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## RUTHENIUM SORPTION BY MINERALS

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### ABSTRACT

Investigations were made of the ruthenium sorptive properties of sulfide minerals. Sorption of ruthenium from synthetic waste solution tagged with Ru-106  $\text{Cl}_3$  was quite high, but sorption of ruthenium from the untreated seep solution of operating waste pits was low. Use of  $\text{Na}_2\text{S}_2\text{O}_4$  as a reducing reagent in alkaline media increased sorption of ruthenium from the seep somewhat. Optimum removal of ruthenium from solution occurred in the pH range, 6 to 10, where polymeric species of ruthenium would be at a maximum.

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## INTRODUCTION

Intermediate-level radioactive effluents at ORNL are discharged to seepage pits and trenches excavated in formations of Conasauga shale. As the highly basic waste solution percolates through the shale, the cesium is quickly removed from solution due to the strong affinity of the ion exchange surfaces of the soil clays, particularly illite (1). That part of the strontium and the rare earths not removed by precipitation during neutralization of the waste stream moves more slowly than the ground water because of continued precipitation of insoluble salts in the ground and because of ion exchange. Ruthenium, on the other hand, moves through the ground nearly as rapidly as the ground water. However, 80-90% of the ruthenium discharged to surface pits is removed within 100 ft of the point of disposal indicating appreciable removal of radioruthenium in the ground. Despite the fact that the permissible concentrations of Ru-106 are comparatively high, movement of radioruthenium in the environment constitutes a serious nuisance, and, in some cases, a possible health hazard.

## PERTINENT RUTHENIUM CHEMISTRY

Ruthenium is a member of the rare group of platinum metals. The chief source of the metal is osmiridium (Os, Ir), but it also occurs naturally as the mineral laurite ( $\text{RuS}_2$ ), which is insoluble in all acids, even in aqua regia, and in fused potassium pyrosulfate (2). Ruthenium is the only element which is known to exist in all oxidation states from 0 to 8. The

characteristics of the various oxidation states are difficult to systematize, and few compounds containing uncomplexed species are known, the oxides and sulfides being exceptions (5).

The lower valent compounds (oxidation states III and IV) are found in acid solution, hydrolyzing to give precipitates of ruthenium hydroxide and hydrous ruthenium dioxide upon neutralization (4).

#### Complex Ion Formation in Nitric Acid Solution (6,7)

In nitric acid the behavior of ruthenium is complicated by the formation of nitrate- and nitro-nitrosyl-hydroxy complexes of varying stability and chemical characteristics. The nitrate complexes have the general formula,  $\left[ \text{Ru NO}(\text{NO}_3)_y(\text{OH})_{3-y}(\text{H}_2\text{O})_2 \right]$ , with the NO, NO<sub>3</sub>, OH, and H<sub>2</sub>O assuming octahedral co-ordination around the ruthenium atom. If the position directly opposite or trans to the NO (nitrosyl) group is occupied by a nitrate group, the complex is cationic in the mono- and di-nitrate, neutral in the tri-nitrate form, and anionic in the tetra- and penta-nitrate forms. Often the trans position is occupied by -OH, rather than -NO<sub>3</sub>, in which case the mono-nitrate form is cationic, the di-nitrate form is neutral, and the tri- and tetra-nitrate forms are anionic. The relative distribution of these forms is a function of the total nitrate concentration, a higher degree of nitrate complexing is favored by higher nitrate concentrations. In solution up to 1 M nitrate concentration, the cationic species of the nitrate complexes are predominant,

while above 9 M  $\text{HNO}_3$  the anionic species are most abundant. When the equilibrium distribution is disturbed, by changing the concentration of nitrate in the solution, new equilibrium is attained following first order reaction kinetics with respect to ruthenium with a rate constant of  $0.024 \text{ min}^{-1}$  at  $20^\circ\text{C}$ . These are fairly weak complexes and, in dilute acid, they oxidize to Ru (IV) polymer, unless light and air are excluded. Above pH 2 the complexes are completely hydrolyzed.

The Ru (NO) nitro complexes, in which  $\text{NO}_2$ (nitro) groups replace one or more  $\text{NO}_3$  groups(nitrato) are much more stable than the nitrato complexes. Their formation requires the presence of nitrous acid, but 30% to 70% of the total ruthenium may be involved in nitro complexing in 2 M to 4 M  $\text{HNO}_3$  with as little as  $10^{-3}$  M to  $10^{-2}$  M  $\text{HNO}_2$ . Because of their pronounced stability, once the nitro complexes have been formed, they are resistant to destruction and are likely to persist through subsequent treatments.

Uncomplexed Ru (NO) cations,  $[\text{Ru NO} \cdot \text{OH}]^{2+}$  or  $[\text{Ru NO}]^{3+}$ , may occur when the nitrate concentration is low. Below 1 M  $\text{HNO}_3$  they may contribute significantly to the total ruthenium concentration. As the acidity falls, polymeric species of the cation may appear. Complete conversion to the hydroxide can be effected by boiling on the alkaline side to displace the complexing ions, and oxidation of the Ru (IV) in strongly alkaline solution gives alkali ruthenates (8).

Behavior of Ruthenium in Alkaline Solution (4)

The higher oxidation states of ruthenium are stable in alkaline media. Ruthenate ( $\text{RuO}_4^-$ ) and perruthenate ( $\text{RuO}_4^+$ ) are the usual species but ruthenium dioxide ( $\text{RuO}_2$ ) or ruthenium tetroxide ( $\text{RuO}_4$ ) may be present, depending on the basicity, the amount of oxidants present, and the presence or absence of catalysts (9,10). Below pH 10 perruthenate disproportionates into ruthenium tetroxide and insoluble ruthenium dioxide so rapidly that perruthenate is only in solution for a matter of minutes. In the region pH 10 to 10.65 the reaction proceeds more slowly; the disproportionation of perruthenate taking place over a period of hours with the dioxide forming as a colloid. Above pH 10.65 the perruthenate reacts with excess alkali to yield ruthenate with evolution of oxygen. However, traces of ruthenium dioxide, from the disproportionation of perruthenate or the decomposition of ruthenate, persist until the pH is raised above 12.

Ruthenate solutions are unstable below pH 12. The ruthenate disproportionates to yield ruthenium dioxide and perruthenate, which further reacts as described above. The rate of disproportionation increases rapidly as the solution pH approaches 7. The ruthenium tetroxide formed is easily reduced to the dioxide.

POSTULATED BEHAVIOR OF RUTHENIUM IN THE ORNL

INTERMEDIATE-LEVEL WASTE EFFLUENTS SYSTEM

As described by Browder (11), the ORNL intermediate-level waste stream has the highest level of activity of any waste produced at ORNL, though it is much lower in activity level than the

waste streams produced in the chemical reprocessing of power reactor fuels. These wastes arise from a variety of ever changing chemical operations, pilot plant operations, uranium recovery, and hot-cell drainages. The liquid waste is collected in underground tanks and is made sufficiently alkaline, with sodium hydroxide, to precipitate the insoluble hydroxides. This operation removes the major portion of several radionuclides, including the rare earths, yttrium, zirconium, niobium, strontium, and a fraction of the ruthenium along with the hydroxide and carbonate precipitates of iron and calcium.

The species of ruthenium entering the collection tanks undoubtedly comprise a wide spectrum of complexed and noncomplexed ruthenium in oxidation states III and IV. Removal of ruthenium upon neutralization is probably due to the formation of polymeric hydroxides of  $\text{Ru}(\text{NO})$ , ruthenium dioxide, and ruthenium hydroxide. In the basic supernatant solution, which is discharged to the seepage pits, aquo-hydroxy complexes of  $\text{Ru}(\text{NO})$  and ruthenate are likely to be the predominant species of ruthenium. A very small per cent of the total ruthenium may exist as neutral or anionic nitro complexes. Perruthenate is not likely to persist for very long in these streams because of its disproportionation into ruthenium tetroxide - ruthenium dioxide and its tendency to react with excess alkali to give ruthenate.

As the waste solution moves through the soil, cationic species of ruthenium, whether complexed or not, would tend to be removed by ion exchange, and polymeric species would be subject to filtration. However, the ruthenium concentration is so

low that the solubility of these ruthenium species may not be exceeded; actual removal may require precipitation on a pre-existing surface or co-precipitation with an element of higher concentration. In addition, the buffering action of the soil reduces the pH of the percolating solution resulting in the decomposition of ruthenate to ruthenium tetroxide and polymeric ruthenium dioxide. In the presence of organic matter the tetroxide is easily reduced to the dioxide. Ruthenium dioxide is very insoluble in water, behaving much like manganese dioxide, and as the waste stream percolates through the soil, this insoluble species would be removed from solution by surface precipitation and filtration. The rate of the disproportionation reaction increases with decreased pH so that complete removal of ruthenates ruthenium would be likely.

The non-complexed nitrosyl ruthenium and the nitro complexes, if they have been formed before discharge as waste, would conceivably resist oxidation to the higher oxidation states and move through the soil as uncharged or negatively charged species.

#### PURPOSE AND SCOPE OF THE EXPERIMENTAL WORK

In view of the chemical nature of ruthenium, a twofold approach was made in the study of ruthenium retention. First, an attempt was made to take advantage of the insolubility of laurite ( $\text{RuS}_2$ ) by replacing ruthenium for other lattice ions at the surface of a number of sulfide minerals. Secondly, attempts were made to reduce ruthenium to positively charged species for subsequent sorption by natural cation exchangers.

Radioactive solution was obtained from a seep near Waste Pit 4, and analyses were made for its radiochemical and stable-chemical content (Table 1). Ruthenium 106-Rhodium 106 was by far the most abundant radionuclide and  $\text{NaNO}_3$  the major stable salt of the seep solution (Analysis was not made for sodium, but it is the major cation of the intermediate-level waste stream discharged to the seepage pits.). The pH of the seep solution, 8.6, is considerably lower than the discharged waste stream which averages 0.2 M NaOH.

The seep solution was diluted to decrease the activity level and brought to the chemical concentration of the discharged waste stream (Table 2). Increasing the hydroxyl concentration of the solution to 0.22 M  $\text{OH}^-$  resulted in precipitation of  $\text{Mg}(\text{OH})_2$  which scavenged ~ 9% of the ruthenium activity. The supernate was decanted and used for subsequent experiments. Experiments were also conducted using a synthetic waste solution of this same composition, containing Ru-106  $\text{Cl}_3$  obtained from the ORNL Isotopes Division. The four sulfide minerals used as sorptive media - pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), and stibnite ( $\text{Sb}_2\text{S}_3$ ) - were obtained from Wards Natural Science Establishment, Rochester, New York; vermiculite (BO-4) was from the Zonolite Co., Traveler's Rest, South Carolina.

#### EXPERIMENTAL RESULTS AND DISCUSSION

Slurry studies of the effect of particle size of the sulfide minerals were inconclusive. Sorption of ruthenium by 0.1 g pyrite or stibnite ore from 100 ml of diluted seep solution at pH 11.8 was negligible for all particle size ranges

Table 1. Analysis of Solution Obtained from a Seep Near Waste Pit 4  
April 3, 1961

Radiochemical Analysis		Stable-Chemical Analysis	
Radionuclide	Concentration (dis/min/ml)	Ion	Concentration (ppm)
Ru-106-Rh-106	$9.30 \times 10^5$	$\text{NO}_3^-$	4,770
Co-60	5.51	$\text{SO}_4^{=}$	500
Cs-137	2.90	$\text{Mg}^{++}$	85
Sr-90	~1	$\text{Ca}^{++}$	28
TRE	1.8	$\text{Ni}^+$	10
		$\text{Sr}^{++}$	5
		$\text{Fe}^{++} - \text{Fe}^{+++}$	< 15
		$\text{Mn}^{++}$	< 5

Table 2. Weighted Average Composition of Waste Stream  
Discharged to Seepage Pits 2, 3, and 4\*

Waste Constituent	Molarity
NaOH	0.22
$\text{NH}_4\text{NO}_3$	0.025
$\text{Al}(\text{NO}_3)_3$	0.022
$\text{NaNO}_3$	0.315
$\text{Na}_2\text{SO}_4$	0.037
NaCl	0.006

\*Calculated from data furnished by K. E. Cowser.

from 100-mesh to less than 270-mesh ore. Sorption by chalcopyrite and chalcocite was measurable, but there was no regular dependence of sorption on particle size.

With varying hydrogen ion concentration (pH 3 to 0.22  $\text{M OH}^-$ ), ruthenium removal was greatest between pH 6 and pH 10. This is the range in which the maximum formation of polymeric ruthenium species would be expected. These systems contained 1 g of chalcopyrite ore per 100 ml of solution.

Ruthenium removal from diluted seep solution (pH 11.8) by 270-mesh chalcopyrite ore was maximum with 1 g of ore per 100 ml of solution (Fig. 1). The amount of ore varied from 0.1 g to 4.0 g per 100 ml, and removal actually decreased when the amount of ore was increased from 1 g to 2 g per 100 ml, then increased slowly with higher amounts of sorbent. Analysis of the supernatant solution for iron, copper, sulfide ion, and for pH failed to show significant differences. Addition of 100 ppm copper ( $\text{Cu}^{++}$ ) or iron ( $\text{Fe}^{+++}$ ) did not eliminate the peak sorption at 1 g ore per 100 ml, but sorption was decreased slightly with all amounts of ore. The addition of 100 ppm sulfide ion not only decreased ruthenium sorption, but also eliminated the peak in the sorption curve. No explanation was found for the occurrence of the peak in the sorption curve nor for its elimination by the addition of sulfide ion. Furthermore, the sorption peak did not occur when the series was reproduced using the same solution but with fairly ground chalcopyrite ore.

Sorption of ruthenium by the formation of  $\text{RuS}_2$  at the surfaces of sulfide minerals should be facilitated by the reduction of the

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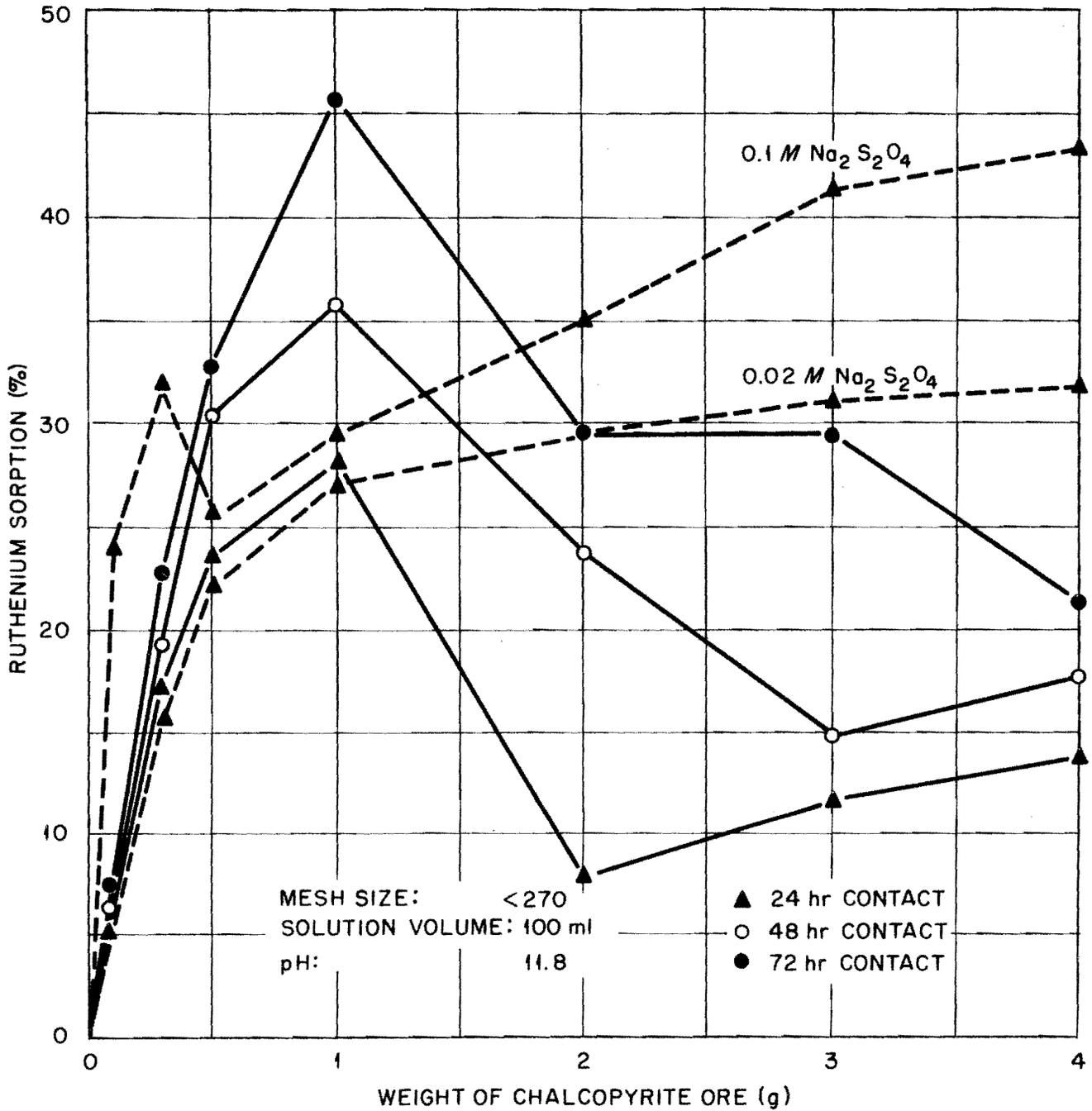


Figure 1. Sorption of Ruthenium on Chalcopyrite Ore in the Presence and Absence of Sodium Hydrosulfite.

ruthenium, and the addition of increasing concentrations of hydrosulfite did increase ruthenium sorption (Fig. 1). Use of the reducing agent also yielded a smooth sorption isotherm, eliminating the sorption peak at 1 g ore per 100 ml. The effect of the past history of the ruthenium on its chemical properties was most evident when experiments were conducted using Ru-106  $\text{Cl}_3$ , purchased from Isotopes Division, in the synthetic waste solution. In all cases the sorption of ruthenium from the synthetic solution was much higher than that from the seep solution (Fig. 2). The lower sorption of ruthenium from diluted seep solution, coupled with a sorptive isotherm that asymptotically approaches less than 100% sorption with increasing amounts of sorbent, suggests the presence of more than one species of ruthenium in the seep solution.

Even though it was evident that it would be necessary to establish the identity and distribution of various species of ruthenium present in the seep solution before a complete analysis of sorption experiments could be made, a series of experiments were carried out using 100- to 150-mesh sulfide ores under the same conditions as the slurry studies. Columns were run at flow rates of approximately 2 to 4 ml per min in 1/2-in. dia columns. The leakage of ruthenium through the columns was quite high (on the order of 60%), and very little ruthenium was sorbed by chalcopyrite or by stibnite. This was confirmed by dividing the columns into six portions after the run and counting duplicate samples from each section (Table 3). For pyrite and chalcocite, retention was somewhat greater. The results

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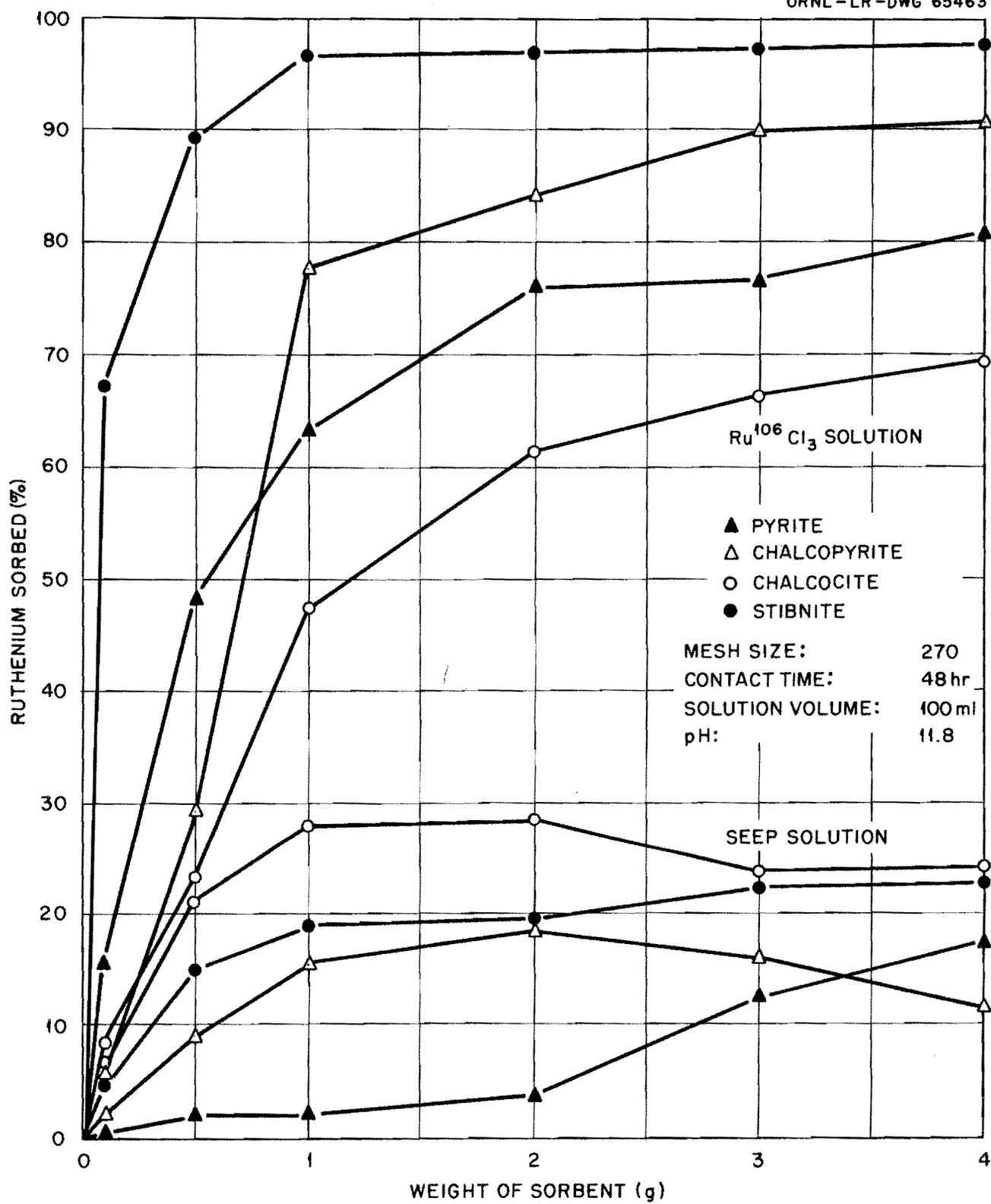


Figure 2. Sorption of Ruthenium on Various Ores from Seep Solution and from Synthetic Solution.

Table 3. Distribution of Ruthenium Activity in the Sulfide Ore Columns

Section	Counts per min per g/counts per min per ml in Influent			
	Pyrite	Chalcopyrite	Chalcocite	Stibnite
1 (top)	11.8	0.7	6.5	2.4
2	14.1	0.92	7.4	2.4
3	8.5	0.98	14.3	2.3
4	6.6	1.02	18.8	2.4
5	5.2	1.04	13.5	3.1
6 (bottom)	4.4	1.19	13.4	3.4

compare favorably with those of Rimshaw and Winkley (12), who obtained  $K_d$ 's of ~ 33 ml to 40 ml per g at pH 7. Vermiculite columns removed negligible amounts of ruthenium (Table 4) when placed after

Table 4. Distribution of Ruthenium Activity in Vermiculite Columns

Section	Counts per min per g/counts per min per ml of Influent			
	Alone	After Pyrite	After Chalcocite	Alone with 0.01 33 M $\text{Na}_2\text{S}_2\text{O}_4$
1 (top)	1.14	0.44	0.34	16.0
2	1.10	0.39	0.32	3.2
3	0.99	0.50	0.40	2.4
4	0.86	0.56	0.48	2.2
5	0.73	0.55	0.58	2.7
6 (bottom)	0.78	0.55	0.51	1.9

columns of pyrite or chalcocite, indicating that these materials are not effective in reducing the ruthenium to an exchangeable species. Sodium hydrosulfite was more effective as a reducing reagent, but the quantities required were too great to suggest its use on a practical basis. When the sodium hydrosulfite was used it was also noted that most of the ruthenium was retained by the topmost portion of the column indicating filtration of a precipitate rather than ion exchange.

Counting of the solids from the sulfide mineral columns showed that the maximum loading of ruthenium was not on the initial fraction of the column, but at some distance down the column (Table 3). It was felt that a change was taking place in the sorbent phase with the continued leaching action of the sulfide minerals with the  $\text{NaNO}_3$  waste solution. To determine the effect of sodium saturation of the mineral surface, two columns of pyrite ores were prepared. One column was leached continuously for 3 hr with 3 M  $\text{NaCl}$ ; the second was untreated. Seep solution was then passed through the two columns under the same conditions. The results of the solids counting data showed that sodium saturation of the sulfide mineral surface reduced the removal of ruthenium by 50%.

#### SUMMARY

Sorption of ruthenium from untreated waste pit seepage solution by vermiculite or by sulfide minerals was quite low. However, the more easily sorbed species (about 80-90% of the total ruthenium discharged) removed with the other cationic radionuclides as the

waste percolates through the ground to the seep. Appreciable sorption can be obtained on sulfide minerals if the ruthenium is present in a suitable chemical form, as indicated by the sorption of ruthenium from synthetic waste solution tagged with Ru-106  $\text{Cl}_3$ . Strong reducing reagents in alkaline media (for example,  $\text{Na}_2\text{S}_2\text{O}_4$ ) improve sorption of ruthenium, but rather large quantities are necessary. The sulfide minerals do not do an effective job in reducing the ruthenium to an easily sorbed form. Optimum removal of ruthenium at pH 6 to pH 10 suggests that in the ground the continued removal of ruthenium results primarily from the filtration of polymeric ruthenium species.

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