Effect of Organic Complexants on the Mobility of Nickel and Cobalt in Soils: Status Report

J. L. Swanson

September 1982

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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

Pacific Northwest Laboratory is conducting a study of the effect of organic complexing agents on the behavior of low-level waste radionuclides in soil/groundwater systems. This report contains the results of recent work with Ni and Co, two elements that have radioactive isotopes that are important to low-level waste disposal.

The complexants studied were EDTA, DTPA, oxalate, and citrate. Data were obtained from experiments using soils from both an arid site (Hanford, Washington) and a humid site (Savannah River, South Carolina). Some work with cobalt was done in the absence of air to allow the behavior of the lower oxidation state to be studied.

Important variations were observed in both the rates at which equilibrium was approached (from both the precomplexed and the presorbed directions) and the equilibrium positions themselves. The oxalate and citrate complexes are weaker and dissociate more rapidly than the EDTA and DTPA complexes. Dissociation of the EDTA and DTPA complexes occurred much more rapidly in solutions contacting Savannah River soil than in solutions contacting Hanford soil.

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INTRODUCTION

This report is an update on the status of a program at Pacific Northwest Laboratory (PNL) 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. Previous results of this program were reported by Swanson (1981). This study showed that while the sorption of Cs or Sr by Hanford soil was essentially unaffected by the presence of organic complexing agents, the sorption of Ni or Co was strongly affected. It was noted that kinetic effects were very important in the Ni and Co cases; the long-term behavior of these elements in Hanford soil systems varied widely, depending on whether the elements had been precomplexed before they were exposed to the soil.

This report describes results of subsequent complexant tests with Ni and Co, elements that have radioactive isotopes that are present in large quantities in low-level wastes. The program has been expanded to include other organic complexants commonly used in the nuclear industry and thus likely to be present in low-level wastes, and another soil that came from the Savannah River site. Very important differences in both the kinetic and the thermodynamic effects of organic complexants on radionuclide behavior in soil systems were observed between complexants and between soils. This report describes the status of the work through July 1982.

MATERIALS AND METHODS

The radionuclide distribution between solution and soil phases was measured at room temperature in batch-type contacts containing different amounts of organic complexing agents. These distributions were measured by radioactive counting techniques. The soil-to-solution ratio in these contacts was about 0.033 g/mL unless otherwise stated. For a further discussion of materials and methods see Swanson's previous work (1981).

As before, results are expressed as percent of the initial radionuclide 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.)

In addition to the complexants used previously (Na_2EDTA AND DTPA), measurements were made this year in the presence of oxalate and citrate. Solutions of these complexants were prepared by dissolving the ammonium salts in water.

The study was also expanded to include soil from a burial site at the Savannah River Plant, in addition to that from the Hanford Plant. A 150- to 500- μm -size fraction of the dry-sieved soils was used in most cases.

Some measurements in cobalt systems were made in an inert atmosphere chamber to eliminate oxidation of Co(II) to Co(III) by air.

The solution samples were filtered before counting to assure that the measured concentrations truly represented soluble species. In addition to the ultrafiltration membrane cones (made from an inert, non-ionic polymer) with a 2-nm pore size, filter disks of different materials were also used. This was done primarily in measurements in the absence of complexing agents, where some radionuclides appeared to be retained by the membrane cones by a process such as sorption rather than by retention of solid particles. One type of filter disk used was made of polycarbonate material, and the other of cellulose ester material. The polycarbonate material sorbed little, if any, of the uncomplexed soluble species. In the presence of the organic complexing

agents, sorption of soluble species by the filter media was not observed with any of the filters and the membrane cones were used for convenience.

In a few experiments, the concentrations of metal ions leached from soils into complexant solutions were determined. These measurements were made by emission spectroscopy using an inductively coupled plasma (ICP) for excitation.

Results this year have emphasized the importance of approaching equilibrium from both the precomplexed and the presorbed directions. This technique has uncovered some apparently anomalous behavior that might otherwise have gone unnoticed, since it would not have been detected by the "second contact" test of equilibrium that has provided an independent test.

In approaching equilibrium from the precomplexed direction, the element of interest is complexed in solution before it is exposed to the soil, which then sorbs a portion of the element. To approach equilibrium from the presorbed direction, the element is first sorbed from solution onto the soil, and complexant is then added to the soil-solution mixture so that a portion of the element is desorbed from the soil and re-enters the solution. At equilibrium the portion of the element in solution should be the same in the two cases, under a given set of conditions.

RESULTS

Experimental results obtained this year for Ni and Co will be presented here. Results include those without complexants as well as those with EDTA, DTPA, oxalate, and citrate complexants. Many of the element/complexant systems were tested with Savannah River soil as well as Hanford soil. Data are also presented on the concentrations of metal ions leached from the soil by the complexant solutions.

NO COMPLEXANT

Element distribution values in the absence of complexants are necessary as a baseline from which the effects of such complexants can be measured. Values reported last year (Swanson 1981) are now thought to have been unreasonably high because the filters used evidently removed some soluble species from solution by a sorption process. One indication of this was that when successive portions of a solution were passed through the same membrane filter cone, the element concentration found in successive filtrate portions gradually increased. Another indication was that when portions of a solution were passed through filters of different materials (with different pore sizes), the amount of element retained by the filter varied widely (but not in proportion to pore size). These observations were made with both Ni and Co in the absence of complexants.

To solve this problem, a type of disk filter made of polycarbonate material and available in a variety of pore sizes was used in the absence of complexants. Nearly all ($\geq 80\%$) of the elements contained in "pure" solutions passed through such filters (whether 0.015 or 0.1 μm -pore size), and there was no change when successive portions were passed through the same filter.

Nickel/No Complexant

When Ni solutions ranging from 2×10^{-7} to 5×10^{-9} M were contacted with Hanford soil at a soil-to-solution ratio of 0.033 g/mL for time periods of 2 to 19 days, about 2.2% of the Ni remained in solution (giving an apparent K_d value of 1300 mL/g), with the pH being about 9. Such constancy with varying Ni concentration suggests that this apparent K_d value might truly represent a reversible sorption equilibrium. However, higher apparent K_d values were

obtained at lower soil-to-solution ratios, which would not be the case for a simple, reversible sorption equilibrium case. The reason for the discrepancy is not known. Data are contained in Table A.1 in the Appendix.

Another experiment with Hanford soil was done, this time at a lower pH. The apparent K_d value was about tenfold lower at a pH value of 6 than at a value of about 9.

With Savannah River soil, Ni was not sorbed as rapidly as it was with Hanford soil. Figure 1 contains data illustrating this slow sorption, and more complete data are contained in Table A.2 of the Appendix. Good agreement was obtained between analyses performed on the solution after only centrifugation and after filtration through a polycarbonate filter; this provides additional evidence that the polycarbonate filters did not remove any Ni by a sorption process. Also, as was the case with Hanford soil, initial Ni concentration does not seem to affect the fraction of Ni sorbed by the soil.

FIGURE 1. Rate of Sorption of Uncomplexed Ni by Savannah River Soil

Cobalt/No Complexant

No measurements have been made of the distribution of Co(II) between soils and solutions in the absence of organic complexants. However, distribution coefficients higher than 10^3 have been measured at low complexant concentrations with both Hanford and Savannah River soils. It appears to be safe to assume that Co(II) distribution coefficients at least that high would result when complexants are absent.

EDTA

Ethylenediaminetetraacetic acid (EDTA) is a relatively strong complexing agent widely used as a decontaminating agent in the nuclear industry and thus will be present in untreated nuclear waste. Our earlier work (Swanson 1981) showed that kinetic effects were especially important in Hanford soil systems containing this complexant and Ni or Co.

Nickel/EDTA

When in contact with Hanford soil for a year, Ni that was precomplexed by EDTA remained completely in solution; this has been observed in eight experiments at EDTA concentrations ranging from 1×10^{-7} to 3.5×10^{-9} M and soil-to-solution ratios of 0.033 to 0.010 g/mL. Thus, Ni that has been complexed by EDTA would be expected to migrate through Hanford soil at the same rate as ground water.

When Ni was sorbed onto Hanford soil before EDTA was added to the system, the Ni tended to dissolve, but only very slowly (see Figure 2). After 6 months only about half of the Ni had dissolved into 1×10^{-5} M EDTA, but, with precomplexed Ni, all of the Ni remained in solution even though the EDTA concentration was much lower. Little additional Ni dissolved in another 9 months, but it is not known whether this was because of the attainment of an equilibrium position.

FIGURE 2. Rate of Desorption of Ni from Hanford Soil by 10^{-5} M EDTA

With Savannah River soil, however, an apparent equilibrium position was attained within several weeks. Figure 3 contains data in which equilibrium was approached from both the precomplexed direction, where Ni was complexed by EDTA before being exposed to the soil, and the presorbed direction, where Ni was sorbed by the soil before EDTA was added. When a 2-day sorption period was allowed before the EDTA was added, the fraction of Ni found in solution reached agreement with that found from the sorption direction within 23 days, indicating that an equilibrium position had been reached. When a 33-day period was allowed before the EDTA was added, the equilibrium position was approached more slowly. This apparent dependence of the rate of desorption on the length of the sorption period may warrant additional investigation.

The relatively rapid approach to equilibrium with Ni/EDTA solutions in contact with Savannah River soil indicates that precomplexed Ni would migrate through Savannah River soil at a rate much lower than the rate of groundwater migration, in contrast to the behavior indicated for Hanford soil. This

FIGURE 3. Ni/EDTA/Savannah River Soil

contrast is quite important, and the reason for this difference will be the subject of future investigations. One possible reason is solution pH (solutions in contact with Savannah River soil have a much lower pH than solutions in contact with Hanford soil), but this has not been proved to be the reason for the marked difference.

Cobalt/EDTA

Preliminary data from the Co(II)/EDTA system (in an argon atmosphere) with Hanford soil are shown in Figure 4. As in the corresponding Ni/EDTA system, slow kinetics are a problem; a large difference still exists after a month between the data obtained from the precomplexed and presorbed directions. It does appear that Co is equilibrating more rapidly than Ni, however.

FIGURE 4. CO(II)/EDTA/Hanford Soil Data

In EDTA solutions in the presence of air, as in the earlier experiments (Swanson 1981), the Co(II) is likely oxidized to Co(III), which forms more stable complexes. Some results obtained with Hanford soil in such experiments are presented in Figure 5. These results were obtained with dilutions of a stock solution containing 1×10^{-5} M Co + 2×10^{-5} M EDTA, with the dilutions made just before contact with the soil. Little difference was observed in the results of using stock solution 2 days or 1 month old, but a marked difference was observed with the 11-month old stock solution. It appeared that after this period of time only a portion of the Co was still complexed; perhaps enough of the EDTA decomposed during this time that not enough remained to complex all of the Co.

The slow changes with time of soil contact indicate that the Co(III)-EDTA complex is slowly dissociating so that the uncomplexed Co can be sorbed by the soil. The rate of this dissociation appears to vary inversely with EDTA concentration.

FIGURE 5. Co(III)/EDTA/Hanford Soil Data

An important conclusion from these data is that even though the reaction is slow, the Co(III)-EDTA complex does dissociate in Hanford soil systems. Therefore, the EDTA-complexed Co would not be expected to travel through Hanford soil at the same rate as water if the water flow rate is low enough to allow time for the dissociation to occur. This expectation has been substantiated by extended field studies (Kirkham and Jones 1982); in this work very little (if any) movement of EDTA-complexed Co was observed over a 3-year period in lysimeter experiments using Hanford soil and water fluxes typical of those encountered at the Hanford site.

Data obtained with Savannah River soil in the Co(II)/EDTA system are presented in Figure 6. With 5×10^{-5} M EDTA, approaching equilibrium from both the precomplexed and the presorbed directions gave the same concentration of Co in solution after about 2 weeks, but the concentrations then diverged

FIGURE 6. Co/EDTA/Savannah River Soil Data

again. This increase and subsequent decrease in Co concentration has also been observed in other systems to be covered later. It is postulated that such behavior is due to a reduction in free complexant concentration with time. Such a reduction might occur because of complexant destruction and/or complexing by elements leached from the soil. Such behavior will be the subject of future investigations.

Preliminary results for the Co(III)/EDTA/Savannah River soil system are shown in Figure 7. As with the Co(II) case, the Co(III) concentration changes more rapidly over time with Savannah River soil than with Hanford soil. Also, an initial increase in Co concentration was followed by a decrease in one of these Co(III) presorption-type experiments.

DTPA

Diethylenetriaminepentaacetic acid (DTPA) is another complexing agent used in the nuclear industry. It is even stronger than EDTA and thus, at equilibrium, it should take less DTPA than EDTA to affect the behavior of

FIGURE 7. Co(III)/EDTA/Savannah River Soil

radionuclides in soils. Earlier work (Swanson 1981) showed that kinetic effects were also quite important in Hanford soil systems containing this complexant and Ni or Co, although not to the extent that they are with EDTA.

Nickel/DTPA

Nickel that was precomplexed by DTPA and then contacted with Hanford soil at low DTPA concentrations is gradually being sorbed by the soil. The reaction roughly followed first-order kinetics for nearly a year, as shown by the data plotted in Figure 8. It should be recalled that similar experiments involving EDTA gave no decrease in Ni concentration over this time period, demonstrating that the Ni-DTPA complex dissociates more rapidly than the Ni-EDTA complex. In these experiments the soil-to-solution ratio had little effect on the concentration of Ni in solution in the short term, as would be expected for the situation where the complex dissociation rate is the controlling factor.

FIGURE 8. Rate of Dissociation of Ni-DTPA in Contact with Hanford Soil

It is possible that all of the Ni will eventually be sorbed by the soil in the experiments shown in Figure 8. Some experiments have thus been started at higher DTPA concentrations. These experiments include sets involving both precomplexed and presorbed Ni at given DTPA concentrations; the equilibrium condition at a given DTPA concentration must lie within the range of these two measurements. Results obtained thus far are presented in Figure 9. At the relatively short time intervals involved, the range is very large.

As in the Ni/EDTA system, the Ni/DTPA system reached equilibrium much more rapidly with Savannah River soil than with Hanford soil (see Table A.3). Figure 10 contains data showing typical changes in Ni concentration with time, and Figure 11 is a plot of the steady-state apparent K_d values as a function of added DTPA concentration. With 0.033 g soil/mL solution, the apparent K_d value was about 10 mL/g at an added DTPA concentration of about 1×10^{-3} M. The K_d value was decreasing approximately tenfold for each tenfold

FIGURE 9. Ni/DTPA/Hanford Soil Data

FIGURE 10. Ni/DTPA/Savannah River Soil Data

FIGURE 11. Equilibrium Data in Ni/DTPA Savannah River Soil System

increase in DTPA concentration, so that the K_d value would be expected to be 1 at about 1×10^{-2} M DTPA. Additional experiments should be done in this system to measure the effects (if any) of Ni concentration and soil-to-solution ratio.

Cobalt/DTPA

Preliminary results of tests in the Co(II)/DTPA/Hanford soil system are shown in Figure 12. As in the corresponding Ni case, the approach to equilibrium is slow. One of the desorption experiments also gave an initial increase in Co concentration followed by a decrease, as has been observed in some other systems.

In earlier experiments in the presence of air, results were obtained that appear to reflect the oxidation of Co(II) to Co(III). A stock solution containing 1×10^{-5} M Co + 2×10^{-5} M DTPA was prepared, and portions were diluted after different time intervals for contact with Hanford soil, in analogous manner to some of the Co/EDTA experiments described earlier. With Co/DTPA, the variation in Co concentration with the time of contact with soil was a function of the age of the stock solution at the time it was diluted for contact with soil, as shown by Figure 13. Much less Co was sorbed from a

FIGURE 12. Co(II)/DTPA/Hanford Soil Data

FIGURE 13. Co(III)/DTPA Hanford Soil Data

dilution of the aged stock solution than from a dilution of the fresh stock solution, presumably because of oxidation of Co(II) to Co(III) in the stock solution as it stands.

No data have yet been obtained with Savannah River soil in the Co/DTPA system.

OXALATE

Oxalate is another organic complexing agent widely used as a decontaminating agent and thus will be present in untreated nuclear waste. Oxalate is known to form much weaker complexes with metal ions than does EDTA or DTPA.

Nickel/Oxalate

This system reached equilibrium with Hanford soil quite rapidly (within a few days), in contrast to the behavior observed with EDTA and DTPA. Many experiments were done here to vary the concentrations of nickel and oxalate, the solution-to-soil ratio, the soil particle size, and the direction of approach to equilibrium. Data from experiments using ammonium oxalate are summarized in Table A.4.

Typical equilibrium data for the $\text{Ni}/(\text{NH}_4)_2\text{Ox}$ /Hanford soil system are plotted in Figure 14. There appears to be no great effect of any of the investigated variables except for the complexant concentration. The dependence of the apparent K_d value on the added oxalate concentration is greater than the dependence observed in the Ni/DTPA/Savannah River soil system discussed previously or in the Eu/EDTA/Hanford soil system studied earlier (Swanson 1981). Whereas the apparent K_d values in those systems decreased approximately tenfold for a tenfold increase in complexant concentration, in the $\text{Ni}/(\text{NH}_4)_2\text{Ox}$ /Hanford soil system, the apparent K_d values decreased approximately 100-fold for a tenfold increase in complexant concentration. Extrapolation of these data indicates that the K_d value would be expected to be 1 at about 0.08 M ammonium oxalate.

FIGURE 14. Equilibrium Data in Ni/Oxalate/
Hanford Soil System

Before these experiments with ammonium oxalate were done, a few tests were made with oxalic acid. The results were similar to those with ammonium oxalate except that lower pH values were obtained with oxalic acid. For example, with 0.01 M oxalic acid and a soil-to-solution ratio of 0.033 g/mL, the pH was about 5, and the apparent K_d was about 22 mL/g. This k_d value is about one-third that obtained at a pH of about 9 at the same oxalate concentration (Figure 14).

Some of the preliminary results obtained with Savannah River soil in the Ni/oxalate system are shown in Figure 15. As was also observed in the Ni/EDTA Savannah River soil system, the results obtained in presorption-type experiments depend on the length of time before complexant addition. Also, initial increases in Ni concentration were followed by decreases, as has been observed in several other systems. Results of precomplexed-type experiments at other oxalate concentrations indicate that the apparent K_d depends much less strongly on the added oxalate concentration with Savannah River soil than with Hanford soil (Figure 14).

FIGURE 15. Ni/Oxalate/Savannah River Soil Data

Cobalt/Oxalate

The $\text{Co(II)}/(\text{NH}_4)_2\text{Ox}$ system also reached equilibrium quite rapidly with Hanford soil. Comparison of data in this system in the presence and absence of air (Figure 16) shows the importance of excluding air. In an argon atmosphere an equilibrium position was reached rapidly, and remained stable for many days. In air, however, the apparent equilibrium position gradually shifted to give more Co in solution, presumably because of oxidation to Co(III) .

The data obtained in the $\text{Co(II)}/(\text{NH}_4)_2\text{Ox}$ /Hanford soil system are tabulated in Table A.5, and the apparent K_d values are plotted as a function of oxalate concentration in Figure 17. As in the $\text{Ni}/(\text{NH}_4)_2\text{Ox}$ /Hanford soil system, the apparent K_d values decreased approximately 100-fold for a tenfold increase in added oxalate concentration. Extrapolation of these data indicates that the K_d value would be expected to be 1 at about 0.2 M ammonium oxalate.

FIGURE 16. Effect of Air in Co/Oxalate/
Hanford Soil System

FIGURE 17. Equilibrium Data in Co(II)/Oxalate/
Hanford Soil System

No data have been obtained for the cobalt/oxalate/Savannah River soil system.

CITRATE

Citrate is another organic complexing agent used in the nuclear industry that forms much weaker complexes with metal ions than does EDTA or DTPA.

Nickel/Citrate

Experiments in the Ni/citrate/Hanford soil system have yielded some unexpected results. Typical data are shown in Figure 18. In the precomplexed-type experiments, the rate of decrease in Ni concentration was faster at low citrate concentrations. Of greater interest, however, is the fact that in presorption-type experiments, in which the Ni is sorbed onto the soil before the complexant is added, the Ni concentration first rose rapidly and then decreased.

FIGURE 18. Ni/Citrate/Hanford Soil Data

As mentioned earlier, this behavior is attributed to changing (decreasing) free citrate concentrations during the experiments. This could occur by decomposition of the citrate and/or by complexing of the citrate by metal ions that are slowly leaching from the soil. To test these hypotheses, a 0.005 M citrate leachate of Hanford soil was analyzed for metal ions after 2 and 14 days. The concentration of calcium, which is the predominant metal ion in leachates of this soil, was 0.003 M after 2 days and 0.00078 M after 14 days. This drop in calcium concentration with time is just the reverse of that predicted by the hypothesis involving complexing by soil-derived metal ions, but is consistent with the hypothesis that citrate is decomposing. Additional work would be required to test this hypothesis, however.

Results with Savannah River soil in the Ni/citrate system are shown in Figure 19. As in the Hanford soil system, the change over time in the concentration of Ni indicates that the free complexant concentration is decreasing. This effect was especially pronounced in the experiment at the lower citrate concentration.

FIGURE 19. Ni/Citrate/Savannah River Soil Data

LEACHING OF METAL IONS FROM SOILS

While the majority of experimental work has involved measuring the distribution of radionuclides between soil and solution phases in the presence of various complexants, the leaching of metal ions from the soils by complexants has also been studied. More data of this type will likely be required before the radionuclide behaviors can be understood well.

The data available are summarized in Table A.6. Some general observations follow:

- Calcium and Mg are the major elements in Hanford soil leached by the complexant solutions. The resultant concentration of Ca is generally equal to or greater than the concentration of complexant added. Since Ca forms reasonably strong complexes with EDTA and DTPA, the concentration of free complexant must be very low in these solutions. It is the concentration of free complexant, not the concentration of total complexant, that will affect radionuclide behavior in these systems. The radionuclide distribution data were discussed earlier in terms of total complexant concentration, assuming that the free complexant concentration was a constant fraction of the total.
- With Savannah River soil and citrate leachant, less Ca and Mg and more Al and Fe were found in solution than in the corresponding Hanford soil experiment.

DISCUSSION

Several of the points raised earlier warrant more general discussion. An overall comparison of some of the equilibrium results is also desirable, even though only fragmentary information is available for many of the systems examined.

In Figure 20 are plotted K_d results as a function of total complexant concentration for the systems in which appropriate data are available. In some cases, error bars are included to represent the spread between the values obtained in precomplexed- and presorbed-type experiments at the time of writing; much smaller error bars are expected after longer time periods. The Eu/EDTA data reported earlier (Swanson 1981) are plotted as well as the data contained in this report. There is quite a difference in results; some systems show a higher dependence of K_d on complexant concentration, and some complexants require a higher concentration to give an appreciable effect.

Data for many of these systems are still incomplete, but a few points appear to be valid. With Hanford soil, the trend agrees in most cases with that expected from the published values of the stability constants for the various complexes. That is, of the systems examined, the Co(II)/oxalate complex is the weakest and Ni/oxalate is next weakest; Ni/DTPA is the strongest complex and Co(II)/DTPA is the next strongest; however, the fact that the Eu/EDTA complex is stronger than the Co(II)/EDTA complex is not reflected in these data. The data from Savannah River soil do not reflect the fact that the Ni/DTPA complex is stronger than the Ni/EDTA complex. In the Ni/DTPA system, where data are available for both soils, a higher concentration of DTPA is necessary to give a low K_d value with Savannah River soil than with Hanford soil.

The results shown in Figure 20 were obtained at a soil-to-solution ratio of about 0.033 g/mL. A variation of K_d with the soil-to-solution ratio has been observed in some systems; it is assumed that this is due to differences in the free complexant concentration (the quantity that actually governs the equilibria), as varying amounts of the complexant are complexed by metal ions

FIGURE 20. Summary of Equilibrium Data

that leach from the soil. Thus, at a higher soil-to-solution ratio, a lower free complexant concentration would be obtained with a given total complexant concentration, and the lines in Figure 20 would shift to the right (a higher total complexant concentration would be required to produce a given change in the K_d value).

Also, it is important to note the complexant concentrations at which the K_d values are estimated to reach a value of 1 mL/g. While such a K_d value is really not very high, it is still sufficient to provide an appreciable retardation of the radionuclide in a groundwater system. The K_d value affects the radionuclide retardation factor, which is the ratio of the rate of water movement to the rate of radionuclide movement, according to the equation (Relyea et al. 1980):

$$\text{Retardation Factor} = 1 + \frac{(\text{bulk density})(K_d)}{(\text{effective porosity})}$$

If the bulk density is 2 g/cm³ and the effective porosity is 0.2, values in the range of typical ground water systems, a K_d value of 1 mL/g gives a

retardation factor of 11. That is, the radionuclide would move through the soil 11 times more slowly than the water. Similarly, a K_d value of 10 mL/g would give radionuclide movement 100 times slower than the groundwater movement for these conditions.

It can be seen in Figure 20 that the complexant concentrations required to give a K_d value as low as 1 are quite high for several systems. Thus, unless very high complexant concentrations are maintained in these systems, the mobility of these radionuclides in systems where equilibrium is obtained rapidly would not be high unless groundwater flows were very high. However, if groundwater flows are high, there may be appreciable dilution of the complexant, which would result in increased K_d values and thus increase the retardation factor. It is thus thought to be relatively unlikely that pronounced mobility of Ni and Co would occur in several of these complexant/soil systems in which equilibrium is obtained rapidly.

However, the systems that reach equilibrium slowly do afford the possibility of appreciable organic complexant-caused movement of Ni or Co. In such cases, data such as those presented in Figure 20 are of lesser importance; what is important are the rates of complex dissociation and the rate at which the water moves through the soil, since the associated complexes will move as fast as the water.

The data obtained with the Hanford and Savannah River soils provide examples of different mechanisms for limiting the migration of radionuclides from waste disposal sites. With the Hanford soil/groundwater system, where the Ni-EDTA complex dissociates very slowly and the Ni migrates through the soil at the same rate as the groundwater, the rate of migration of precomplexed Ni from a disposal site would still be low because the low rainfall rate gives a low rate of water migration. With the Savannah River soil/groundwater system, where a relatively high rainfall rate could give a high rate of water migration through the soil, the Ni-EDTA complex dissociates more rapidly and the uncomplexed Ni can then be sorbed by the soil. Thus little of the precomplexed Ni may migrate at the same rate as the water.

Another important factor in the systems that reach equilibrium slowly is whether the radionuclide is precomplexed before it is exposed to the soil. In the slow-equilibrating systems, this factor has a tremendous effect on the extent of radionuclide migration to be expected for a given distance of water

migration. While the precomplexed radionuclide may migrate at the same rate as the ground water if the rate of complex dissociation is sufficiently slow; if the radionuclide is sorbed by the soil before it is exposed to the complexant, it may not travel far, even if the same quantity of complexant is present. This is because of slow desorption rates, especially at low complexant concentrations.

Another factor of importance to the rate of desorption of a presorbed radionuclide may be the length of time the radionuclide has been sorbed before it is exposed to the complexant. This has been observed in two radionuclide/complexant systems with Savannah River soil but has not yet been examined with Hanford soil.

A factor that would tend to reduce the likelihood of serious complexant-caused movement of radionuclides is that of complexant decomposition or degradation, which results in higher radionuclide K_d values as the free complexant concentration decreases. Such decomposition appears to have occurred in the citrate experiments discussed earlier. The environmental chemistry of several complexants has recently been summarized by Means and Alexander (1981). Little quantitative data are available on the rates at which such reactions occur, but such decomposition or degradation would tend to reduce the extent of complexant-caused movement of radionuclides, at least in systems that reach equilibrium rapidly. The effect of such decomposition on slowly equilibrating systems is not known; depending on what factors control the rate of complex dissociation, complexant decomposition may not have a significant effect.

Several factors discussed here point to a conclusion regarding the effect of certain organic complexants on radionuclide mobility. The presence of oxalate or citrate in low-level waste would be much less likely to cause radionuclide mobility problems than would EDTA or DTPA. This is not only because oxalate and citrate form weaker complexes than do EDTA and DTPA, but also because oxalate and citrate do not form kinetically-inert complexes with Co and Ni, as do EDTA and DTPA under some conditions. Also, the decomposition rate of citrate appears to be quite rapid.

Perhaps this conclusion regarding the relative desirabilities of having the different complexants present in low-level waste could affect decisions regarding the degree of treatment required for wastes before they can be

disposed of. Such decisions could, in turn, aid in determining which complexants are used in the nuclear industry. Such "trade-off" considerations are beyond the scope of this program, however.

PROCEDURES FORMAT

The procedures format developed previously (Swanson 1981) has been generally followed in the current work, but one aspect has been found to be more useful than was previously realized. That is to initially perform simultaneous experiments at the same complexant concentration from both the precomplexed and presorbed directions. This has allowed earlier recognition of problems such as those observed in several of the systems, where the concentration of free complexant appears to change with time. In doing presorption-type experiments, the effect of the length of the presorption time period should also be examined; this has recently been found to be important in some cases.

Another modification of the previously recommended procedure would be to use shorter time intervals between measurements until it is determined that the kinetics are slow in the system under investigation.

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APPENDIX

SUPPLEMENTAL DATA ON RADIONUCLIDE SORRPTION
AND
THE LEACHING OF METAL IONS FROM SOILS

TABLE A.1. Sorption of Ni by Hanford Soil in the Absence of Complexants

Tube	Initial Ni, M	g Soil/ mL Solution	Time, Days	Ni in Soln., %	Apparent Kd, mL/g	pH
409	2×10^{-7}	0.033	4	2.2 ^(a)	1,300	9.1
			11	2.2 ^(a)	1,300	8.8
435	1×10^{-7}	0.033	7	2.1 ^(a,b)	1,400	8.8
426	2×10^{-8}	0.033	6	2.3 ^(a)	1,300	
			13	3.9 ^(a)	740	8.9
			19	2.9 ^(a)	1,000	8.8
534	5×10^{-9}	0.033	3	2.6 ^(c)	1,100	9.3
553	4×10^{-9}	0.033	1	7.9 ^(d)		9.5
			2	7.9 ^(d)		
			3	2.2 ^(c)	1,300	9.3
				7.2 ^(d)		9.3
			6	9.1 ^(d)		
				2.1 ^(c)	1,400	8.9
<hr/>						
427	9×10^{-8}	0.010	6	4.7 ^(a)	2,000	
			13	5.2 ^(a)	1,800	9.1
NS-4	8×10^{-8}	0.0034	14	3.2 ^(a)	8,800	8.0
			42	2.3 ^(a)	13,000	8.1
441	2×10^{-8}	0.0033	7	3.6 ^(a)	8,000	9.5
<hr/>						
425	1×10^{-7}	0.033	6	24 ^(a,e)	100	6.3

(a) 0.1 μ m polycarbonate filter.

(b) Initial solution was 0.01 M NaCl.

(c) 0.015 μ m polycarbonate filter.

(d) Centrifuged only.

(e) Initial solution was 0.01 M HCl.

TABLE A.2. Sorption of Ni by Savannah River Soil in the Absence of Complexants

Tube	Initial Ni, M	Time, Days	Ni in Soln., %	Apparent K _d , ^(a) mL/g	pH
447	2×10^{-8}	4	6.3 ^(b)	440	6.0
		12	1.6 ^(b)	1,800	6.1
		26	0.8 ^(b)	3,800	6.2
547	5×10^{-9}	1	21 ^(c)	110	
			21 ^(d)	110	
498	5×10^{-9}	1	15 ^(c)	180	7.4 (?)
			17 ^(d)	150	
		5	2.5 ^(d)	1,200	6.1
		32	0.8 ^(c)	3,500	
			0.4 ^(d)	7,500	
548	5×10^{-9}	8	3.8 ^(c)	760	
			4.0 ^(d)	720	
552	4×10^{-9}	1	16 ^(d)	150	6.2
		2	8.7 ^(c)	310	
			11 ^(d)	230	
		3	10 ^(d)	260	6.0
		6	4.5 ^(c)	640	5.9
			6.0 ^(d)	470	

(a) Using 150- to 500- μ m soil. Soil-to-solution ratio = 0.033 g/mL.

(b) 0.1 μ m polycarbonate filter.

(c) 0.015 μ m polycarbonate filter.

(d) Centrifuged only.

TABLE A.3. Ni/DTPA Savannah River Soil Data

Tube	Added Concentrations		Time, Days	Ni in Soln., %	Apparent Kd, (a) mL/g	pH
	DTPA, M	Ni, M				
<u>Precomplexed Direction</u> ^(b)						
513	5.0 x 10 ⁻⁷	5 x 10 ⁻⁹	3	4.0	720	6.8
			7	4.0	720	6.0
514	5.0 x 10 ⁻⁶	3 x 10 ⁻⁹	3	4.9	580	6.1
			7	4.6	620	6.0
521	5.5 x 10 ⁻⁵	4 x 10 ⁻⁹	3	27		6.0
			6	16	160	
			10	16	160	5.5
			18	16	160	
			26	20	120	6.0
522	5.0 x 10 ⁻⁴	4 x 10 ⁻⁹	3	71	12	4.0
			7	73	11	4.0
			15	55	25	
			23	47	34	
555	1.0 x 10 ⁻³	5 x 10 ⁻⁹	3	96	1	3.0
			7	79	8	
			14	79	8	3.8
<u>Presorbed Direction</u>						
514 ^(c)	1.6 x 10 ⁻⁵	3 x 10 ⁻⁹	3	13	200	
			7	13	200	5.9
513 ^(c)	5.2 x 10 ⁻⁵	5 x 10 ⁻⁹	3	21	110	
			10	23	100	5.9
554	1.0 x 10 ⁻³	5 x 10 ⁻⁹	3	57	23	3.3
			7	64	17	
			14	64	17	4.1

(a) Using 150- to 500- μ m soil. Soil-to-solution ratio = 0.033 g/mL.

(b) Ni stood in $>5 \times 10^{-5}$ M DTPA for 2 days before the solution was diluted and soil was added.

(c) More DTPA was added to sorption experiments after apparent equilibrium was reached.

TABLE A.4. Ni/Oxalate/Hanford Soil Data

Tube	Added Concentrations, M		g Soil/ mL Solution	Time, Days	Ni in Soln., %	Apparent Kd, mL/g	pH
	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	Ni					
Precomplexed Direction							
440	0.0020	2×10^{-8}	0.010 ^(a)	7	25	300	7.5
				15	10	890	7.6
429	0.0020	2×10^{-8}	0.033 ^(a)	7	3.6	800	8.2
				14	4.2	680	8.1
				31	3.6	800	
468	0.0030	6×10^{-9}	0.033 ^(b)	1	3.0	1,000	9.3
				4	2.9	1,000	9.2
				10	2.1	1,400	
438	0.0040	4×10^{-8}	0.033 ^(a)	5	5.7	500	9.1
				22	6.6	420	8.2
483	0.0080	2×10^{-9}	0.033 ^(b)	1	20	120	8.8
				4	17	140	8.9
				8	22	110	
467	0.0080	6×10^{-9}	0.033 ^(b)	1	17	140	8.9
				4	14	190	8.8
				10	17	140	
473	0.0080	6×10^{-9}	0.033 ^(b)	1	85	52	7.7
				4	86	51	7.2
482	0.0080	2×10^{-8}	0.033 ^(b)	1	17	150	8.8
				3	14	180	8.9
				6	16	160	
				10	19	130	
531	0.010	6×10^{-9}	0.033 ^(b)	4	32	64	
				11	35	55	
				22	40	45	8.1
				35	6.0	470	
449	0.010	4×10^{-8}	0.033 ^(a)	5	32	65	8.5
				11	31	67	
430	0.010	1×10^{-7}	0.033 ^(a)	7	38	48	8.6
				14	43	40	7.7

TABLE A.4. (contd)

Tube	Added Concentrations, M		g Soil/ mL Solution	Time, Days	Ni in Soln., %	Apparent Kd, mL/g	pH
	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	Ni					
471	0.015	2×10^{-9}	0.033 ^(b)	1	49	31	8.6
				4	51	29	8.5
466	0.015	6×10^{-9}	0.033 ^(b)	1	54	26	8.6
				4	48	33	8.5
				10	52	27	
				25	62	19	
464	0.015	2×10^{-8}	0.033 ^(b)	1	68	14	8.4
				4	67	15	8.4
				11	70	13	8.4
				19	73	12	8.2
499	0.015	3×10^{-8}	0.033 ^(b)	4	48	33	8.4
				11	47	34	
465	0.028	2×10^{-8}	0.033 ^(b)	1	85	5	8.2
				4	84	6	8.2
472	0.030	6×10^{-9}	0.033 ^(b)	1	75	10	8.3
				4	76	9	8.3
				25	80	8	7.2
<u>Presorbed Direction</u>							
479	0.015	5×10^{-9}	0.033 ^(b)	1	36	53	8.5
				3	40	46	8.5
				6	42	41	
				10	45	37	
480	0.030	5×10^{-9}	0.033 ^(b)	1	78	9	8.3
				3	67	15	8.3
				6	73	11	
				13	76	9	
<u>Second Contact</u>							
499b	0.015 ^(c)	$1 \times 10^{-8(c)}$	0.033 ^(b)	3	40	45	8.8
				10	46	36	

(a) Using 75- to 150- μm soil.(b) Using 150- to 500- μm soil.

(c) The equilibrated solution from the first contact.

TABLE A.5. Co(II) Oxalate/Hanford Soil Data

Tube	Added Concentrations, M		g Soil/ ^(a) mL Solution	Time, Days	Co in Soln.,%	Apparent Kd, mL/g	pH
	(NH ₄) ₂ C ₂ O ₄	Co					
Precomplexed Direction							
475	0.010	1 x 10 ⁻⁷	0.0035	8	71	120	7.4
				18	72	110	
474	0.010	1 x 10 ⁻⁷	0.035	8	5.6	480	8.4
				18	5.2	520	
476	0.010	1 x 10 ⁻⁶	0.035	8	6.4	510	8.4
				18	5.8	460	
460	0.020	1 x 10 ⁻⁶	0.033	4	23	100	8.3
				7	21	110	
				14	20	120	
Presorbed Direction							
461	0.0070	1 x 10 ⁻⁶	0.033	4	1.8	1,600	8.8
				7	1.8	1,600	
				14	1.8	1,600	
459	0.020	1 x 10 ⁻⁶	0.033	4	18	140	8.2
				7	19	130	
				14	20	130	
462	0.050	1 x 10 ⁻⁶	0.033	4	60	20	8.0
				7	63	18	
				14	64	17	

(a) Using 150- to 500- μm soil.

TABLE A.6. Metal Ions Leached From Soils

Leachant	g Soil/ mL Solution	Time, Days	Concentration Found in Filtered ^(a) Leachate, M x 10 ⁴												
			Na	K	Mg	Ca	Sr	Ba	Zn	Al	Fe	Cr	Mn	Cu	Si
Hanford Soil															
H ₂ O	0.033	7	5.2	0.28	0.42	0.90	0.004	0.001	0.06	0.02	--	0.005	--	--	3.9
9 x 10 ⁻⁵ M Na ₂ EDTA	0.010	1	3.9	0.20	0.31	1.5	0.003	--	0.28	0.02	--	--	0.01	0.003	1.3
		7	3.2	0.12	0.42	2.0	0.005	0.002	0.27	0.03	0.003	--	0.01	0.004	1.5
Add Ca to increase its concentration by 5 x 10 ⁻⁴ M															
		+7	2.8	0.16	0.89	5.4	0.01	0.003	0.33	0.02	--	--	0.02	0.008	1.2
9 x 10 ⁻⁵ M Na ₂ EDTA	0.033	7	7.6	0.28	0.50	1.8	0.004	0.001	0.29	0.02	--	--	0.01	0.006	4.0
1 x 10 ⁻⁴ M DTPA	0.010	7	1.6	0.16	0.87	3.9	0.01	0.003	0.36	0.01	0.04	0.007	0.03	0.007	1.5
1 x 10 ⁻⁴ M DTPA	0.033	7	5.8	0.38	1.0	3.1	0.01	0.002	--	0.02	0.02	--	0.05	0.02	3.9
1 x 10 ⁻³ M DTPA	0.010	7	1.1	0.25	4.5	11.0	0.02	0.02	0.30	1.3	0.43	--	0.26	0.05	3.9
5 x 10 ⁻³ M Citrate	0.033	2	5.9	1.0	6.9	30.0	0.06	0.03	0.55	1.2	0.21	0.02	0.36	--	5.6
		14	7.7	2.0	6.8	7.8	0.04	0.01	0.26	--	--	0.02	0.02	--	6.0
Savannah River Soil															
5 x 10 ⁻³ M Citrate	0.033	2	0.87	0.13	0.50	1.1	0.001	0.01	0.66	5.9	0.32	0.07	0.02	0.02	3.3
		14	1.8	0.41	0.33	0.58	0.001	0.01	0.62	7.7	0.90	0.02	0.02	0.01	5.9

(a) Using 2-nm membrane filter cores.

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