

# Sorption of Radioactive Cobalt and Ruthenium on Soil Minerals

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## ABSTRACT

The sorption of radioactive cobalt and ruthenium on alumina, silica gel, zeolite 3A, kaolin and Na-bentonite has been studied as a function of pH, nuclide concentration and ionic strength. Retardation factor for cobalt and ruthenium on soil minerals was determined through porosity measurement.

Hydrolysed species, cobalt and ruthenium interact with solid surfaces by physical adsorption processes. Freundlich sorption isotherms for cobalt and ruthenium are effectively linear. The sorption decreases with increasing ionic strength for cobalt and ruthenium. The effect of increasing porosity on the retardation factor countered the effect of a significant increase in the distribution coefficient.

## 1. Introduction

The disposal of radioactive wastes generated by nuclear installations has been receiving growing attention. The method for disposing of low-level solid wastes is shallow land burial and that of high-level solid wastes is disposal to the deep geologic formations.

Cobalt-60 is one of the predominant radionuclides at nuclear power plants as low-level radioactive wastes. Ruthenium-106 is one of the hazardous fission products which are contained in the spent nuclear fuels as high-level radioactive wastes. Kinetics and adsorption of ruthenium are complex and slow due to the large number of chemical forms and complexes of ruthenium under varying conditions. Because of their low permeability, high sorption capacity and plasticity, clay minerals are used for a surface seal to minimize excessive infiltration of rain water and for sealing or backfilling of waste repositories to prevent or retard fluid flow and radionuclide migration by

sorption [1-15].

The objective of this study is to examine some of the factors such as the effects of pH, nuclide concentration, ionic strength and retardation factors affecting sorption and migration of cobalt and ruthenium by both soil minerals and some individual soil components.

The distribution coefficient,  $K_d$  ( $m^3/kg$ ), of radionuclides on soil minerals is calculated by

$$K_d = (c_0 - c)v/cm$$

where  $c_0$  = initial count rate of solute in solution (cpm)

$c$  = count rate of solute in solution after equilibrium (cpm)

$v$  = volume of aqueous phase ( $m^3$ )

$m$  = mass of solid phase (kg)

The amount of isotopically exchangeable, sorbed nuclides is calculated by

$$c_e = \text{nuclide concentration in solution} \times \frac{c_1 - c_f}{c_f}$$

where  $c_s$  = amount of isotopically exchangeable, sorbed nuclide  
 $c_i$  = initial activity of nuclide in the solution  
 $c_f$  = final activity of nuclide in the solution

Sorption of nuclide as a function of nuclide concentration in solution is described by the Freundlich equation

$$C_s = aC_i^b$$

where  $C_s$  = nuclide concentration adsorbed on the soil minerals ( $\mu\text{g/g}$ )  
 $C_i$  = nuclide concentration in solution ( $\mu\text{g/cm}^3$ )  
 $a, b$  = coefficients

The retardation factor, ratio of the groundwater velocity to the radionuclide migration velocity, is obtained from experimental porosities, experimental bulk densities, and from batch distribution coefficient based on the assumption that the exchange reaction is described by a linear adsorption isotherm<sup>3)</sup>.

$$R = V_w / V_n = 1 + K_d \rho_s (1 - \epsilon) / \epsilon$$

where  $R$  = retardation factor  
 $V_n$  = velocity of nuclide (m/s)  
 $V_w$  = velocity of groundwater (m/s)  
 $K_d$  = distribution coefficient ( $\text{m}^3/\text{kg}$ )  
 $\rho_s$  = density of solid ( $\text{kg}/\text{m}^3$ )  
 $\epsilon$  = porosity of solid

## 2. Experimental

### 2.1. Materials

Approximately 3 $\mu\text{m}$  samples of the soil mine-

erals: bentonite (light grey power, Aldrich Chemical Co. Ltd.), kaolin, (heavy, BDH Chemicals Ltd.) and zeolite (type 3A, Union Carbide Co. Ltd.) were used with the soil components: aluminium oxide, activated acidic, (150 mesh, Aldrich Chemical Co. Ltd.), silica gel (70-230 mesh, Aldrich).

For their preconditioning, both soil minerals and soil components were prewashed and equilibrated with simulated groundwater for 3 days. The composition of the simulated groundwater is given in Table 1. The solids phases in the system were allowed to settle by gravity or by centrifugation with MSE 'High speed 18' Refrigerator Centrifuge (Measuring and Scientific Equipment Ltd., Crawley, Sussex, England), and the aqueous phases were discharged, and then fresh simulated groundwater was added. The system was allowed to equilibrate for 1 week. The solids recovered were dried in an air-circulation oven at 105°C.

Liquid sources of cobalt-60 (cobalt(II) chloride in 0.1M HCl, 2.0 $\mu\text{gCo}/\text{cm}^3$ , 0.114mCi/ $\text{cm}^3$ ) and ruthenium-103 (ruthenium(III) chloride in 3.67M HCl, 2.7mgRu/ $\text{cm}^3$ , 1.07mCi/ $\text{cm}^3$ ) obtained from Amersham International plc were neutralised and diluted to have concentration of 0.04 $\mu\text{gCo}/\text{cm}^3$  (2.28 $\mu\text{Ci}/\text{cm}^3$ ) and 27 $\mu\text{gRu}/\text{cm}^3$  (10.7 $\mu\text{Ci}/\text{cm}^3$ ) for <sup>60</sup>Co and <sup>103</sup>Ru, respectively.

### 2.2. Sorption measurements

Samples of sorbent (100 mg) were equilibrated in a 250- $\text{cm}^3$  stoppered Erlenmeyer flask with 10  $\text{cm}^3$  of the simulated groundwater containing 0.01 $\text{cm}^3$  of the prepared <sup>60</sup>Co tracer solution and 0.01 $\text{cm}^3$  of 10<sup>-4</sup>M cobalt(II) chloride solution, and containing 0.01 $\text{cm}^3$  of <sup>103</sup>Ru solution. The pH of the aqueous solution was adjusted by adding small volumes of 0.05M-, 0.1M-, 1M-NaOH and 0.1M-, 1 M-HCl solution. Sorption of cobalt and ruthenium was carried out by shaking gently the flasks

Table 1. Composition of simulated groundwater.

Ion	mg/dm <sup>3</sup>	Salt added	meq/dm <sup>3</sup>	mg/dm <sup>3</sup>
Na <sup>+</sup>	30	NaHCO <sub>3</sub>	0.95	79.8
K <sup>+</sup>	8	Na <sub>2</sub> SO <sub>4</sub>	0.35	24.85
Ca <sup>2+</sup>	6.5	MgSO <sub>4</sub> · 7H <sub>2</sub> O	0.08	9.85
Mg <sup>2+</sup>	1.0	CaSO <sub>4</sub>	0.07	4.76
HCO <sub>3</sub> <sup>-</sup>	58	CaCl <sub>2</sub> · 2H <sub>2</sub> O	0.26	19.10
SO <sub>4</sub> <sup>2-</sup>	23	KCl	0.20	14.91
Cl <sup>-</sup>	16			

on the shaker, Shaking Incubator (The Mickie Laboratory Engineering Co., Gomshall, Surrey, England) at 20°C for 4 hours and standing at ambient temperature for 1 day. After the period of equilibration, the mixtures of soil and groundwater were centrifuged and aliquots of the supernatant solutions were taken for measurements of pH and radioactivity by using a well-type NaI(Tl) crystal gamma scintillation counter with scaler-ratemeter SR 7 (Nuclear Enterprises Ltd.).

The measurements of the nuclide concentration dependence on the sorption were carried out with 10<sup>-6</sup>M-, 10<sup>-8</sup>M-, 10<sup>-10</sup>M-cobalt(II) chloride solution and 10<sup>-7</sup>M-, 10<sup>-8</sup>M-, 10<sup>-9</sup>M-ruthenium(III) chloride solution with the procedure similar to that of the sorption measurement.

The measurement of ionic strength dependence on the sorption were carried out with 0.1 M- and 4 M-sodium chloride with the procedure similar to that of the sorption measurement.

The porosity, ratio of the volume of the voids in the soil minerals to the total volume of the soil minerals, was calculated by

$$\epsilon = 1 - \frac{\rho_b}{\rho_p}$$

where  $\rho_b$ =bulk mass density of the soil minerals

$\rho_p$ =particle mass density of the soil minerals

The bulk mass density is the oven-dried mass of the soil minerals divided by its field volume. The particle mass density is the oven-dried mass divided by the volume of the soil particles, determined by a water-displacement test.

### 2.3. Paper-electrophoresis

The investigation of the hydrolysis products of <sup>60</sup>Co and <sup>103</sup>Ru was carried out by the paper-electrophoresis method using LKB 3276 paper-electrophoresis apparatus(LKB-Produkter AB, Stockholm, Sweden). 725 cm<sup>3</sup> of 0.1 M-NaCl solution were poured into the cathode and anode electrode vessels, respectively. 0.01cm<sup>3</sup> of the nuclide solution was applied at the fiducial point of a strip of Whatman No. 1 filter paper, 40×410 mm. A potential of 300 volts was applied for 5 hours. After the electrophoresis run was over, the strip was dried and cut into 1-cm pieces, and the activity was measured by the well-type NaI(Tl) crystal gamma scintillation counter.

## 3. Results and discussion

### 3.1. Effect of pH

The pH dependence of distribution coefficients for cobalt and ruthenium on soil minerals is shown in Table 2 and 3. All results show the mean values of determination carried out on duplicate

samples. Differences in values between duplicates were small, less than 6%. The change in pH of aqueous phase on soil-groundwater mixture after contact time are shown brackets.

On alumina  $K_d$  increases from low value at pH

Table 2. Distribution coefficients,  $K_d(m^3/kg)$ , for cobalt-60 on soil minerals from batch experiment.

	Basic groundwater (pH=10.5)	Simulated groundwater (pH=8.2)	Acidic groundwater (pH=4.8)
Alumina	1.647±0.0065 (8.7)	3.832±0.077 (6.5)	0.017±0.001 (6.3)
Silica gel	0.640±0.019 (9.0)	0.354±0.0015 (8.2)	0.0840.0005± (7.4)
Zeolite 3A	0.473±0.017 (10.6)	19.075±0.915 (10.0)	25.668±1.597 (9.8)
Kaolin	0.479±0.0025 (9.4)	2.481±0.173 (8.2)	0.045±0.0005 (6.5)
Na-bentonite	0.375±0.008 (9.9)	1.322±0.044 (8.9)	1.396±0.051 (8.6)

( ) pH at defined distribution coefficient after 4 h shaking time and 1 d standing time.

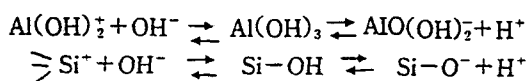
Table 3. Distribution coefficients,  $K_d(m^3/kg)$ , for ruthenium-103 on soil minerals from batch experiment.

	Basic groundwater (pH=10.2)	Simulated groundwater (pH=8.3)	Acidic groundwater (pH=4.2)
Alumina	4.822±0.080 (8.6)	11.799±0.239 (7.5)	2.560±0.033 (5.9)
Silica gel	0.050±0.0005 (8.8)	0.051±0.0001 (8.1)	0.479±0.003 (7.4)
Zeolite 3A	0.027±0.0005 (10.5)	0.032±0.0005 (10.1)	0.207±0.0005 (9.9)
Kaolin	3.112±0.025 (8.6)	34.102±4.293 (8.0)	2.834±0.069 (4.6)
Na-bentonite	0.889±0.033 (9.5)	0.373±0.0005 (8.7)	2.767±0.113 (8.4)

( ) pH at defined distribution coefficient after 4 h shaking time and 1 d standing time.

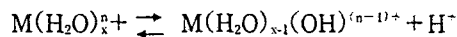
below 5 to maximum value at pH 8 and then decreases at pH above 10 for cobalt and ruthenium. On silica gel  $K_d$  increases from low value at pH below 5 to high value at pH above 10 for cobalt, while decreases from high value at pH below 5 to low value at pH 8 and levels out at pH above 10 for ruthenium.

Alumina and silica gel show either cation or anion exchangers depending upon the pH of the solution according to the equilibria



Cobalt hydrolyses in higher pH region (higher than .7) and a maximum in sorption is observed

at pH around 8.



Ruthenium exists in aqueous solution in numerous forms. Various hydration processes result in complex shifts of equilibria. The hydrolysis products of cobalt and ruthenium are shown in figs. 3 and 4.

On zeolites 3A  $K_d$  decreases from high value at pH below 5 to low value at pH above 10 for cobalt and ruthenium. The ionic sieve properties of the zeolites make it possible to carry out the exchange of cations. The rate of exchange is dependent upon the ionic radii, that is, the extent of exchange of cobalt is greater than that of ruthenium and

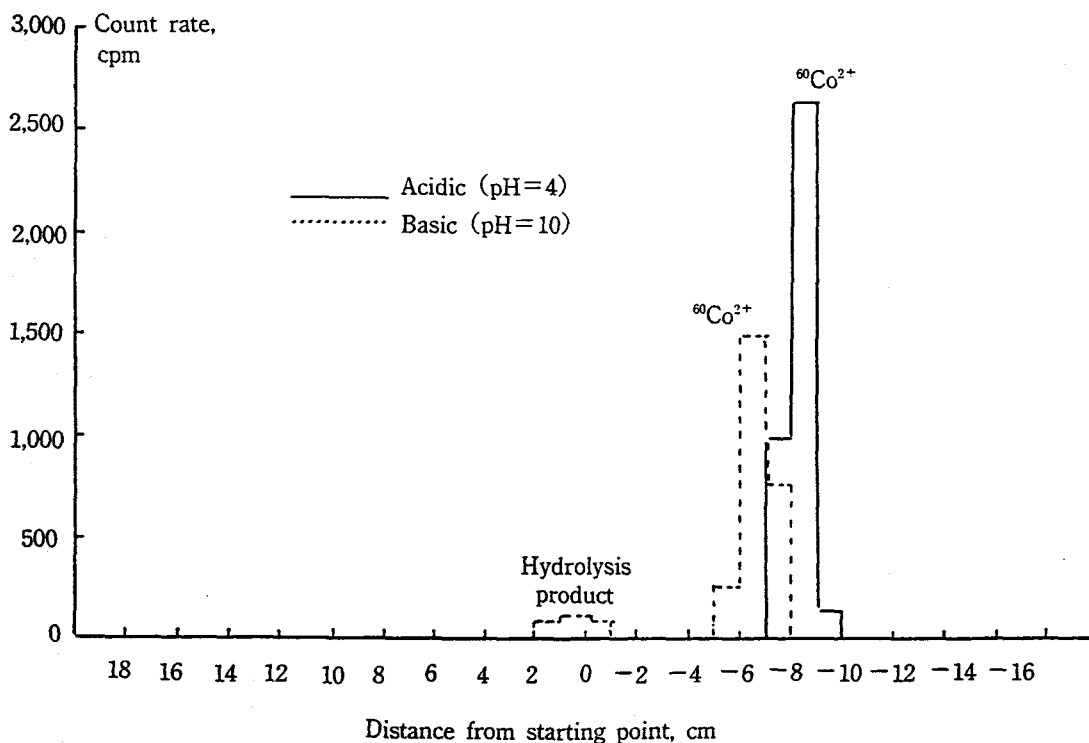


Fig. 3. Paper-electrophoresis histogram of cobalt-60 labelled cobalt(II) chloride. Paper wet with 0.1 M NaCl. Running time, 5 hrs. at 300 V.

the hydrolysis products have lower rate of exchange.

On kaolin  $K_d$  increases from low value at pH below 5 to maximum value at pH 8 and then decreases at pH above 10 for cobalt and ruthenium. On Na-bentonite  $K_d$  decreases from high value at pH below 5 to low value at pH above 10 for cobalt and decreases from high value at pH below 5

to low value at pH 8 and then increases at pH above 10. In clay minerals cation adsorption is described as exchange of interlayer ions and complexation with surface OH groups, while anion adsorption is due to surface exchange only<sup>12)</sup>.

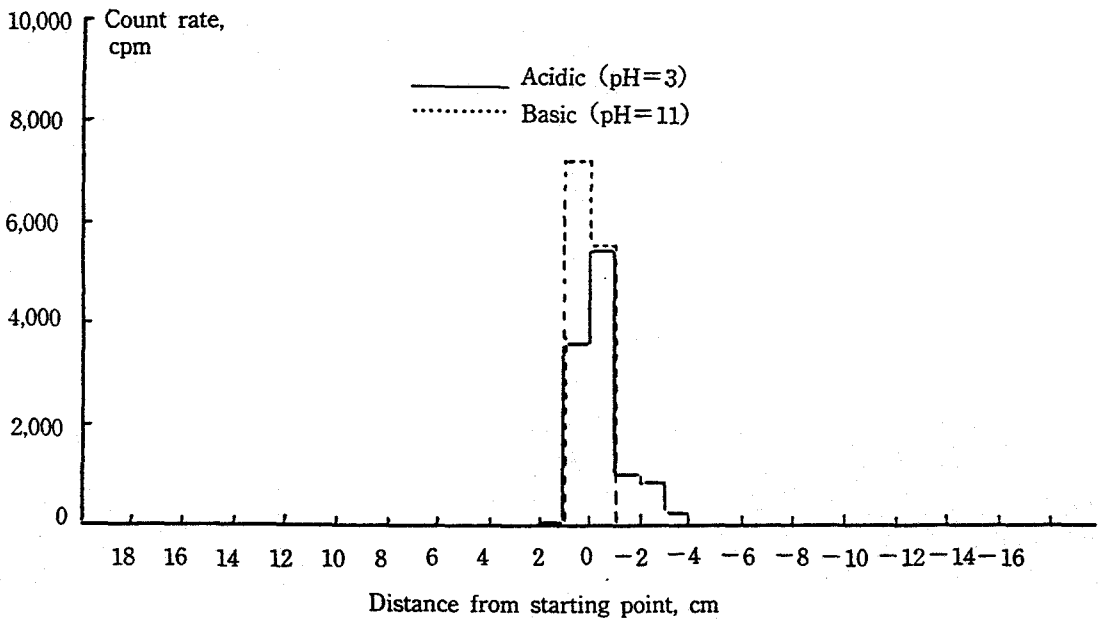
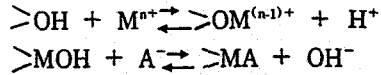


Fig. 4. Paper-electrophoresis histogram of ruthenium-103 ruthenium(III) chloride. Paper wet with 0.1 M NaCl. Running time, 5 hrs. at 300 V.

### 3. 2. Effect of nuclide concentration

Cobalt adsorption isotherm for silica gel, zeolite 3A, kaolin, Na-bentonite and ruthenium adsorption isotherm for silica gel, zeolite 3A, Na-bentonite are shown in figs. 1 and 2, respectively.

Freundlich plot of the logarithm of the soil phase nuclide concentration against the logarithm of the aqueous nuclide concentration is effectively linear and described by the equations :

For cobalt,

$$\begin{aligned} C_s &= 34.21(C_w)^{1.09} && \text{on silica gel} \\ C_s &= 76.10(C_w)^{1.17} && \text{on zeolite 3A} \\ C_s &= 104.71(C_w)^{1.16} && \text{on kaolin} \\ C_s &= 7.29(C_w)^{1.02} && \text{on Na-bentonite} \end{aligned}$$

For ruthenium,

$$\begin{aligned} C_s &= 7.66(C_w)^{1.21} && \text{on silica gel} \\ C_s &= 2.01(C_w)^{0.98} && \text{on zeolite 3A} \\ C_s &= 48.15(C_w)^{1.22} && \text{on Na-bentonite} \end{aligned}$$

### 3. 3. Effect of ionic strength

The dependance of the ionic strength on distri-

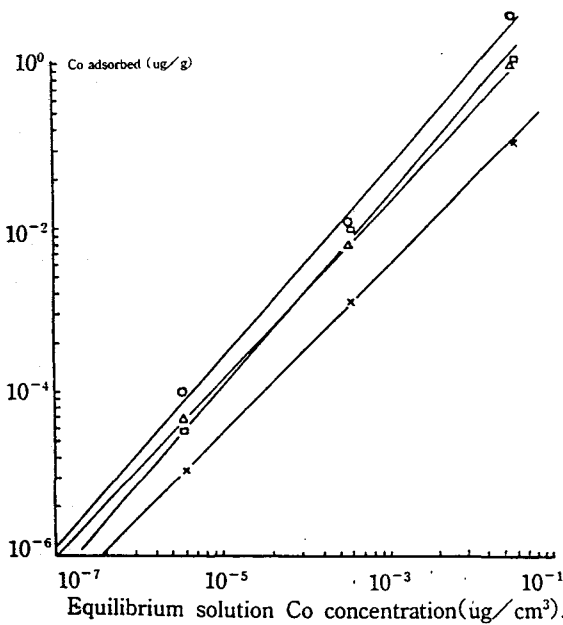


Fig. 1 Cobalt adsorption isotherm for individual soil minerals at pH 8.2. Silica gel( $\Delta$ ), zeolite 3A( $\square$ ), kaolin( $\circ$ ), Na-bentonite ( $\times$ ).

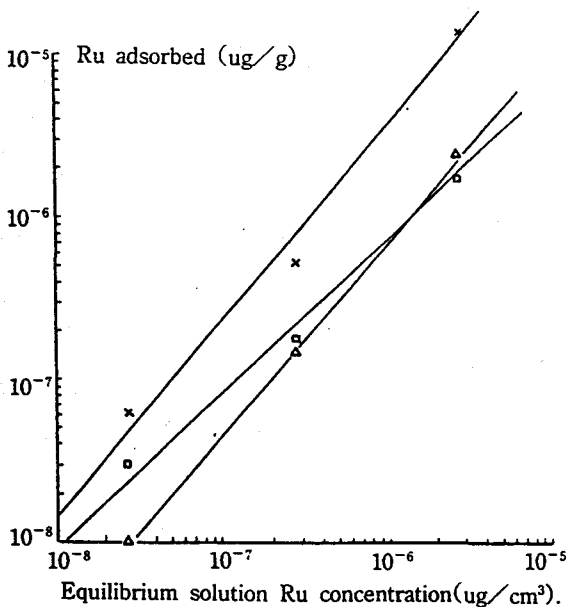


Fig. 2 Ruthenium adsorption isotherm for individual soil minerals at pH 8.3. Silica gel ( $\Delta$ ), zeolite 3A( $\square$ ), Na-bentonite( $\times$ ).

bution coefficients for cobalt and ruthenium on soil minerals is shown in Table 4 and 5. The sorption is decreasing with increasing ionic strength for soil minerals. The sorption is less effective for radionuclides in brines than for those in dilute groundwater, because ions of the brine compete with the radionuclide ions from sorption sites, that is, electrolytes which do not supply a common ion generally have the opposite effect from the common ion effect, making the solubility greater.

#### 3. 4. Retardation factors

Retardation factors for cobalt and ruthenium on soil minerals are shown in Table 6. The retardation factor is proportional to the distribution coefficient ( $K_d$ ) and to the bulk density ( $\rho_b$ ), but inversely proportional to the porosity ( $\epsilon$ ).

As shown in Table 6, the resulting retardation factors ( $R$ ) increased as the  $K_d$  values increased. The decreases of porosity in zeolite 3A and kaolin than that in silica gel is attributed to clay-size particles filling the pore space. The porosity increased as the Na-bentonite occupied more space than that provided by the larger pores of the silica gel.

The retardation factor for cobalt increases six-fold in zeolite 3A than in silica gel as  $K_d$  increases two-fold, due to the decrease of porosity on zeolite 3A and increases six-fold in kaolin as  $K_d$  increases three-fold, while decreases one-third in Na-bentonite as  $K_d$  decreases one-fifth and porosity increases. The retardation factor for ruthenium decreases seven-tenth in zeolite 3A than in silica gel as  $K_d$  decreases three-tenth and porosity decreases, while increases eight-fold in Na-bentonite as  $K_d$  increases six-fold and porosity increases.

Table 4. Effect of ionic strength on distribution coefficients for cobalt-60 on soil minerals

	$K_d, m^3/kg$	
	0.1M NaCl (pH=8.25)	4M NaCl (pH=7.6)
Alumina	5.120±0.055 (7.9)	6.645±0.416 (7.15)
Silica gel	0.293±0.012 (8.1)	0.002±0.0003 (6.75)
Zeolite 3A	42.547±2.734 (9.05)	0.089±0.004 (7.75)
Kaolin	0.784±0.003 (8.25)	0.209±0.003 (7.4)
Na-bentonite	12.048±0.814 (8.45)	8.986±0.377 (7.85)

( ) pH at defined distribution coefficient after 4 h shaking time and 1 d standing time.

Table 5. Effect of ionic strength on distribution coefficients for ruthenium-103 on soil minerals

	$K_d, m^3/kg$	
	0.1M NaCl (pH=8.2)	4M NaCl (pH=7.45)
Alumina	3.748±0.084 (7.85)	2.873±0.050 (7.25)
Silica gel	0.671±0.001 (7.95)	0.820±0.005 (7.35)
Zeolite 3A	4.243±0.181 (0.95)	1.312±0.016 (7.65)
Kaolin	101.824±11.467 (8.15)	12.328±0.069 (7.4)
Na-bentonite	5.466±0.041 (8.45)	3.182±0.118 (7.85)

( ) pH at defined distribution coefficient after 4 h shaking time and 1 d standing time.



Table 6. Retardation factors cobalt-60 and ruthenium-103 on soil minerals.

Soil	Nuclide	$K_d$	$\rho_b$	$\rho_p$	$\epsilon$	R
Silica gel	$^{60}\text{Co}$	$34.21 \times 10^{-3}$	$0.497 \times 10^{-3}$	$1.599 \times 10^{-3}$	0.689	25.69
	$^{103}\text{Ru}$	$7.66 \times 10^{-3}$	$0.497 \times 10^{-3}$	$1.599 \times 10^{-3}$	0.689	6.53
Zeolite 3A	$^{60}\text{Co}$	$76.10 \times 10^{-3}$	$0.974 \times 10^{-3}$	$2.004 \times 10^{-3}$	0.514	145.19
	$^{103}\text{Ru}$	$2.01 \times 10^{-3}$	$0.974 \times 10^{-3}$	$2.004 \times 10^{-3}$	0.514	4.81
Kaolin	$^{60}\text{Co}$	$104.71 \times 10^{-3}$	$0.900 \times 10^{-3}$	$2.205 \times 10^{-3}$	0.592	160.14
	$^{103}\text{Ru}$	-	-	-	-	-
Na-bentonite	$^{60}\text{Co}$	$7.29 \times 10^{-3}$	$0.959 \times 10^{-3}$	$11.282 \times 10^{-3}$	0.915	8.64
	$^{103}\text{Ru}$	$48.15 \times 10^{-3}$	$0.959 \times 10^{-3}$	$11.282 \times 10^{-3}$	0.915	51.46

#### 4. Conclusion

The pH dependence indicates that the hydrolysis of cobalt and ruthenium, and the complex formation of ruthenium seem to be the prime factor determining the sorption and migration. Hydrolysed species, cobalt and ruthenium interact with solid surfaces by physical adsorption processes.

Freundlich sorption isotherms for cobalt and ruthenium are effectively linear and have exponents close to 1. There is a dependence on ionic strength indicating that the sorption is decreasing with increasing ionic strength for cobalt and ruthenium. The effect of increasing porosity on the retardation factor countered the effect of a significant increase in the distribution coefficient of cobalt and ruthenium.

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## 방사성 코발트 및 루테튬의 토양 흡착

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요 약

알루미나, 실리카겔, 제오라이트 3A, 카올린 그리고 나트륨-벤토나이트에 대한 방사성코발트 및 루테튬 흡착을 수소이온농도, 핵종 농도 그리고 이온강도를 함수로 고찰하였다. 토양에 대한 코발트 및 루테튬의 지연계수는 공극을 측정으로 결정하였다.

코발트 및 루테튬의 가수분해 분자종은 물리적 흡착반응으로 고체 표면과 상호작용한다. 코발트 및 루테튬의 후로인드릿히 흡착 등온식은 직선이다. 코발트 및 루테튬의 흡착은 이온강도의 증가에 따라 감소한다. 지연계수에서 공극을 증가효과는 분배계수의 증가효과와 반한다.