Effect of Organic Complexants on the Mobility of Low-Level Waste Radionuclides in Soils: Status Report

J. L. Swanson

September 1981

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MOBILITY OF LOW-LEVEL WASTE RADIONUCLIDES
IN SOILS: STATUS REPORT

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Richland, Washington

SUMMARY

The effects of some organic complexants on the sorption by soil of some elements typical of those present in low-level wastes are being evaluated and procedures are being developed to efficiently obtain valid sorption data. Data have been obtained with Hanford soil and the elements europium, nickel, cobalt, cesium, and strontium. Complexants studied to date include ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and humic acid.

The sorption of cesium and strontium has been found to be affected very little by EDTA or DTPA, as expected. However, these complexants have been found to greatly reduce the sorption of europium, nickel, or cobalt by the soil. The Eu/EDTA system was found to be well behaved, and the effect of the complexant on the sorption by soil was quantified. With nickel and cobalt, however, kinetic problems have been encountered, and the effects of complexants on the sorption by soil have not yet been quantified.

The problems encountered in the nickel and cobalt systems have further emphasized the need for the development of methods to assure the general validity of the data obtained in the experiments. Series of experimental results that looked very good within themselves were found by additional procedures to be artifacts of the conditions used. One procedure that has been of great value in identifying invalid data is that of contacting the "equilibrated" solution from a soil contact with a second batch of soil. Unless the sorption coefficient in the second contact is equivalent to that in the first contact, the data are likely invalid.

Efforts are continuing to develop procedures that will allow generally valid data to be obtained in an efficient manner and to employ such procedures to obtain data in a variety of systems pertinent to low-level waste disposal.

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INTRODUCTION

Low-level radioactive wastes are traditionally disposed of by underground burial in trenches or pits designed for that purpose and operated in accordance with governmental regulations. The waste has been packaged at the time of burial, although the packages, generally wood boxes or metal drums, are not required to maintain their integrity for long periods of time. Thus, radioactive elements contained in the wastes can become exposed to the actions of nature, unless their half-lives are short enough that they will disappear by radioactive decay before the container integrity is breached. The action of nature of most concern is that of soil moisture, which can leach the radionuclides from the waste forms and transport them through the soil. As the moisture passes through the soil, the soil tends to remove many radionuclides from solution, thus preventing or greatly delaying their transport from the disposal site into natural water bodies. This retardation of radionuclide mobility by soil is one important factor in assuring the safety of low-level waste disposal.

The retardation of radionuclide migration by soils and rocks has been studied for many years. Methods for determining retardation factors were recently discussed by Relyea, Serne, and Rai (1980). These authors also discussed various mechanisms by which retardation of migration can occur. Such mechanisms include sorption by ion exchange processes, physical adsorption on the surface of soil particles, precipitation of compounds of the element of interest, and carrying of the element of interest on precipitates of other elements. Other mechanisms may also be important.

Organic complexants can affect the retardation of radionuclide mobility either positively or negatively. They can decrease the retardation (increase the mobility) by forming soluble complexes that shift radionuclide ion exchange, physical sorption, or solubility equilibria; by dissolving soil-originated materials that were sorbing the radionuclide; or by the complexant itself sorbing onto the soil and "blinding" sorption sites. Organic complexants can also have the opposite effect, that is, increase the retardation (decrease the mobility) by forming insoluble complexes with the radionuclide.

The potential influence of organic compounds on the transport of radionuclides from a geologic repository was recently considered by Silviera (1981).

Several reports in the literature address organic complexants that affect the mobility of various radionuclides in soil/water systems. Means, Crerar, and Duguid (1978) concluded that the presence of EDTA was causing the migration of ^{60}Co from waste disposal pits and trenches at Oak Ridge National Laboratory. Gee and Campbell (1980) presented data that illustrated a large decrease in ^{60}Co sorption when ^{60}Co was complexed by EDTA. Clayton, Sibley, and Schell (1981) studied the effect of several complexants on several radionuclides added to sediment/water systems from natural environments and found that EDTA and humic acids decreased the sorption of ^{241}Am and ^{57}Co , while other complexants such as 1-nitroso-2-naphthol and 1,10-phenanthroline actually increased the affinity of these radionuclides for the sediments. Some of the organic materials present in leachates from low-level radioactive waste disposal sites have been characterized by Francis, Iden, Nine, and Chang (1980).

A knowledge of the effects of organic complexants on the mobility of radionuclides in soils is essential for the accurate prediction of the migration of radionuclides from a disposal site. This current report describes some results of a project at Pacific Northwest Laboratory to develop and employ standard procedures for evaluating how and to what extent organic complexants affect the mobility of low-level waste radionuclides in soils. This status report describes the results up to July 1981.

MATERIALS AND METHODS

The effect of organic complexants on the mobility of radionuclides in soils has been determined in experiments in which the distribution of a radionuclide between liquid and solid phases was measured. The distribution of the radionuclide was determined by comparing the concentration of radionuclide in solution before and after a batch-type contact.

Radioactive tracers were purchased from various suppliers. Stock solutions of the various tracers were maintained in dilute HCl. Total element concentrations were calculated from data provided by the suppliers except for cesium, which was obtained as carrier-free ^{137}Cs and mixed with known concentrations of inert cesium.

Organic complexing agents were also obtained from commercial suppliers, and were used without purification. Complexing agents examined include ethylenediaminetetraacetic acid (EDTA), used as the disodium salt $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$; diethylenetriaminepentaacetic acid (DTPA); and humic acid, obtained as "humic acid, sodium salt" from Aldrich Chemical Company. Solutions were prepared using distilled water.

The soil used in all the experiments to date was a calcareous, sandy loam Hanford soil (pH ~8.2). Most of the work was done with a 75- to 150- μm -size fraction.

All work done so far has involved the use of air-equilibrated solutions. No steps have been taken to exclude air from any of the experiments. The temperature was generally about 21°C, but variations of 3 to 4°C sometimes occurred.

The concentrations of the elements of interest were determined by gamma counting of ^{152}Eu , ^{137}Cs , ^{85}Sr , and ^{60}Co , and by beta counting of ^{63}Ni . Standards of each radionuclide were counted daily so that corrections could be made for variations in counting efficiency. Such corrections were minor.

The pH values of the soil/solution mixtures were measured periodically. A combination glass electrode was used for this purpose.

The radionuclide distribution data were expressed as percent of the initial concentration remaining in solution and/or as the apparent K_d value. The apparent K_d value for an element is defined as the quantity of element per gram of soil divided by the quantity of element per milliliter of solution. The term "apparent K_d " is used rather than merely " K_d " because a true K_d signifies a reversible sorption equilibrium position, which is not always obtained.

The solution/soil mixtures were contained in screw-capped polypropylene centrifuge tubes and were agitated with a reciprocating shaker operating at about 150 cycles/min. The tubes were held horizontally on the shaker and were generally only about half-full so that good mixing would occur. This batch-type procedure was chosen over a column-type procedure because of its simplicity and the ease of performing many such experiments at one time.

To assure that the measured values were truly representative of soluble species, samples were passed through a 2-nm filter prior to counting. The soil/solution mixture was centrifuged before the samples were removed for filtration to assure that the total amount of soil remained in the tube.

The procedure initially used involved the sequential addition to the tube of a weighed amount of soil, a measured volume of water, and known spikes of complexant and radionuclide solutions. A subsequent procedure involved mixing the water, complexant, and radionuclide, and removing a portion for analysis before the soil was added. In both of these procedures, the contents were mixed gently after each addition, and the total procedure was completed within a few minutes. Still later, the procedure was modified to include preparation of concentrated radionuclide/complexant solutions that were aged for several days before being diluted, analyzed, and mixed with soil. The latter procedure is felt to be the best to follow.

Another type of procedure, which proved to be very valuable in verifying the meaningfulness of data points, involves contacting the separated solution from a soil/solution mixture with a second batch of fresh soil. In these experiments, the first mixture was centrifuged and a portion of the centrate was filtered and analyzed as usual. Another portion of the centrate was then

transferred to another tube (where it was mixed and analyzed without filtration to obtain the total radionuclide input), and fresh soil was added for the second contact.

Other types of procedures that have been of value in testing the validity of apparent K_d values include varying the initial element concentration, varying the soil-to-solution ratio, and varying the direction of approach to equilibrium (comparing the apparent K_d values obtained by sorbing elements from element/complexant solutions with those obtained by first sorbing the element in the absence of complexant and then adding complexant to desorb the element).

If the apparent K_d values obtained by all of these techniques were comparable (at a given complexant concentration), it was concluded that those values were true K_d values and could be used with confidence in predicting the effect of the complexant on the mobility of the element in a soil/water system. If the apparent K_d values obtained by all of these techniques were not comparable, it was concluded that more work was needed to define conditions where generally valid K_d values could be measured or to determine that the K_d concept was not valid for the system being studied.

RESULTS AND DISCUSSIONS

The results will be presented and discussed separately for the elements studied (europium, nickel, cobalt, cesium, and strontium). Data are available for EDTA complexant with each of these elements, for DTPA complexant with each except for europium, and for humic acid complexant with nickel. EDTA and DTPA are often used in nuclear facilities, and thus are likely to be present in some of the disposed waste. Humic acid is present in many soil systems. Many of the data are still preliminary in nature but are presented to provide a description of the current status of the work.

All results to date have been obtained with Hanford soil and air-equilibrated solutions.

EUROPIUM

The behavior of europium in complexant/soil systems should be fairly typical of that of the other lanthanides and also of the trivalent actinides such as americium and curium that may be present in low-level waste disposal sites. The examination of the europium/EDTA system was begun last fiscal year and was continued during the current year to test the applicability of various procedures.

Table 1 contains some of the early results obtained in the Eu/EDTA/Hanford soil system at different concentrations and with different directions of approach to equilibrium. As seen, the measured apparent K_d value is strongly affected by the EDTA concentration; it is about 1×10^5 in the absence of EDTA and about 1×10^2 in the presence of 5×10^{-5} M EDTA. The apparent K_d values appeared to change very little with times greater than 2 weeks, except in the experiment at 4.5×10^{-7} M EDTA where the value gradually became comparable to that observed in the absence of EDTA.

The effect of the EDTA concentration on the apparent europium K_d is illustrated in Figure 1 where selected data from Table 1 are plotted. The data fall quite close to the line having a slope of -1.0, which suggests that

TABLE 1. Eu/EDTA/Hanford Soil System: Effects of Concentrations and Direction of Approach to Equilibrium

<u>Tube</u>	<u>Na₂EDTA, M</u>	<u>Eu, M</u>	<u>Time, Days</u>	<u>Apparent Kd, ^(a) mL/g</u>	<u>pH</u>
<u>Sorption Direction^(b)</u>					
11	---	2.7 x 10 ⁻⁷	31	~1 x 10 ⁵	7.9
211	4.5 x 10 ⁻⁷	8.6 x 10 ⁻⁸	12	1.2 x 10 ⁴	8.4
			25	2.1 x 10 ⁴	8.1
			39	2.8 x 10 ⁴	8.1
			70	~1 x 10 ⁵	
204	4.5 x 10 ⁻⁶	2.7 x 10 ⁻⁷	15	1.2 x 10 ³	8.0
			28	1.4 x 10 ³	8.0
205	4.5 x 10 ⁻⁶	2.7 x 10 ⁻⁷	28	1.5 x 10 ³	8.0
210	4.5 x 10 ⁻⁵	8.6 x 10 ⁻⁸	12	1.1 x 10 ²	8.4
			25	0.9 x 10 ²	8.1
<u>Desorption Direction^(c)</u>					
201	4.5 x 10 ⁻⁶	2.7 x 10 ⁻⁷	15	1.3 x 10 ³	8.0
			28	1.3 x 10 ³	7.9
202	4.5 x 10 ⁻⁶	2.7 x 10 ⁻⁷	28	1.2 x 10 ³	8.0
7	4.5 x 10 ⁻⁵	2.7 x 10 ⁻⁷	27	0.7 x 10 ^{2(d)}	7.9
54	4.5 x 10 ⁻⁵	2.7 x 10 ⁻⁹	25	1.1 x 10 ^{2(e)}	8.0

(a) Using <500- μ m Hanford soil. Soil-to-soil solution ratio = 0.033 g/mL.

(b) Europium spiked into solution/soil mixture shortly after the complexant was added.

(c) Europium solution contacted with soil for 4 days before complexant was added, unless indicated otherwise.

(d) Agitation was not as vigorous in this experiment.

(e) Europium solution contacted with soil for 97 days before complexant was added.

FIGURE 1. Effect of EDTA Concentration on Europium Kd

a 1:1 complex of EDTA with europium is responsible for decreasing the sorption of europium by the soil.

All of the europium results discussed previously were obtained at one soil-to-solution ratio (0.033 g/mL). In the ideal sorption case, the measured K_d value should be independent of this ratio. However, this was found to not be quite the case in the Eu/EDTA/Hanford soil system, as shown in Table 2. At a given EDTA concentration, the apparent K_d is seen to increase as the soil-to-solution ratio increases. It is thought that this variation may be due to variations in the solution macroion concentration. For example, calcium was found to be the major component of solutions after contact with Hanford soil; perhaps a higher calcium concentration results in the higher soil-to-solution cases, and the higher calcium concentration further reduces the free EDTA concentration so that a higher K_d value is obtained.

The effect of soil particle size on the sorption of europium was also evaluated. The data in Table 3 show that particles $<75 \mu\text{m}$ in dia were more efficient in sorbing europium from a $4.5 \times 10^{-6} \text{ M}$ EDTA solution than were larger particles. This is not surprising since, although K_d is defined and measured on a soil weight basis, sorption could be expected to depend more on the surface area.

TABLE 2. Effect of Soil-to-Solution Ratio in the Eu/EDTA/Hanford Soil System

<u>Tube</u>	<u>Na₂EDTA, M</u>	<u>Soil-to-Solution Ratio, g/mL</u>	<u>Time, Days</u>	<u>Apparent K_d, mL/g</u>	<u>pH</u>
218	4.5×10^{-6}	0.0067	15	320	8.0
			42	520	7.9
204	4.5×10^{-6}	0.033	15	1200	8.0
			28	1400	8.0
210	4.5×10^{-5}	0.033	12	110	8.4
			25	90	8.1
221	4.5×10^{-5}	0.33	7	200	8.4
			14	280	8.3
			22	330	8.2

TABLE 3. Effect of Soil Particle Size on Europium Sorption

Tube	Soil Particle Diameter, μm	Time, Days	Apparent K_d , (a)	pH
			mL/g	
204	<500 ^(b)	15	1200	8.0
		28	1400	8.0
217	150 to 500	7	1100	8.5
		14	1100	8.3
216	75 to 150	1	80	8.8
		3	180	8.7
		7	900	8.5
		14	980	8.3
218	<75	7	2200	8.5
		14	3300	8.1
		23	5000	8.2

(a) With 4.5×10^{-6} M Na_2EDTA and a soil-to-solution ratio of 0.033.

(b) Found to contain 18% in the 150- to 500- μm -dia range, 35% in the 75- to 150- μm -range, and 48% <75 μm in dia.

The data in Table 3 also indicate that a longer time is needed to reach a constant apparent K_d value when the soil particles are small (<75 μm), with appreciable differences being observed between the 1-week, 2-week, and 3-week equilibration periods. With the 75- to 150- μm -dia portion, steady state appeared to be reached within 7 days, but not within 3 days. The data with the 75- to 150- μm material are presented differently in Figure 2. This is a semi-logarithmic plot of the difference in concentration of europium at a given time and the concentration at steady state (which was 3.0% of the initial concentration) versus time. The fit of the data to a straight line indicates that the rate of approach to equilibrium was first order with respect to this concentration difference. The slope of the line indicates a half-time of about 0.8 days.

FIGURE 2. Rate of Approach to Steady State in Eu/EDTA/Hanford Soil System

The data presented for the Eu/EDTA/Hanford soil system have indicated that this system is well behaved, and that the apparent K_d values could be used to meaningfully model the transport of europium in soil systems. This conclusion was further verified by an experiment in which comparable apparent

Kd values were obtained in each of three successive contacts with fresh portions of soil. At the end of each contact, the suspension was centrifuged, and a portion of the centrate was removed for filtration and analysis. The bulk of the remaining centrate was then transferred to another tube, where it was mixed and analyzed to provide the value of the total amount of europium introduced to the next contact, and fresh soil was added for the next contact. Good agreement was observed between the final europium concentration of one contact with the initial europium concentration of the next contact, demonstrating that carry-over of europium-containing soil particles was negligible in this experiment. The results are given in Table 4.

The soil and residual solution from the first contact were also equilibrated with fresh 1×10^{-4} M EDTA solution for 7 days to obtain the apparent Kd for the desorption direction. A value of 37 mL/g was measured, which is in excellent agreement with the values obtained in the sorption direction. This provides still more evidence that the Eu/EDTA system is, indeed, well behaved.

NICKEL

In contrast to the well-behaved Eu/EDTA system, the nickel/complexant systems have proved to be quite difficult. Considerable effort has been

TABLE 4. Behavior of Europium on Successive Contacts of EDTA Solution with Soil

Contact Number	Soil-to-Solution Ratio, g/mL	Eu, counts/min, mL		Apparent Kd, mL/g ^(c)
		Initial ^(a)	Final ^(b)	
1	0.033	8774	4834	24
2	0.030	5221	2471	37
3	0.10	2580	475	44

(a) Measured without filtration to obtain the total amount present.

(b) Measured after filtration to obtain the amount truly in solution.

(c) After a 7-day contact period with 75- to 150- μ m soil. The Na_2EDTA concentration was 1×10^{-4} M. The initial Eu concentration in the first contact was 8×10^{-9} M.

expended in studying these systems, but results suitable for general predictions of the mobility of nickel in soil systems in the presence of complexants still have not been achieved. Many of the results will be presented here, however, as illustrations of how extensive procedures should be used to assure the validity of the measured apparent K_d values.

The initial experiments with nickel employed the same procedures that had been successful with europium; that is, both the sorption and desorption directions were used to approach equilibrium, with the nickel added to the solution/soil mixture shortly after the complexant was added in the experiments from the sorption direction. Results of these initial experiments are presented in Table 5. The data obtained when equilibrium was approached from the sorption direction appear within themselves to be quite good. Steady-state conditions appear to be achieved within a week of soil contact, and there appears to be a regular decrease in apparent K_d with increasing EDTA concentration. However, subsequent results have shown that these data are artifacts of the experimental method used, and that they are not of general validity.

The first clue that the Ni/EDTA system is not as well behaved as the Eu/EDTA system became apparent in the results of the desorption experiments shown in Table 5. Desorption of the nickel by 1×10^{-5} M EDTA is seen to occur quite slowly and to not reach the same apparent K_d value as was measured from the sorption direction within 2 months. There seemed to be little, if any, effect on the rate of desorption by EDTA of the time allowed for nickel sorption to occur before EDTA was added.

Conclusive proof that the sorption-direction data of Table 5 involving EDTA were not valid was provided by contacting some of the "equilibrium" solutions with a second batch of soil. In neither of the cases tested (Tubes 246 and 247) did the concentration of nickel in solution change at all during a 7-day contact with fresh soil. The apparent K_d values in the second contacts were thus zero in both cases, compared with values of 180 and 60 in the two cases in the first contacts. For the apparent K_d values to be valid, the

TABLE 5. Initial Data in Ni/EDTA/Hanford Soil System (Data are Not Generally Valid)

Tube	Na ₂ EDTA, <u>M</u>	Ni, <u>M</u>	Time, Days	Apparent K _d , ^(a) mL/g	pH
<u>Sorption Direction^(b)</u>					
248	---	1.1 x 10 ⁻⁷	3	9.5 x 10 ³	9.2
228	---	1.1 x 10 ⁻⁵	7	7.1 x 10 ³	7.8
			20	4.3 x 10 ³	8.5
263	---	1.1 x 10 ⁻⁷	55	1.2 x 10 ⁴	8.1
234	1.0 x 10 ⁻⁶	1.1 x 10 ⁻⁷	8	2.1 x 10 ³	8.9
			14	1.9 x 10 ³	8.7
246	3.0 x 10 ⁻⁶	1.1 x 10 ⁻⁷	6	1.8 x 10 ²	9.1
			17	1.8 x 10 ²	8.7
229	1.0 x 10 ⁻⁵	1.1 x 10 ⁻⁷	7	1.3 x 10 ²	7.8
			14	1.2 x 10 ²	8.6
247	3.0 x 10 ⁻⁵	1.1 x 10 ⁻⁷	6	6.4 x 10 ¹	9.0
			17	5.2 x 10 ¹	8.6
<u>Desorption Direction^(c)</u>					
248	1.0 x 10 ⁻⁵	1.1 x 10 ⁻⁷	3	5.2 x 10 ³	8.8
			63	2.6 x 10 ²	8.2
228	1.0 x 10 ⁻⁵	1.0 x 10 ⁻⁷	3	3.3 x 10 ³	8.6
			16	1.2 x 10 ³	
			69	3.0 x 10 ²	8.1
263	1.0 x 10 ⁻⁵	1.1 x 10 ⁻⁷	10	2.3 x 10 ³	
			21	1.5 x 10 ³	8.1

(a) Using 75- to 150- μ m Hanford soil. Soil-to-solution ratio = 0.010 g/mL.

(b) Nickel spiked into solution/soil mixture shortly after the complexant was added.

(c) Nickel contacted with soil for varying periods (see corresponding tube number under sorption) before complexant was added.

values obtained in the second contacts should agree with those obtained in the first contacts (as was the case in the Eu/EDTA system).

The first hypothesis as to the reason for this behavior was that a portion of the nickel was removed from solution in the first contacts by precipitation, and that no further precipitation occurred in the second contacts because the nickel concentration was then lower. However, this hypothesis was not substantiated by the results of the experiments performed to test it.

Table 6 contains the results of experiments designed to test this solubility effect hypothesis. At nickel and EDTA concentrations the same as in some of the experiments listed in Table 5, only a small fraction of the nickel was found to disappear from solution in these experiments in the absence of soil. Thus, the disappearance of nickel from the solutions in the Table 5 experiments could not have been due to precipitation of a simple nickel compound. To see if some precipitant could have originated in the soil, some soil was subsequently added to the solubility experiments of Table 6. However, no nickel disappeared from solution then either. Thus, not only was no precipitation of nickel observed in these solutions, but no sorption onto the soil was observed either. Obviously, the data of Tables 5 and 6 are quite contradictory.

TABLE 6. Test of Solubility Hypothesis in Ni/EDTA System

<u>Tube</u>	<u>Na₂EDTA, M</u>	<u>Ni, M</u>	<u>Time, Days</u>	<u>Ni Found in Solution, %</u>	<u>pH</u>
<u>Before Soil Added</u>					
277	1.0×10^{-6}	1×10^{-7}	7	81	7.2
			14	84	7.0
269	1.0×10^{-5}	1×10^{-7}	6	91	7.0
<u>After Soil Added (0.010 g/mL)</u>					
277	1.0×10^{-6}	1×10^{-7}	6	100	9.0
269	1.0×10^{-5}	1×10^{-7}	7	98	9.1

The explanation for the contradictory data appears to be that the formation of the Ni-EDTA complex did not proceed rapidly under the conditions of the Table 5 experiments, and that the uncomplexed portions of the nickel were sorbed by the soil. In the experiments in Table 6, there was a 1- to 2-week period before the soil was added, and this evidently was sufficient for complete complexation to occur so that no nickel was sorbed by the soil.

A more quantitative illustration of the importance of time of complexation before soil contact is contained in the data of Table 7. These data were obtained by preparing a Ni-EDTA solution and removing portions for contact with soil after various time intervals. The behavior of nickel in the soil contacts is seen to be highly dependent on the time allowed for complexation before the soil contact was begun, and to be essentially independent of the time of contact with soil.

TABLE 7. Effect of Ni-EDTA Complexation Time on Sorption of Ni by Soil

Time, Days		Ni Found in Solution, %	pH
Before Soil Contact Begun (a)	After Soil Contact Begun (b)		
0.0007	2	2.6	8.3
	14	2.9	
0.0035	2	2.8(?)	8.3
	7	9.7	
	14	9.7	
0.010	2	12	8.3
	7	12	
	14	13	
5	2	29	8.3
	9	29	
19	2	41	

(a) 1.1×10^{-7} M Ni + 3.3×10^{-7} M Na₂EDTA at pH = 7.3.

(b) Soil-to-solution ratio = 0.010 g/mL.

Other experiments provide examples of the importance of concentrations during the complexation period prior to contact with soil. Such data are contained in Table 8. When a 1×10^{-7} M EDTA solution of nickel was aged 1 day before soil contact, all of the nickel was sorbed by the soil. However, when a 1×10^{-5} M EDTA solution of nickel was aged for the same period and was then diluted to the same EDTA concentration and contacted with soil, none of the nickel was sorbed by the soil. The extent of complexation was obviously much greater in the more concentrated solution.

The current status of the work in the Ni/EDTA system is that a stock solution containing 1×10^{-5} M Ni and 2×10^{-5} M EDTA was prepared and allowed to react for several days before being diluted and contacted with soil under a variety of conditions. After a contact period of 3 weeks, no significant sorption of Ni has been observed, even at the lowest EDTA concentration of 3.5×10^{-9} M.

A few experiments have also been completed with the DTPA complex of nickel. Sorption data that look good within themselves have been shown by second-contact experiments to be invalid, as was the case in the Ni/EDTA system. However, the desorption of nickel by DTPA appears to proceed much more rapidly than does the desorption by EDTA. The current status of the work in the Ni/DTPA system is the same as in the Ni/EDTA system; that is, dilutions of a concentrated stock solution are being contacted with soil. After 3 weeks of contact, only a slight sorption of nickel has been observed.

TABLE 8. Effects of Concentrations During Complexation Time on Sorption of Ni by Soil

Tube	Complexation Conditions			Ni Found in Solution, (a) %	pH
	Na ₂ EDTA, M	Ni, M	Time, Days		
295	1×10^{-7}	1×10^{-9}	1	0	8.9
303	1×10^{-5}	1×10^{-6}	1	99	

(a) After a 5-day contact with soil (0.033 g/mL) at an EDTA concentration of 1×10^{-7} .

Results of experiments with the Ni/humic acid system are shown in Table 9. These results should be considered as quite preliminary, especially in light of the kinetic problems observed in the other nickel systems, but they do show some interesting trends. The presence of the humic acid is seen to decrease the apparent K_d value for nickel compared to that observed in the absence of complexant. The sodium humate used in these experiments was not

TABLE 9. Preliminary Results in Ni/Humic Acid System

<u>Tube</u>	<u>Humate</u>	<u>Time, Days</u>	<u>Ni Found in Solution, %^(a)</u>	<u>Apparent K_d, mL/g</u>	<u>pH</u>
<u>In the Presence of Soil (0.010 g/mL)</u>					
228	---	7	1.4	7.1×10^3	7.8
		20	2.3	4.3×10^3	8.5
252	Filtrate ^(a)	7	20	4.1×10^2	8.8
		14	18	4.6×10^2	
272	Suspension ^(b)	7	11	7.8×10^2	9.6
		14	12	7.5×10^2	9.4
<u>In the Absence of Soil</u>					
287	---	3	0.5	---	8.2
		5	0.8	---	7.4
279	Filtrate ^(a)	0.01	22	---	7.3
		3	40	---	7.1
		9	37	---	7.0
278	Suspension ^(b)	0.01	5.1	---	7.9
		2	8.2	---	7.7
		10	9.2	---	7.5

(a) Initial nickel concentration was 1.1×10^{-7} M in each case. The nickel was spiked into the diluted humate solutions just prior to contact with soil in the cases where soil was added.

(b) Complexant solution prepared by 10-fold dilution of 2-nm filtrate of 2 g/L sodium humate suspension.

(c) Complexant solution prepared by 10-fold dilution of 2 g/L sodium humate suspension.

completely soluble in water; lower apparent K_d values were obtained in the presence of the undissolved humate material, suggesting that nickel is sorbed by such material as well as by soil. In fact, the presence of soil had no great effect on the concentration of nickel found in solution when the humate suspension was used. With dilutions of the filtered humate solution, about twice as much nickel was found in solution in the absence of soil than in the presence of soil.

The experiment in Table 9 in the absence of both humate and soil is of special interest in that nearly all of the nickel disappeared from solution. Assuming that this was due to the precipitation of $\text{Ni}(\text{OH})_2$, these data give a value of about 10^{-23} for the solubility product. Since this value is lower than that reported (Dean 1973) for $\text{Ni}(\text{OH})_2$ by a factor of about 10^8 , it is not reasonable to attribute the disappearance of nickel to precipitation of this compound. Perhaps the nickel was carried on a precipitate of some impurity, but this has not been verified. More work is needed in this aspect of nickel behavior since it could affect the results in all of the complexant systems.

COBALT

Examination of the effect of organic complexants on the behavior of cobalt in soil systems has not been as extensive as that with nickel. The cobalt systems were generally ignored as the problems with nickel were attacked. However, some cobalt data are now available from on-going experiments. These preliminary data indicate that kinetic factors may be less of a problem with cobalt than with nickel, but further work will be required before such a statement can be made with confidence.

Cobalt is strongly sorbed by Hanford soil in the absence of complexants. An apparent K_d value of 1×10^5 was measured in an experiment where a 1×10^{-7} M Co solution was contacted for 4 days with soil at a soil-to-solution ratio of 0.033 g/mL.

In the Co/EDTA system, experiments are in progress using solutions prepared by dilution of a 1×10^{-5} M Co plus 2×10^{-5} M EDTA stock solutions. Current results (Figure 3) show that the concentration of cobalt in solution

FIGURE 3. Preliminary Data in the Co/EDTA System

is decreasing very slowly with time; at each initial concentration, the rate of decrease is first-order in residual cobalt concentration and the half-time is about 20 days. In the two cases where comparative data are available, the rate of decrease is the same at two different soil-to-solution ratios. This suggests that the amount of cobalt sorbed by the soil so far in these

experiments is a function of the rate of dissociation of the Co-EDTA complex rather than of the attainment of any equilibrium condition involving the cobalt, the complexant, and the soil.

Experiments are also in progress in the Co/DTPA system that use solutions prepared by dilution of a $1 \times 10^{-5} \text{ M}$ Co plus $2 \times 10^{-5} \text{ M}$ DTPA stock solution. The results so far (Figure 4) show that in this system the decrease in cobalt concentration occurs more rapidly than it did in the Co/EDTA system (Figure 3). Also, some of the Co/DTPA experiments appear to be nearing an apparent steady-state condition within 3 to 4 weeks. In one pair of experiments, the cobalt concentration remaining after various times is the same at two different soil-to-solution ratios, as observed in the Co/EDTA system. However, in another pair of experiments, different results are being obtained at different soil-to-solution ratios.

CESIUM AND STRONTIUM

Only a few experiments were done with cesium and strontium to verify the expected lack of effect of organic complexants on their sorption by soil. The results are given in Table 10. The slight reduction in the apparent K_d for cesium in the presence of $3.3 \times 10^{-3} \text{ M}$ Na_2EDTA may have resulted from competition by sodium for the sorption sites. The strontium experiments at $3.9 \times 10^{-7} \text{ M}$ Sr show no effect of either EDTA or DTPA at the 10^{-4} M level on the sorption of strontium by the soil. Later experiments at higher strontium concentrations gave markedly lower apparent K_d values (both in the presence and absence of complexant). The reason for this is not known.

FIGURE 4. Preliminary Data in the Co/DTPA System

TABLE 10. Results with Cesium and Strontium

Tube	Complexant	Complexant Concentration, <u>M</u>	Cs or Sr Concentration, <u>M</u>	Apparent Kd, ^(a) mL/g	pH
<u>Cesium</u>					
341	---	---	1.0×10^{-8}	1.4×10^4 (b)	9.0
222	---	---	1.0×10^{-7}	7.4×10^3 (c)	8.5
223	Na ₂ EDTA	9.0×10^{-5}	1.0×10^{-7}	5.5×10^3 (c)	8.4
224	Na ₂ EDTA	3.3×10^{-3}	1.0×10^{-7}	2.0×10^3 (c)	5.1
340	DTPA	4.5×10^{-4} (d)	1.0×10^{-7} (d)	8.7×10^3 (b)	7.8
<u>Strontium</u>					
225	---	---	3.9×10^{-7}	180(c)	7.7
339	---	---	5.9×10^{-6}	16(b)	6.3
226	Na ₂ EDTA	9.0×10^{-5}	3.9×10^{-7}	180(c)	7.6
227	DTPA	1.0×10^{-4}	3.9×10^{-7}	180(c)	8.4
338	DTPA	5.0×10^{-4} (d)	4.1×10^{-6} (d)	58(b)	7.8

(a) After contact with soil (75- to 150- μ m fraction) for 1 week.

(b) Soil-to-solution ratio = 0.033 g/mL.

(c) Soil-to-solution ratio = 0.010 g/mL.

(d) Obtained by 10-fold dilution of a 5-day-old stock solution. In the other cases, the Cs or Sr was spiked into the solution/soil mixture shortly after the complexant was added.

PROCEDURES FORMAT

One of the objectives of this project has been to develop a "procedures format" that can be followed to obtain truly meaningful results in an efficient and economic manner. Such a format has been under development throughout the course of the experimental work described earlier. As that work demonstrates, it is often easier to obtain data than it is to be assured that the data are indeed valid.

Unfortunately, the optimum procedures format to use to gain the desired information in a minimum amount of time is probably not the same as the optimum format to use to minimize the expenditure of money. Thus, certain choices must be made in deciding on the number of experiments to be done at one time within a given system.

To obtain the desired data with a minimum number of experiments (which is assumed to minimize the cost) the format discussed below is recommended, based on the experience gained in the work described earlier in this report. Figure 5 contains a schematic representation of this format. To obtain the data in a minimum amount of time, work in several of the phases can be conducted concurrently. This will likely result in some wasted effort, but the savings in time is sometimes worth that price.

Phase 1. Perform two experiments to measure the apparent K_d of an element in a soil/water system, one without complexant and one with a high concentration of complexant. The experiment that contains complexant should employ an element/complexant stock solution that had aged for at least several days to allow slow complex formation to occur. If the apparent K_d values measured in these two experiments (after a week or two) are the same, as it was in the cesium and strontium systems discussed earlier, it can be concluded that the complexant has no effect and no further study of the system is necessary. If the apparent K_d value measured in the presence of complexant is higher than the value measured in the absence of complexant, the complexant must be enhancing the sorption and/or precipitation of the element, and further study may be desired. Such a case has not been observed in this work

DEFINITIONS:

K = K_d MEASURED IN THE ABSENCE OF COMPLEXANT

$K_c(h)$ = K_d MEASURED AT A HIGH CONCENTRATION OF COMPLEXANT

$K_c(h/n)$ = K_d MEASURED AT AN N-FOLD LOWER COMPLEXANT CONCENTRATION

K_{ca} = K_d MEASURED UNDER CONDITIONS SUCH THAT 20 TO 80% OF THE RADIONUCLIDE REMAINS IN SOLUTION

K^{*ca} = K_d MEASURED WHEN SOLUTION FROM K_{ca} MEASUREMENT CONTACTED WITH SECOND PORTION OF SOIL

FIGURE 5. Recommended Procedures Format

and the procedures to follow have not been addressed. If the effect of the complexant is to decrease the apparent K_d value, the complexant must be diminishing the sorption and/or precipitation of the element. To quantify the magnitude of the effect, additional experiments must be done. If the decreased apparent K_d value and the soil-to-solution ratio are such that about 20 to 80% of the element remains in solution, proceed directly to Phase 3. Otherwise, proceed to Phase 2.

Phase 2. If the conditions in the Phase 1 complexant experiment were such that >80% of the radionuclide remained in solution, experiments should be done at several lower complexant concentrations to establish the concentration range suitable for more detailed study. These experiments should also (as in Phase 1) employ dilutions of aged, concentrated element/complexant stock solutions to minimize the chance of the data being affected by slow kinetics of complexation, as were the initial nickel data described earlier. Apparent K_d values should be determined after 1- and 2-week time periods (and longer time periods if they are necessary to demonstrate attainment of a steady-state condition). In order to establish conditions that leave the desired 20 to 80% of the element in solution, the soil-to-solution ratio can be adjusted instead of (or in addition to) the complexant concentration.

Phase 3. Perform experiments that involve removal of portions of the solution from experiments showing appropriate residual element concentrations and contact them with fresh batches of soil. Measure these apparent K_d values after time intervals similar to those used in Phase 2. If the second-contact apparent K_d values agree with the first-contact apparent K_d values, as they did in the europium experiment described earlier, the data can be considered to be validated, but additional verification may still be desired, as discussed under Phase 4. If the first- and second-contact data do not agree, as was the case in the nickel experiments described earlier, the first-contact data cannot be considered to be generally valid and additional experiments must be done, as discussed under Phase 5.

Phase 4. Additional data may be desired under somewhat different conditions to further verify the validity of the data. Parameters to be

investigated here include the soil-to-solution ratio and the element concentration. Experiments may also be done in which equilibrium is approached from the desorption direction, by adding complexant to a soil/solution system containing previously sorbed (or precipitated) element. If not already done in Phase 2, data should also be obtained at a variety of complexant concentrations.

Phase 5. It is difficult to specify the best course of action to follow if the first- and second-contact data do not agree or if the additional data do not agree. Each case should be considered separately, and plans should be developed as additional data are obtained. Two starting points can be suggested, however. The first one involves the use of longer-aged and/or more concentrated stock solutions to see if conditions of complexation prior to contact with soil are affecting the data, as was observed to be the case with nickel and cobalt. The second one involves the use of lower-element concentrations to see if the element was precipitated, rather than sorbed, from solution. Second-contact experiments should also be used to check appropriate data obtained in these experiments. If conditions are found that appear to give valid data, additional verification may still be desired as discussed under Phase 4.

The preceding discussion has assumed that the mechanism that controls the removal of the element from solution was the reversible sorption by soil, which is the only mechanism for which the K_d concept is strictly valid. If some other mechanism (e.g., precipitation or slow kinetics) controls, the experimental format outlined here should demonstrate that fact and also provide other data of potential value in predicting element migration through soils. Knowing when not to use the simple K_d concept in predicting migration may actually be more important than knowing the precise K_d values to use in situations where the K_d concept is truly valid.

FUTURE WORK

Future work is planned in these areas: 1) continuation of study of the nickel and cobalt systems currently being examined; 2) initiation of studies with other complexants and soils; 3) initiation of studies under controlled-atmosphere conditions; and 4) modification (as required) of the procedures format. Future work may also include additional emphasis on comparison of the data with predictions based on known thermodynamic properties, and verification of data obtained in batch experiments with continuous-flow (column) techniques.

The currently available results with nickel and cobalt and EDTA or DTPA are obviously not sufficiently definitive, and more work is needed. Detailed kinetic studies may be required if kinetic factors appear to be more important than thermodynamic factors.

The effect of organic complexants should be determined with other soils since magnitude of the effect could well vary with the type of soil. The effect of other complexants likely to be present in low-level waste disposal sites should also be examined.

Controlled-atmosphere conditions should also be employed to allow studies to be made under anoxic and/or reducing conditions. Natural ground waters often have low oxidation potentials because of the absence of air and the presence of decaying organic matter. Since the oxidation potential can affect not only the oxidation state of multivalent radionuclides but also the presence or absence of radionuclide-sorbing hydrous oxides of multivalent soil elements, this is an important factor to investigate.

The results of continued experimentation will be evaluated for their effect on the recommended procedures format. The format will be modified and/or expanded if the added data point out improvements that can be made.

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