0.1
Arsenopyrite	26.1	27.8	45.3	6.4	< 0.1
Baddeleyite	47.6	58.9	56.9	9.3	1.3
Cassiterite	31.8	53.1	61.4	10.9	7.9
Celestite	17.8	30.6	25.9	1.5	< 0.1
Chalcocite	29.3	48.3	82.2	19.5	26.1
Chromite	41.9	57.9	37.8	2.7	< 0.1
Collinsite	39.9	49.7	50.5	1.4	< 0.1
Copper	45.9	72.8	91.1	30.9	19.2
Copper in Conglomerate	53.7	73.7	92.7	18.7	25.2
Descloizite	46.3	72.3	91.5	2.9	9.3
Dufrenite	46.7	71.7	56.8	4.2	8.7
Franklinite	23.9	40.8	39.1	< 0.1	4.2
Galena	17.3	45.1	33.7	8.5	14.1
Griphite	20.5	32.9	55.6	1.7	7.5
Ilmenite	16.3	55.3	43.9	1.0	7.3
Langbeinite	14.3	22.6	25.5	0.7	3.8

Mineral	Reducing Conditions, pH 7		Oxidizing Condition, pH >13		
	Percent Removed, Contact = 1 day	Percent Removed, Contact = 4 days	Percent Removed Four Days Plus 16 hr at 60°C	Percent Removed 1 day	Percent Removed 4 days
Lepidomelane	29.9	40.6	18.7	1.1	2.9
Leucite	33.4	43.5	53.7	2.6	3.9
Limonite	30.0	61.2	70.8	7.2	21.5
Magnetite	17.5	25.1	21.9	1.5	2.6
Molybenite	25.1	36.9	32.4	5.1	12.4
Pentlandite	18.4	18.3	52.5	5.6	15.8
Psilomelane	62.4	70.9	50.9	10.8	18.8
Pyrite	37.8	40.1	52.8	7.2	1.7
Pyrolusite	58.1	67.9	43.2	6.6	17.2
Pyrrhotite	18.1	29.4	66.2	5.8	16.4
Rammelsbergite	20.8	26.2	56.7	7.6	44.4
Realgar	52.6	66.5	74.9	11.0	21.0
Rhodachrosite	28.9	53.1	39.3	4.0	10.4
Rhodonite	19.0	53.5	52.7	3.4	10.7
Rutile	29.2	55.1	38.8	3.6	8.4
Scorodite	25.0	55.9	47.4	1.8	7.7
Smaltite	31.3	62.4	77.8	5.9	11.4
Sphalerite	28.1	41.9	60.3	8.8	17.4

Mineral	Reducing Conditions, pH 7		Oxidizing Condition, pH >13		
	Percent Removed, Contact = 1 day	Percent Removed, Contact = 4 days	Percent Removed Four Days Plus 16 hr at 60°C	Percent Removed 1 day	Percent Removed 4 days
	22.4	28.2	37.9	4.0	13.2
Wavellite	42.1	56.5	47.0	8.4	7.6
Marcasite	22.9	39.9	47.0	1.9	5.3
Cinnabar	19.8	32.2	47.3	3.9	10.4
Cobaltite	23.7	45.7	73.5	2.7	9.5
Columbite	26.0	57.6	58.8	1.0	2.1
Wolframite	24.5	25.4	39.8	1.1	5.0
Cuprite	56.2	78.6	85.7	4.5	14.5
Cryolite	29.9	25.5	21.5	1.8	4.4
Digenite in Pyrite	22.1	19.9	43.5	19.2	25.2
Glauconite	30.1	61.1	76.6	3.8	17.2
Kalinite	9.6	11.7	14.2	1.4	< 0.1
Lepidomelane	54.6	57.0	66.6	1.7	8.4
Microcline	17.9	25.1	24.9	1.6	2.5
Muscovite	26.7	48.2	64.1	1.0	5.3
Fuchsite	72.2	80.7	89.7	15.4	24.7
Niccolite	25.0	53.3	74.7	6.9	11.5

Mineral	Reducing Conditions, pH 7		Oxidizing Condition, pH >13		
	Percent Re- moved, Contact = 1 day	Percent Re- moved, Contact = 4 days	Percent Removed Four Days Plus 16 hr at 60°C	Percent Removed 1 day	Percent Removed 4 days
	37.1	40.0	74.0	8.3	13.6
Pollucite	33.1	25.5	16.6	3.3	0.7
Florida Pebble Phosphate	52.9	57.2	56.5	2.5	9.3
Dowex 50W	17.2	17.4	13.2	1.0	2.1
1RC-50	8.0	10.0	11.6	2.5	12.9
Permutite	15.7	49.3	59.0	1.3	0.9
BaCrO <sub>4</sub>	49.7	78.6	81.0	4.0	10.5
Dowex 1	30.3	39.5	46.1	12.4	3.0
Zr.Moly.	7.4	50.9	61.9	3.4	6.8
Zr Phosphate	57.0	79.0	87.0	6.7	17.2
Al Silicate	17.5	23.2	21.9	1.9	0.3
Silica Gel	26.5	22.0	17.6	3.9	8.6

APPENDIX 3

Removal of Cesium and Ruthenium by Various Minerals

Mineral	K <sub>D</sub> of Cs (3 days Contact)	% Ru Removed From Solution at pH 13.0 (4 days Contact)	% Ru Removed From S6- lution at pH 7.0, 0.02 M Sodium Hydrosulfite Added (2 days Contact)
<b>Amphibole</b>			
Actinolite	11.8	3.51	37.5
Asbestos	0.95	2.08	37.1
Hornblende	59.4	2.41	39.2
Tremolite	5.64	4.68	40.2
Hexagonite	16.5	4.99	34.7
<b>Gneiss</b>			
Biotite gneiss (NY)	36.6	0.93	33.3
Biotite gneiss (Mass)	227	2.62	47.7
Hornblende gneiss (NY)	14.2	2.26	52.5
<b>Peridotite</b>			
Mica peridotite	218	28.3	51.1
Mica-augite peridotite	1146	8.30	37.0
Dunite	2.84	5.83	56.3
Peridotite changing to serpentine	2.84	12.3	50.1
<b>Serpentine</b>			
Chrysotile	1.35	14.4	52.1
Maryland	12.6	10.2	50.0
Vermont	3.51	7.12	60.1
Quebec	10.8	7.25	46.2

Mineral	K <sub>D</sub> of Cs (3 days Contact)	% Ru Removed From Solution at pH 13.0 (4 days Contact)	% Ru Removed From Solution at pH 7.0, 0.02 M Sodium Hydrosulfite Added (2 days Contact)
<b>Shale</b>			
Oil shale, Colorado	31.6	18.3	45.4
Oil shale, Tasmania	12.1	25.2	26.6
Oil shale, Tasmanite	415	16.8	63.0
Uintahite, Gilsonite	9.94	1.21	62.8
<b>Schists</b>			
Chlorite schist	1.91	2.54	44.8
Hornblende schist	4.60	< 0.01	31.9
Muscovite biotite schist	66.5	1.56	35.7
Crumpled mica schist	360	5.55	52.8
Chrome mica schist	128	< 0.01	37.0
Graphite mica schist	482	5.19	57.2
Tremolitic mica schist	15.1	< 0.01	38.8
Allophane	342	3.33	85.0
Anglesite	< 0.1	22.5	53.5
Anhydrite	0.78	5.24	50.2
Anorthoclase	63.8	0.96	49.8
Anthophyllite	24.6	7.05	58.6
Amblygonite	8.64	5.36	59.8
Amosite	25.8	3.04	34.9
Barite	<< 0.1	0.40	45.2

Mineral	K <sub>D</sub> of Cs (3 days Contact)	% Ru Removed From Solution at pH 13.0 (4 days Contact)	% Ru Removed From So- lution at pH 7.0, 0.02 M Sodium Hydrosulfite Added (2 days Contact)
Bauxite	9.66	4.08	56.8
Bentonite	199	10.1	59.7
Beryl	5.90	2.00	62.1
Biotite	719	4.66	61.1
Cerussite	6.41	6.42	65.9
Chondrodite	10.3	8.73	50.6
Clay - bentonite (cretaceous)	53.9	1.19	52.0
Crocidolite	109	6.01	53.6
Dacite	402	11.4	67.2
Dumortierite	50.2	5.87	65.8
Fluorite	< 0.1	0.17	38.3
Gypsum	10.9	7.44	60.0
Holloysite	25.8	8.23	74.1
Kaolin	57.5	4.35	55.6
Margarite	4.91	2.23	38.6
Mineral coal	19.5	8.08	45.3
Monazite	94.8	3.55	47.2
Nepheline	7.60	2.75	59.2

Mineral	K <sub>D</sub> of Cs (3 days Contact)	% Ru Removed From Solution at pH 13.0 (4 days Contact)	% Ru Removed From So- lution at pH 7.0, 0.02 M Sodium Hydrosulifte Added (2 days Contact)
Oligoclase	4.50	2.60	64.4
Olivine	1.26	5.24	55.2
Opal	187	1.29	54.0
Peat (pleistocene)	5.75	12.5	26.7
Prochlorite	7.56	4.32	50.3
Prophyllite	78	2.68	45.7
Siderite	0.45	3.49	39.1
Slate - green slate	312	4.71	52.2
Witherite	1.56	0.54	53.2

APPENDIX 4

Sorption of Strontium by Tennessee Phosphate Heated to 600°C  
as a Function of  $\text{NaNO}_3$  Concentration

$\text{NaOH} = 0.1 \text{ N}$  in each experiment. Contact time = 69 hours.

<u><math>\text{NaNO}_3</math> Moles/Liter</u>	<u><math>K_D</math> of Tennessee Phosphate</u>
0	3190
1.0	572
2.0	287
4.0	188

The  $K_D$  is still relatively high in 4.0 N  $\text{NaNO}_3$ . The exchange of strontium is taking place via two mechanisms. Part of the strontium exchange is due to ion exchange which is affected by  $\text{NaNO}_3$  concentration. Another part of the strontium exchange is due to isomorphous replacement of calcium by strontium in the apatite lattice and it is assumed that this exchange is not affected by  $\text{NaNO}_3$  concentration.

1.0 N  $\text{NaNO}_3$   
a. Ion exchange  
b. Isomorphous replacement

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