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Organic Complexant-Enhanced Mobility of Toxic Elements in Low-Level Wastes

Annual Report
July 1983 - June 1984

Prepared by J. L. Swanson

Pacific Northwest Laboratory
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ABSTRACT

This report describes the results obtained during the first year's activities of a project whose objective is to determine how and to what extent organic complexants affect the mobility of toxic elements in subsurface groundwaters at commercial low-level waste disposal sites. This project will study nonradioactive toxic elements as well as elements having radioactive isotopes of importance (e.g. ^{63}Ni, ^{239}Pu, ^{241}Am). Organic complexants used in the nuclear industry are being emphasized, but we also examine others. We are employing generic soil components (e.g. hydrous oxides, silica, clays) so that the results will be broadly applicable.

Data have been obtained with two radionuclides (^{63}Ni and ^{239}Pu) and one nonradioactive toxic element (Cd). Work with ^{63}Ni has been emphasized; it was studied with five different generic soil components (hydrous ferric oxide, silica, titania, kaolinite, and montmorillonite) and five different complexants (EDTA, NTA, picolinate, citrate, and oxalate). EDTA was the complexant studied most extensively and hydrous ferric oxide, $Fe_2O_3 \cdot xH_2O$, was the most studied soil component. Only scouting studies have been done so far with some of the toxic element/complexant/soil component systems.

A wide diversity of effects of organic complexants on toxic element sorption was observed. The effects vary not only among complexants, but also among toxic elements and among soil components. In some systems the complexant results in increased toxic element sorption (decreased mobility) while in other systems the complexant results in decreased toxic element sorption (increased mobility).

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ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the skill and dedication devoted to this project by A. D. Peoples, who performed the experiments. The ICP analyses were performed under the direction of F. T. Hara and C. L. Matsuzaki of PNL. Surface area and particle size distribution measurements were made by M. C. Burt of HEDL.

The report was typed by L. D. Maki and K. M. McCormack, and edited by N. M. Sherer.

EXECUTIVE SUMMARY

The primary mechanism of escape of toxic elements from commercial low-level waste disposal sites to the accessible environment, where they may endanger public health and safety, is migration with subsurface groundwaters. As the water passes through the soil, many of the toxic elements may be removed from solution by sorption or precipitation reactions, with the result that their migration rates (mobilities) are markedly retarded. The degree of retardation depends on the nature of the soil and on the nature of the toxic element species present in the solution, and may be adversely affected by the presence of organic complexing agents.

Organic complexing agents are often used in the nuclear industry to remove radioactive materials from contaminated equipment and facilities. The wastes resulting from such activities therefore contain the organic complexants, unless they are destroyed before disposal of the wastes. These complexants can affect the mobility of toxic elements. Determination of the potential importance of such complexants to the mobilities of toxic elements present in low-level waste is the objective of this research project.

We are measuring the distribution of toxic elements between generic soil components and solution phases in the presence and absence of complexants to determine the effects of complexants. We are using experimental procedures that allow determination of whether the measured distribution coefficients represent equilibruim conditions. In this first year's effort, data have been obtained with two radionuclides (^{63}Ni and ^{239}Pu) and one nonradioactive toxic element (Cd). Work with ^{63}Ni has been emphasized; it was studied with five different generic soil components (hydrous ferric oxide, silica, titania, kaolinite, and montmorillonite) and five different complexants (EDTA, NTA, picolinate, citrate, and oxalate). EDTA was the complexant studied most extensively and hydrous ferric oxide was the most studied soil component.

A wide diversity of effects of organic complexants on toxic element sorption by generic soil components has been demonstrated in the experimental work of this project. The effects vary not only among complexants, but also among toxic elements and among soil components. In some toxic element/complexant/soil component systems, the complexant results in increased toxic element sorption (decreased mobility) while in other systems the

complexant results in decreased toxic element sorption (increased mobility). Kinetically inert behavior, where a complexed toxic element does not rapidly adjust to altered chemical conditions, was observed in only one of the systems studied. Such behavior can be very important since kinetically inert complexes that are not sorbed by the soil can migrate at the same rate as groundwater.

The results of this project indicate that disposal requirements should not be the same for all organic complexants, since different complexants have markedly different effects on toxic element mobilities. These results also suggest that the effect of complexants on toxic element sorption should be examined with soils from specific proposed commercial low-level waste disposal sites.

INTRODUCTION

The primary mechanism of escape of toxic elements from commercial low-level waste disposal sites to the accessible environment, where they may endanger public health and safety, is migration with subsurface groundwaters. As the water passes through the soil, many of the toxic elements may be removed from solution by sorption or precipitation reactions, with the result that their migration rates (mobilities) are markedly retarded. The degree of retardation depends on the nature of the soil and on the nature of the toxic element species present in the solution, and may be adversely affected by the presence of organic complexing agents.

ISSUES ADDRESSED BY THIS RESEARCH

This research addresses two key issues for licensing of low-level waste disposal sites: 1) What restrictions should be placed on the disposal of wastes containing different organic complexants? 2) How can the effects of organic complexants be included properly in predicting the release of toxic elements?

To properly address these key issues, the technical questions below must be examined.

1. What are the important gross mechanisms affecting the retardation of toxic element mobility in soil/groundwater systems? The relative importance of retardation phenomena such as precipitation, coprecipitation, surface adsorption, and diffusion of toxic elements into the bulk sorbent must be assessed.
2. What are the quantitative effects of specific organic complexants with specific soil components on these retardation mechanisms? Among such effects are extent of complex formation (with elements dissolved from the soil components as well as with toxic elements), rates of complex formation and dissociation, and sorption of the complexes themselves.
3. What data need to be obtained to provide the proper input to predictive models so that the toxic element migration rates obtained from such models will be meaningful? For this purpose it is of paramount importance to know whether the data represent a true equilibrium

condition or are merely dictated by the kinetics of the system. Further, if changes with time are observed, it is necessary to know if these changes are caused by changes in the soil component properties (aging) or by changes in the extent of element complexation. It is also necessary to know the effects of element and complexant concentrations and the soil-to-solution ratio.

4. What are the basic mechanisms by which the important gross mechanisms operate? For example, if a complexed toxic element species appears to be sorbed, how does this occur? Is the mechanism really sorption of a performed complex, or does the apparent sorption involve first sorption of the complexant and then complexing of the toxic element by the sorbed complexant? Also, if a toxic element appears to be sorbed by a hydrous oxide or hydroxide, is sorption truly the mechanism or could the mechanism be precipitation caused by a localized high hydroxide ion concentration near the surface? While knowledge of such basic mechanisms may not be necessary for the development of adequate predictive capability, it would certainly lend confidence in the accuracy of such predictions.

BACKGROUND AND OBJECTIVES

Organic complexing agents (e.g. EDTA, NTA, oxalate, citrate) are often used in the nuclear industry to remove radioactive materials from contaminated equipment and facilities. The wastes resulting from such activities therefore contain the organic complexants, unless they are destroyed before disposal of the wastes. These complexants affect the mobility of toxic elements. Toxic element mobilities can also be affected by other manufactured organic complexants that may enter the low-level waste disposal site by other means and by naturally occurring organic complexants. Determination of the potential importance of such complexants to the mobilities of toxic elements present in low-level waste is the objective of this research project.

There have been several reports of enhanced radionuclide mobilities resulting from the presence of organic complexants. The migration of a Co-EDTA complex from a low-level waste burial site was first reported by Means, Crerar, and Duguid (1978). Similar results have also been obtained at a different low-level waste disposal site (Toste, Kirby, and Pahl 1983) for both Co and alpha-emitting radionuclides. A Pu-EDTA complex was also found in leachates from the latter site (Cleveland and Rees 1981). These observations illustrate the potential importance of organic complexants to radionuclide mobilities and also provide a basis of the need for a broader project such as that being pursued here.

This project is an expansion of our previous work in this area (Swanson 1981, 1982, 1983). Three different soils were studied in that work. The elements Co and Ni, which have important isotopes present in low-level wastes, were studied in the most detail. An important activity of that work was the development of procedures to determine whether a radionuclide sorption coefficient that appears to be stable with time is truly an equilibrium value or appears stable only because the rate of change is very slow. An understanding of this is necessary to accurately predict the rate of radionuclide migration.

The effect of organic complexants on the sorption of radionuclides was found in our previous work to vary widely among different complexants. This variation involves not only the concentration of complexant required to have an appreciable effect on the equilibrium sorption coefficient, but also involves how rapidly the equilibrium is attained. The latter factor is more important since, in the extreme case, kinetically inert complexes could migrate at the same speed as groundwater. Rapid dissociation of the complexes is desirable so that the uncomplexed radionuclide can be sorbed by the soil.

The comparison of complexing agents included study of the fate of some of the complexants themselves as well as study of their effects on radionuclide distribution. The results of these tests indicated that all organic complexing agents should not be considered to be equally hazardous from a waste disposal standpoint.

The earlier work also showed that sorption of some kinetically inert radionuclide complexes, as well as sorption of uncomplexed radionuclides, is important with some soils. In these cases, the radionuclide migration rates were lower than they would have been if the complexes had not been sorbed, but were higher than they would have been if the complexes were not kinetically inert, or if complexants were absent.

The three different soils studied affected organic complexant-enhanced radionuclide mobility differently. Two of them sorbed kinetically inert complexes and one did not. Radionuclide complexes dissociated more rapidly in some soil/groundwater systems that they did in others. The soils also differed in their leaching by complexant solutions; different elements were predominant in leachates of different soils, and rates of leaching were different. These differences also affected radionuclide behavior.

SCOPE OF RESEARCH

The current project is continuing and expanding the investigations summarized above. It is employing generic soil constituents (e.g. hydrous oxides, clays and silica) so that the results will be more broadly applicable. The number of toxic elements studied has been expanded by including transuranic elements and nonradioactive toxic elements that may be present in low-level waste. We are continuing to emphasize study of the organic complexing agents used in the nuclear industry but will also examine the effects of some naturally occurring ones.

EXPERIMENTAL METHODS

EXPERIMENTAL CONSIDERATIONS

The principal measurements for this project are of distributions of toxic elements between solutions and soil components in the presence of organic complexants. These measurements are made at various time intervals as the solution and soil are shaken together and thus can provide kinetic data as well as equilibrium data; these experiments are, therefore, being called K&E experiments.

The K&E experiments are simple to perform and allow a wide range of variables to be examined efficiently. Among the variables to be studied are complexant identity and concentration, toxic element identity and concentration, soil component identity and soil-to-solution ratio, pH, Eh, and bulk solution composition. Experiments can also be performed with several soil components present at once to see if the overall effect is that predicted from the results obtained with the individual components. Changes with time are also easily followed; these changes can include sorbent aging before the toxic element sorption is begun as well as changes that occur in the presence of both the element and the sorbent.

One important extension of these K&E experiments involves removing the solution from an experiment that appears to be at steady state (i.e. the toxic element distribution is not changing with time) and contacting it with a second portion of soil. If the toxic element distribution coefficient measured in the "second contact" experiment is the same as in the first contact, it indicates that the measured coefficients are equilibrium (or pseudo-equilibrium) values. If the coefficients in the two experiments do not agree, it shows that (at least) the first value is probably not a meaningful equilibrium distribution coefficient and that additional examination is necessary.

These second contact experiments are especially valuable in determining whether the initial solution contained more than one kinetically inert species of the toxic element having different sorption properties; if it did, different distribution coefficients would be measured in the two contacts. These experiments are also valuable in determining whether toxic elements are precipitating in addition to being sorbed. If precipitation is important in the first contact, the apparent distribution coefficient will be higher than the coefficient for sorption alone, which will be measured in the second contact.

Different distribution coefficients will also be obtained in first and second contact experiments if the distribution coefficient is a function of element concentration in solution or of element loading on the sorbent. These differences would likely be less pronounced than those resulting from the multiple species and/or precipitation conditions discussed above, and can be investigated more fully in additional experiments at different concentrations.

Another important and useful variation of K&E experiments is to approach equilibrium from both the adsorption and the desorption directions; the results from the two directions should agree when equilibrium is truly achieved. This variation often gives useful kinetic information: it provided part of the information critical to demonstrating that the sorption of a complexed species was a pseudo-equilibrium, rather than a true equilibrium, condition (Swanson 1983).

While the K&E experiments will provide the bulk of the data, a few column experiments are planned for verification of these data under a few, carefully selected conditions. Of special interest here will be conditions involving multiple species and/or high soil-to-solution ratio conditions.

By careful planning and execution of the procedures discussed above, plus other measurements, several mechanistic concerns may be addressed. Among these are:

- sorption on the surface of the sorbent
- diffusion of sorbate into the sorbent
- sorbent alteration with time, a special case of which could be conversion of a metastable to a stable sorbent
- the possible importance of localized concentration regimes (e.g. high hydroxide concentrations near the surface of solid hydrous oxides)
- slow dissociation of complexed species
- in cases where the toxic elements complex itself appears to be sorbed, is the mechanism really sorption of the preformed complex or is it first sorption of the complexant and then complexing of the toxic element by the sorbed complexant?

The K&E experiments have generally been performed in polypropylene tubes but glass vials have also been used on occasion. No effects of container type have been observed. The containers rest horizontally on a shaker and are shaken at ambient temperature, which is generally about 30°C on the shaker platform.

GENERIC SOIL COMPONENTS

Initial plans for this project called for the use of a range of well-characterized generic soil types that are prevalent in the U.S., as well as single minerals selected from among those likely to be present in pertinent low-level waste site soils. Subsequent investigation showed that samples of well-characterized generic soil types are not readily available. Further consideration led to the conclusion that this generic study would best be done by starting with individual soil components and later using mixtures of the individual components. This is the approach now being pursued.

$Fe_2O_3 \cdot xH_2O$ Sorbent

Amorphous hydrous ferric oxide (also called amorphous ferric hydroxide or iron oxyhydroxide) is precipitated in situ in the experimental containers by the addition of NaOH solution to raise the pH to 7.5 ± 0.5. The NaOH solutions are fresh dilutions of a 50% NaOH stock solution so that the addition of carbonate, which might affect the behavior of some trace elements, is minimal. The $Fe_2O_3 \cdot xH_2O$ is aged under these conditions for varying times (generally 1 day) before the toxic element is added and the sorption experiment is begun.

Leckie et al. (1980) report that the surface area of similarly prepared $Fe_2O_3 \cdot xH_2O$ ranged from 160 to 260 m^2/g, measured by BET nitrogen adsorption. They also report that the point of zero charge is pH ~7.9 and comment that this value may change during the course of long-term experiments. They also present data on the surface charge density as a function of pH at three different ionic strengths. Presumably these characterization values are valid for our experiments as well because we prepared our $Fe_2O_3 \cdot xH_2O$ in essentially the same manner.

SiO_2 Sorbent

Silica (α-quartz) was obtained and pretreated as described by Leckie et al. (1980). This treatment involves heating to oxidize organic contaminants, refluxing in 4 M HNO_3, rinsing until the pH of the rinse water is approximately 7, and drying at 125°. The BET surface area was measured at 5.0 m^2/g, in reasonable agreement with the 3.3 m^2/g reported by Leckie et al. Those authors also cite literature that states that the PZC on nonporous silica is generally in the range 2.0 to 3.0, and that the surface site density is generally in the range of 3 to 6 sites per nm^2.

TiO_2 Sorbent

Titania powder was used without treatment. It had a BET surface area of 9.5 m^2/g. Particle size distribution measurements showed that 95% had equivalent spherical diameters $\leq$0.13 μm.

Kaolinite and Montmorillonite Sorbents

These clays were obtained from Ward's Natural Science Establishment, from their stock of American Petroleum Industry standard clays. The kaolinite is from Mesa Alta, New Mexico, and the montmorillonite is from Clay Spur, Wyoming. The crude clays were used without purification or chemical pretreatment in the scouting experiments done so far. They were ground and sieved; the experiments employed portions of the 44 to 74-μm size fraction.

SOLUTION CLARIFICATION

As mentioned earlier, the primary measurements of this project are the distribution of a toxic element between liquid (solution) and solid (soil component) phases. It is thus very important to use a good phase separation technique so that the results are not erroneous because of the presence of finely divided solids in the liquid samples. Our past experience in actinide element solubility measurements has indicated that centrifugation, even for long time periods, was not always sufficient. We thus initially adopted filtration as our standard phase separation procedure and generally used 2-nm ultrafiltration membrane cones for this purpose.

However, subsequent work showed that the 2-nm filters were removing uncomplexed Ni from solution, presumably by sorption on the filter medium.

At low pH values the sorption by the filter medium was much greater than that by the soil component.

A similar problem with these filters had been observed earlier in similar systems (Swanson 1982) but was not apparent when the first tests were done in our current work. This was because the effect is much less pronounced in 0.1 M $NaNO_3$ than in 0.01 M $NaNO_3$, and the initial checking was done in a 0.1 M $NaNO_3$ experiment.

Data illustrating the filter sorption problem are contained in Table 1, where results obtained after experimental suspensions were clarified by centrifugation or by filtration are presented. Filters having three different pore sizes were used; they were from three different sources and presumably had three different filter media. Comparable results were obtained with centrifugation or with filtration through the 0.1- or 0.2-μ filters. Only

TABLE 1. Comparison of Apparent Uncomplexed Ni Sorption with Different Solution Clarification Techniques

	% of Ni Sorbed(a)			
Clarification Technique	Expt. 104(b)		Expt. 105(c)	
Centrifugation(d)	0 to 6		-1 to 1	
Filtration through 0.2 μ	5		1	
-second portion		6		2
Filtration through 0.1 μ	8		3	
-second portion		11		1
Filtration through 0.002 μ (2 nm)	48		63	
-second portion		31		26
-third portion		22		19

(a) Calculated from analysis of the initial solution and the solutions after clarification.

(b) pH = 5.9; 5×10^{-4} M $Fe_2O_3 \cdot xH_2O$ in 0.01 M $NaNO_3$.

(c) pH = 4.2; 30 g/L SiO_2 in 0.01 M $NaNO_3$.

(d) At ~1500 G for >10 minutes.

with the 2-nm filter, which is the one we had initially used routinely, was the result different; in these cases the apparent Ni sorption was much higher. Based on the single-portion filtration data, it could be argued that the difference was due to the more efficient removal of finely-divided particulate species by the filter having the smallest pore size. However, data obtained when multiple portions of the suspension were clarified by the same filter show that this was not the case. As multiple portions were clarified by the 2-nm filter, the apparent sorption indicated by the Ni content of each filtrate portion decreased. This is not what would be expected if the 2-nm filter had removed finely-divided particulates more efficiently; if that had been the case, there should have been either no change in the Ni content of consecutive portions, or the Ni content would have decreased (giving an increasing apparent sorption) as the removed particulates decreased the effective pore size. Thus it appears that uncomplexed Ni was sorbed by the medium of the 2-nm filter, and that the sorption sites tended to become loaded as consecutive portions were passed through the same filter.

The different clarification techniques were also compared under a wide variety of other conditions. Close agreement persisted between uncomplexed Ni results obtained by centrifugation and by 0.2-μ filtration at all pH values examined. All four techniques gave comparable results in the presence of complexants, indicating that complexed Ni was not affected by any of the filter media.

EDTA SORPTION MEASUREMENTS

Sorption of EDTA by various materials was measured using ^{14}C-labeled EDTA. The labeled EDTA was mixed with nonlabeled EDTA at least one day before the sorption contact was begun, to allow time for equilibration to occur so that the measured behavior of the labeled EDTA would represent the behavior of all the EDTA.

Pu ANALYSES

Plutonium analyses are being performed by liquid scintillation counting of TTA extracts of treated solution samples. TTA is a highly efficient extractant for Pu(IV), but not for the other Pu oxidation states (or for Am, which is generally present in Pu solutions) at acidities of about 0.1 M or higher.

By performing the TTA extractions after various solution sample treatments, we can differentiate between reduced [Pu(III) and Pu(IV)] and oxidized [Pu(V) and Pu(VI)] Pu fractions in the solution samples.

We are using a Pu speciation method we developed earlier (Rai and Swanson 1981) to differentiate between reduced and oxidized species. This method involves first adjusting the sample to 0.3 $\underline{M}$ HNO_3 + $5x10^{-5}$ $\underline{M}$ $NaBrO_3$ [to oxidize any Pu(III) to Pu(IV)] and then immediately contacting it for 10 minutes with 0.5 $\underline{M}$ TTA in xylene to extract the Pu that had been present initially as Pu(III) and Pu(IV). The aqueous phase from the extraction is then made 10^{-3} $\underline{M}$ in $TiCl_3$ and allowed to stand for ~5 minutes [to reduce Pu(V) and Pu(VI) to Pu(III)], then made 10^{-2} $\underline{M}$ in $NaBrO_3$ [to oxidize the Pu(III) to Pu(IV)], and then contacted immediately with a fresh TTA phase to extract the Pu that had been present initially as Pu(V) and Pu(VI). The total Pu found in the two TTA extracts thus represents the total Pu present in the solution sample.

The presence of $1x10^{-4}$ $\underline{M}$ EDTA was found to cause erroneous results in the TTA extraction method used to differentiate between reduced [Pu(III) and PU(IV)] and oxidized [Pu(V) and Pu(VI)] fractions: the reduced fraction was too low (by up to 50%) and the oxidized fraction was correspondingly high. The EDTA did not appear to affect the measurement of total Pu concentration, however.

COUNTING PROCEDURES

Liquid scintillation counting is used for analyses of ^{63}Ni, ^{239}Pu, and ^{14}C. The Pu analyses are performed on TTA extracts so that Am will not interfere. Gamma counting is used for analysis of ^{109}Cd.

Concentrations of Ni, Cd, and Pu are calculated from their measured activities, previously determined counting efficiencies, and specific activities of the stock supplies. The specific activities of the Ni and Cd were provided by the vendor, while that of the Pu was obtained by earlier analysis.

Some experiments involved both ^{239}Pu and ^{14}C (as labeled EDTA). It was possible to measure both of these radioisotopes by liquid scintillation counting by careful selection of the detection ranges. There was no contribution of ^{14}C in the predominant ^{239}Pu range, but there was some ^{239}Pu contribution in the ^{14}C range that was easily corrected. The ^{239}Pu count in the ^{14}C range amounted to about 9% of the Pu count in its predominant range.

pH MEASUREMENTS

Measurements of pH are made using a combination electrode standardized with buffer solutions. Leckie et al. (1980) discussed potential problems of slow drifts with time in slurries of $Fe_2O_3 \cdot xH_2O$ and used values measuring 30 seconds to 3 minutes after immersion of the electrode. We are recording the measurements after 1 and 4 minutes of immersion; these values generally agree to within 0.1 pH unit.

SOLUTION ANALYSES

Selected solution samples were analyzed to determine the extent of leaching or dissolution of metal ions from the generic soil component sorbents by different solutions. These analyses were performed by emission spectroscopy using an inductively coupled plasma (ICP) for excitation.

RESULTS AND DISCUSSION

Experiments have been performed with three toxic elements (Ni, Pu, and Cd), with five different complexants (EDTA, NTA, picolinate, citrate, and oxalate), and with five generic soil components ($Fe_2O_3 \cdot xH_2O$, SiO_2, TiO_2, kaolinite, and montmorillonite). The sorption of Ni-EDTA and Ni-picolinate complexes by ion exchange resins was also examined. In many of these systems only preliminary results are available, while other systems were studied extensively. Results with Ni will be discussed first, then those with Pu, and finally those with Cd will be presented.

EFFECT OF EDTA ON Ni SORPTION BY $Fe_2O_3 \cdot xH_2O$

In our earlier work (Swanson 1981, 1982, 1983) with actual soils, the Ni-EDTA complex exhibited several properties important to low-level waste disposal. The complex tended to maintain its identity for long periods of time even under conditions where it was thermodynamically unstable, which means that the migration of Ni could be much greater than that predicted from thermodynamics. With some of those soils, the complex itself was shown to be sorbed, which provided some retardation of the migration. For these reasons, the Ni/EDTA system was deemed especially appropriate for examination with individual soil components in this current project. Most of our study of this system so far has been with $Fe_2O_3 \cdot xH_2O$ sorbent.

Figure 1 shows the initial results obtained in 0.1 M $NaNO_3$ solution with Ni-EDTA and $Fe_2O_3 \cdot xH_2O$ as the soil component. In the absence of EDTA, the sorption of Ni was low at low pH and high at high pH. In contrast, when the Ni was first complexed with EDTA and then contacted with the $Fe_2O_3 \cdot xH_2O$, the sorption of Ni was initially high at low pH and low at high pH. This initial Ni sorption was higher at a lower EDTA concentration. However, the effect of EDTA changed on long standing, so that Ni sorption became low at all pH values.

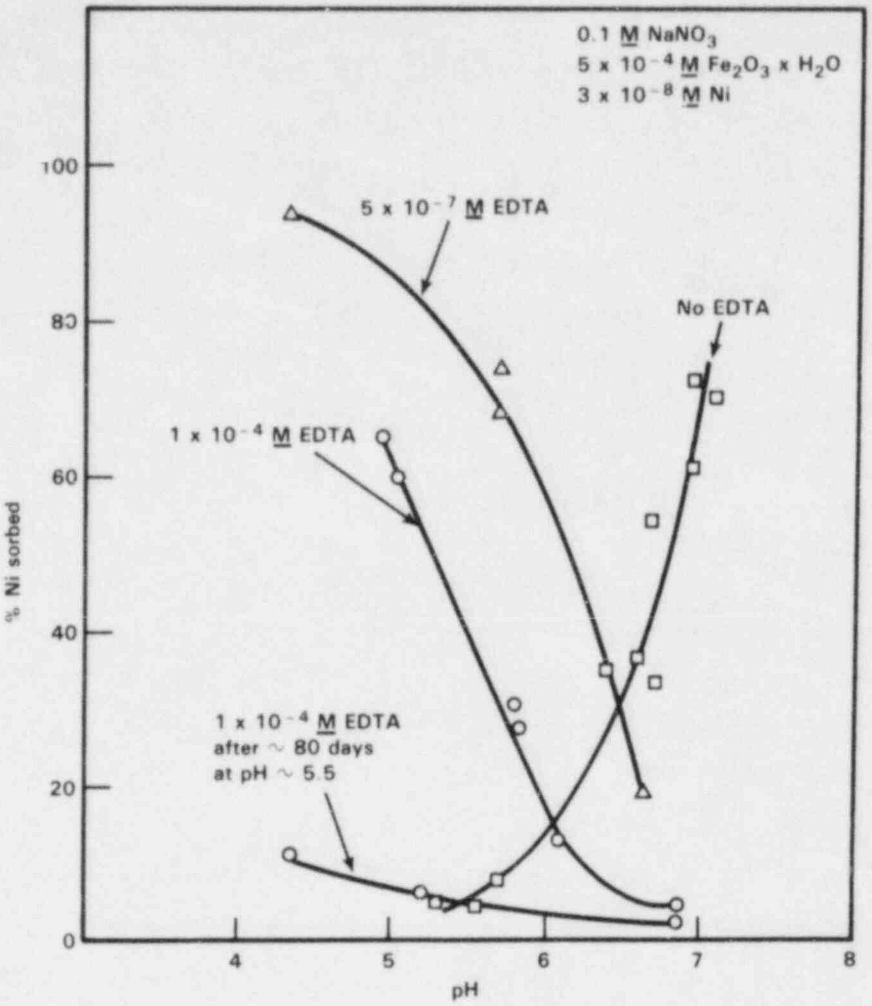


FIGURE 1. Effect of EDTA on Ni Sorption by $Fe_2O_3 \cdot xH_2O$.

The data indicate that the effect of EDTA on the mobility of Ni in the presence of $Fe_2O_3 \cdot xH_2O$ will vary markedly with pH and with the time of contact. In short contact times, EDTA will decrease Ni mobility at pH values below about 6, but will increase Ni mobility at higher pH values. However, changes occur during long contact times that negate the decreased mobility at low pH values. The increased mobility at high pH values persists, so that high Ni mobility occurs at all pH values in aged EDTA/$Fe_2O_3 \cdot xH_2O$ suspensions.

The initial behavior of the precomplexed Ni suggests that the Ni-EDTA complex is sorbed by $Fe_2O_3 \cdot xH_2O$. The changed behavior after longer times indicates that some alteration must have occurred to the sorbent, to the complexant, or to the complex itself. These possibilities will be addressed later.

Figure 2 provides a comparison of the sorption of Ni in the presence of EDTA (presumably sorption of Ni-EDTA) with the sorption of EDTA alone. The similarities in the pH dependencies of the two species suggest that the "sorption of the complex" may be occurring by a mechanism involving partial sorption of the EDTA itself. These data were obtained at a lower ionic strength than those shown in Figure 1; little if any effect of ionic strength on Ni sorption was apparent.

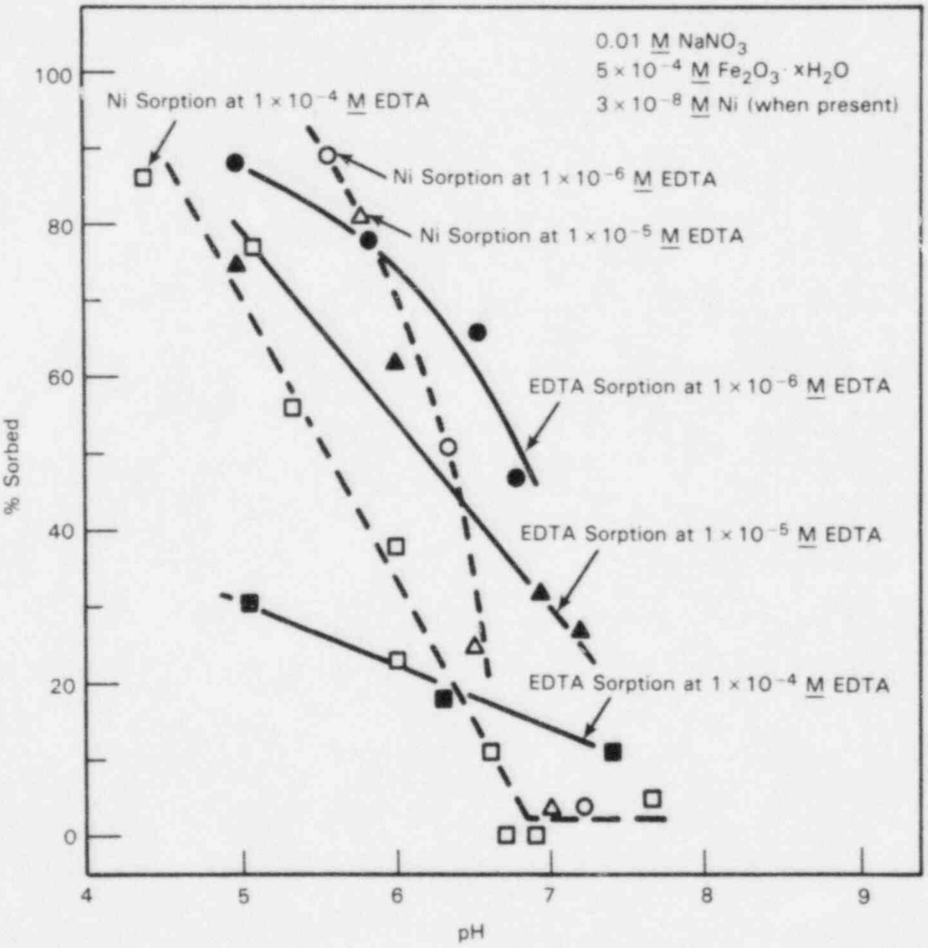


FIGURE 2. Sorption of Ni-EDTA and of EDTA Alone

The increasing degree of EDTA sorption observed as its concentration decreases indicates that the sorptive sites tend to become saturated. With 1×10^{-4} M total EDTA the ratio of solution EDTA to sorbed EDTA is markedly higher than it is at the lower total EDTA concentrations. This suggests that the lower Ni sorption observed at the higher EDTA concentration was caused by an equilibrium shift towards solution species, resulting from the increased solution EDTA-to-sorbed EDTA ratio.

The hypothesis that the "sorption of the Ni-EDTA complex" actually occurs by partial sorption of EDTA, which then competes with the EDTA remaining in solution to complex the Ni, was supported by the results of experiments to measure EDTA sorption in the presence of a macro amount of Ni. These results are compared in Figure 3 with those observed in the absence of Ni. Comparable results were obtained in the presence or absence at both EDTA concentrations

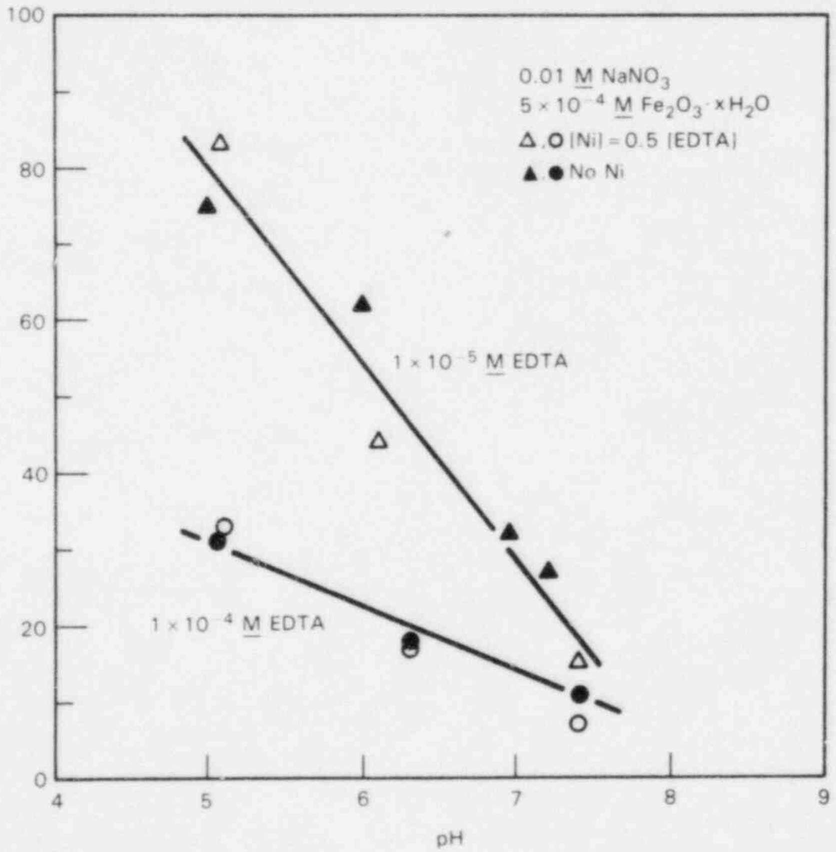


FIGURE 3. EDTA Sorption in the Presence and Absence of Ni

examined; this is the result expected for the proposed hypothesis. If, on the other hand, a preformed Ni-EDTA complex were the sorbing species, the sorption of EDTA would be expected to be higher in the presence of Ni. Such behavior was observed earlier (Swanson 1983) with Ni-EDTA and an iron-containing soil and in the current work in the Pu(IV)/EDTA/$Fe_2O_3 \cdot xH_2O$ system to be discussed later.

Returning to the subject of the changes with time that occur in the Ni/EDTA/$Fe_2O_3 \cdot xH_2O$ system, considerable effort has been devoted to trying to learn the reason for this phenomenon, but with only partial success. Some data illustrating the rate of changes of Ni sorption are shown in Figure 4. The change is seen to be quite gradual under the conditions of these experiments. Limited data from an earlier experiment at a lower pH (~4.5) and higher ionic strength (0.1 M) showed a more rapid rate of change; it is not known which of these variables caused the difference.

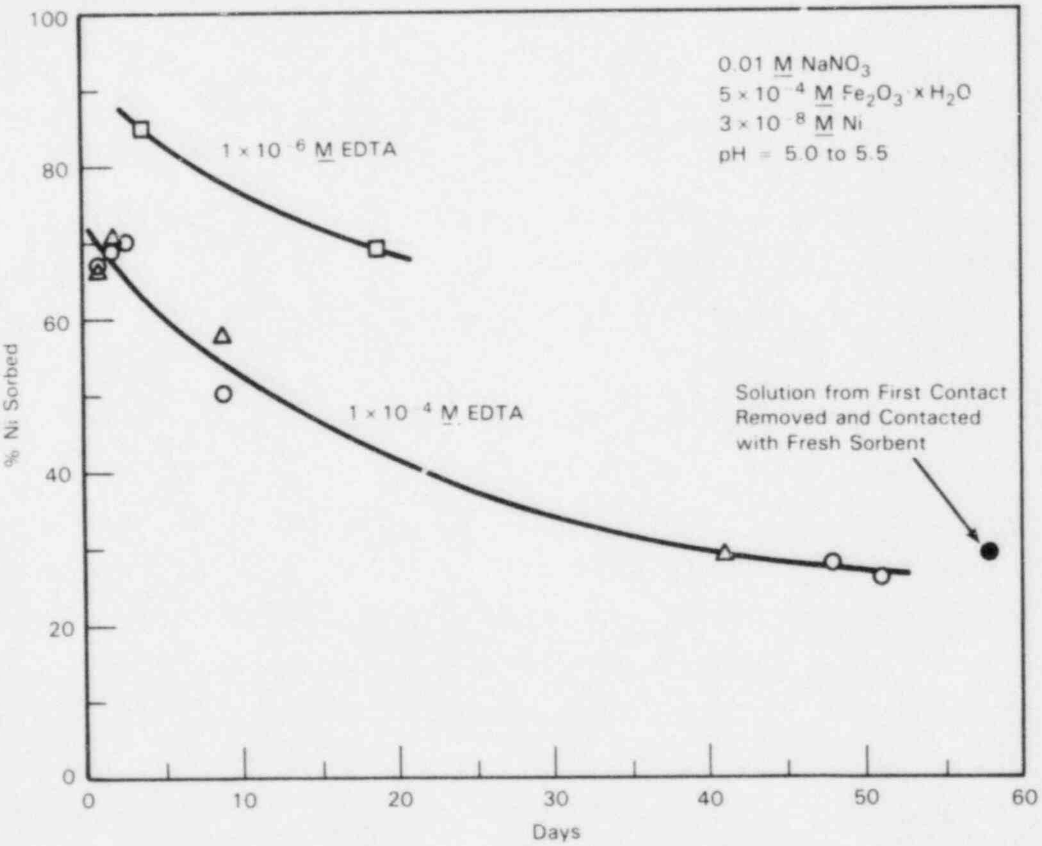


FIGURE 4. Changes in Ni-EDTA Sorption with Time

An important measurement is shown in Figure 4 as the shaded circle datum point. This point provides proof that the change with time was not the result of aging of the sorbent. To obtain this datum point, the $Fe_2O_3 \cdot xH_2O$ suspension that had exhibited ~70% Ni sorption initially and ~27% Ni sorption after 50 days was separated into solid and liquid fractions. The liquid portion was then added to a one day old $Fe_2O_3 \cdot xH_2O$ suspension (under conditions that resulted in a 2-fold dilution of the solution) and the resulting suspension was equilibrated for one day. The Ni sorption by the fresh sorbent was essentially the same as that by the aged sorbent. Thus, the change in Ni sorption with time was not caused by aging of the sorbent.

Earlier, but less definitive, evidence against a sorbent aging effect was obtained by comparing Ni behavior as a function of time after Ni-EDTA addition in two experiments that were identical except for the age of the $Fe_2O_3 \cdot xH_2O$ at the time the Ni-EDTA was added. When the Ni-EDTA was added to a Fe_2O_3 suspension that had been aged for 2 hours at pH ~4 and the pH was maintained at 4.3, the Ni sorption was initially high (94% after 3 hours) but then gradually decreased to 43% after 8 days. In the second experiment, the Fe_2O_3 suspension was aged for 8 days at pH ~4.4 before the Ni-EDTA was added so that any change that might have occurred in the properties of the sorbent in the first experiment could occur before the Ni-EDTA was added. The initial sorption of Ni was 90%, in good agreement with the 94% observed initially in the first experiment, rather than with the 43% observed in the first experiment after the suspension had been at pH ~4.3 for 8 days.

Another phenomenon that might cause a change in Ni sorption with time as shown in Figures 1 and 4 is the disappearance of EDTA. However, this phenomenon does not appear to be responsible for the observed change. Based on the data of Figure 2, the EDTA concentration would have to decrease to less than 1×10^{-6} $\underline{M}$ before Ni sorption might begin to decrease. Analysis (by A. P. Toste of PNL) using gas chromatographic techniques developed in a companion NRC project (Kirby, Rickard, and Toste 1984) showed that the 80 day old solution giving the Ni sorption results shown in Figure 1 still contained 5.5×10^{-5} $\underline{M}$ EDTA, which is in great excess of the concentration below which Ni sorption might begin to decrease.

The aged solution was also analyzed by Toste using a gas chromatographic/mass spectrographic technique in search of EDTA degradation products. Ethylenediaminetriacetic acid (ED3A) was found at a concentration of 8.2×10^{-6} M; giving a total of 6.3×10^{-5} M EDTA + ED3A found in the aged solution. An EDTA sorption of ~20% was measured in a separate experiment at 0.1 M $NaNO_3$ and pH = 5.5 (which was the pH of the aged suspension when it was sampled for EDTA analysis). Thus, ~1.1×10^{-5} M EDTA could have disappeared from the aged suspension by sorption on the $Fe_2O_3 \cdot xH_2O$. The solution EDTA + ED3A and the sorbed EDTA thus add up to ~74% of the EDTA initially present. The fate of the other ~26% is presently unknown.

We have thus shown that the changes with time observed in the Ni/EDTA/$Fe_2O_3 \cdot xH_2O$ system are not due to aging of the sorbent or to disappearance of the EDTA. However, we have not yet determined what is responsible for the observed effect. One possible explanation is that perhaps sorbed EDTA, which does complex Ni to the surface of the sorbent, is displaced by an EDTA degradation product, which does not complex Ni to the surface. Another possibility is that an EDTA degradation product forms more stable complexes in solution with Ni than does EDTA, and thus competes with sorbed EDTA with increasing effectiveness as more degradation product accumulates with time. These are speculative hypotheses, with no data yet available to substantiate or refute them.

The rate of attainment of an initial steady state sorption appears to be quite rapid in the Ni/EDTA/$Fe_2O_3 \cdot xH_2O$ system, which is a very important difference from our earlier results with some soils (Swanson 1981, 1982, 1983). With precomplexed Ni-EDTA (Figures 1 and 2), the Ni distribution achieved within 3 hours was stable for several days. More importantly, insofar as proof of equilibrium is concerned, when equilibrium was approached from the opposite direction by sorbing uncomplexed Ni onto $Fe_2O_3 \cdot xH_2O$ at high pH for several hours and then adding EDTA to desorb the Ni, a rapid desorption removed most of the Ni within 1 day.

However, slower kinetics were observed when uncomplexed Ni was sorbed by $Fe_2O_3 \cdot xH_2O$ for longer time periods before EDTA was added. This phenomenon is illustrated by Figure 5, where the fraction of Ni that remained sorbed by $Fe_2O_3 \cdot xH_2O$ as a function of time after EDTA was added to 1×10^{-4} M is shown

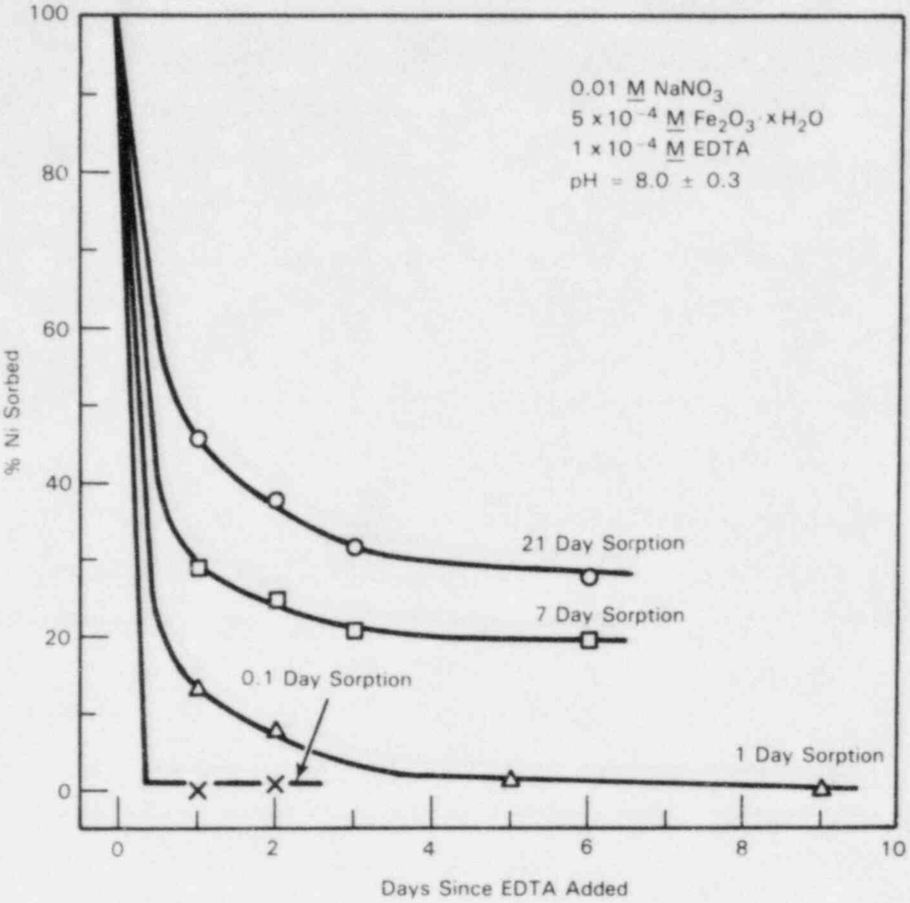
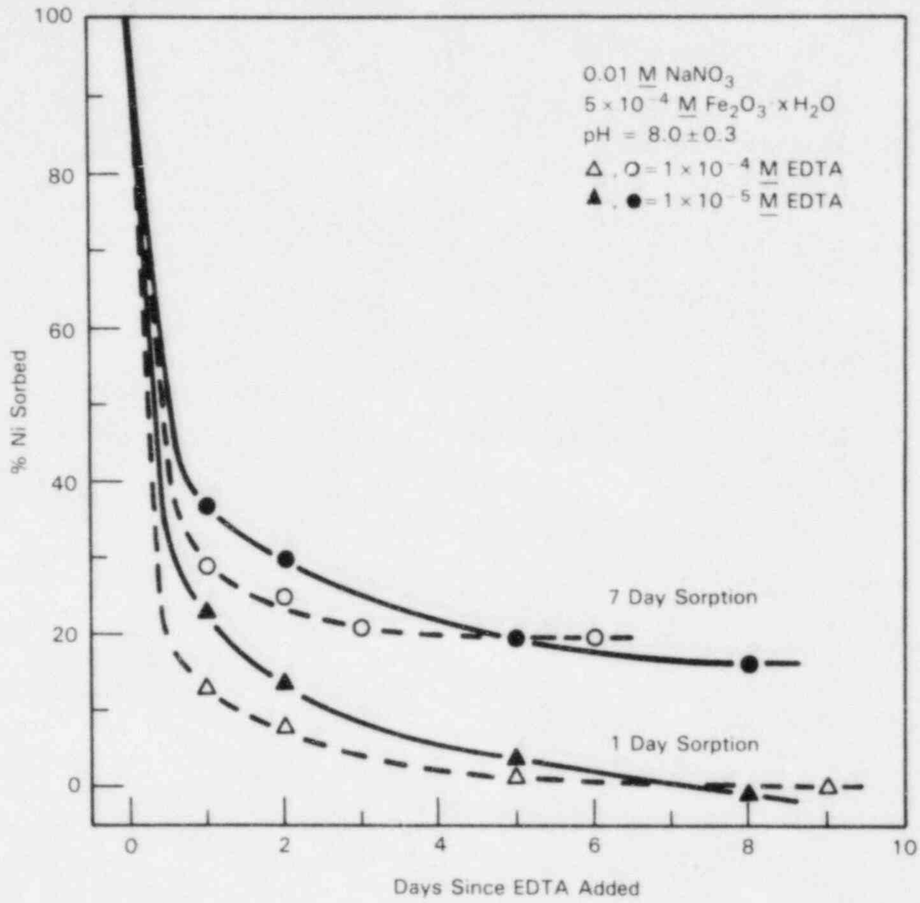


FIGURE 5. Effect of Sorption Time on the Rate of Ni Desorption by EDTA

for experiments involving uncomplexed Ni sorption times of 0.1, 1, 7, and 21 days. These experiments were done at a pH where no sorption of the Ni-EDTA complex occurs (Figures 1 and 2). As the uncomplexed Ni sorption time increased, the time required to desorb the Ni with EDTA also increased. These results suggest that uncomplexed Ni slowly diffuses into the $Fe_2O_3 \cdot xH_2O$ during the sorption process and then slowly diffuses out again after EDTA is added.

Figure 6 contains data on the rate of Ni desorption at two different EDTA concentrations. This rate is seen to be initially somewhat slower with $1x10^{-5}$ EDTA than with $1x10^{-4}$ $\underline{M}$ EDTA. This may be at least partially due to the fact that less $Fe_2O_3 \cdot xH_2O$, and therefore less Ni that had diffused into the $Fe_2O_3 \cdot xH_2O$, would be dissolved by the solution containing less EDTA. When EDTA is added to $Fe_2O_3 \cdot xH_2O$ suspensions, the concentration of Fe in solution increases by an amount equal to the added EDTA concentration.



<u>FIGURE 6.</u> Effect of EDTA Concentration on the Rate of Ni Desorption

Nickel distribution coefficients (Kd's) in the presence and absence of EDTA are plotted in Figure 7. These values are more readily applicable to comparisons and predictions than are the percent sorbed values shown in the earlier figures. These Kd values are expressed in units of mL/g sorbent; they may be converted to values in units of mL/m^2 sorbent by dividing by 200 m^2/g, which is the approximate surface area of similarly prepared $Fe_2O_3 \cdot xH_2O$ reported by Leckie et al. (1980).

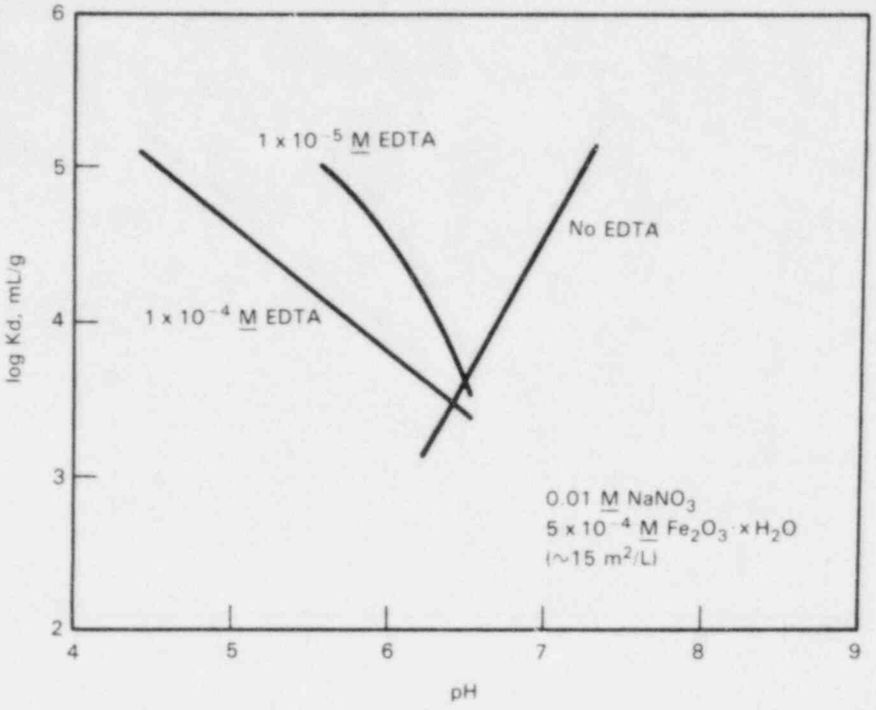


FIGURE 7. Nickel Distribution in Presence and Absence of EDTA

Before the detailed work was completed to indicate that complexing of Ni by sorbed EDTA is responsible for the apparent sorption of the Ni-EDTA complex, experiments were done at different Ni and $Fe_2O_3 \cdot xH_2O$ concentrations to test the general validity of the Ni-EDTA Kd values. The same Kd values were obtained with 3×10^{-7} M Ni-EDTA as with 3×10^{-8} M in suspensions containing 5×10^{-4} M $Fe_2O_3 \cdot xH_2O$, 1×10^{-4} total EDTA and 0.01 M $NaNO_3$. With one-tenth as much $Fe_2O_3 \cdot xH_2O$ (5×10^{-5} M), the Kd values were somewhat different. There is some question regarding the amount of solid $Fe_2O_3 \cdot xH_2O$ actually present at the lower concentration, especially at low pH. In addition, it may be that different Kd values should be expected at different $Fe_2O_3 \cdot xH_2O$ concentrations because of differences in the free EDTA concentration as the $Fe_2O_3 \cdot xH_2O$ concentration is varied at constant total EDTA. More examination will be required to resolve this question.

EFFECT OF OTHER COMPLEXANTS ON Ni SORPTION BY $Fe_2O_3 \cdot xH_2O$

Several other complexants that are used in the nuclear industry as decontaminating agents were also tested to determine their effect on Ni sorption by $Fe_2O_3 \cdot xH_2O$. Those tested were nitrilotriacetic acid (NTA), picolinic acid (which is the primary complexant used in the LOMI reactor decontamination process), citric acid, and oxalic acid. The results obtained with these four complexants are shown in Figure 8.

The effect of NTA was found to be similar to that of EDTA, which was discussed in detail earlier. Ni sorption was increased at low pH but decreased at high pH, and was higher at 10^{-5} M complexant than at 10^{-4} M. Aging of $Ni/NTA/Fe_2O_3 \cdot xH_2O$ suspensions also showed the same reversal of the initially high sorption at low pH that was observed with EDTA. No NTA sorption measurements have been made, but it is likely that complexant sorption is reponsible for the observed effect of NTA on Ni behavior, as discussed in the EDTA case.

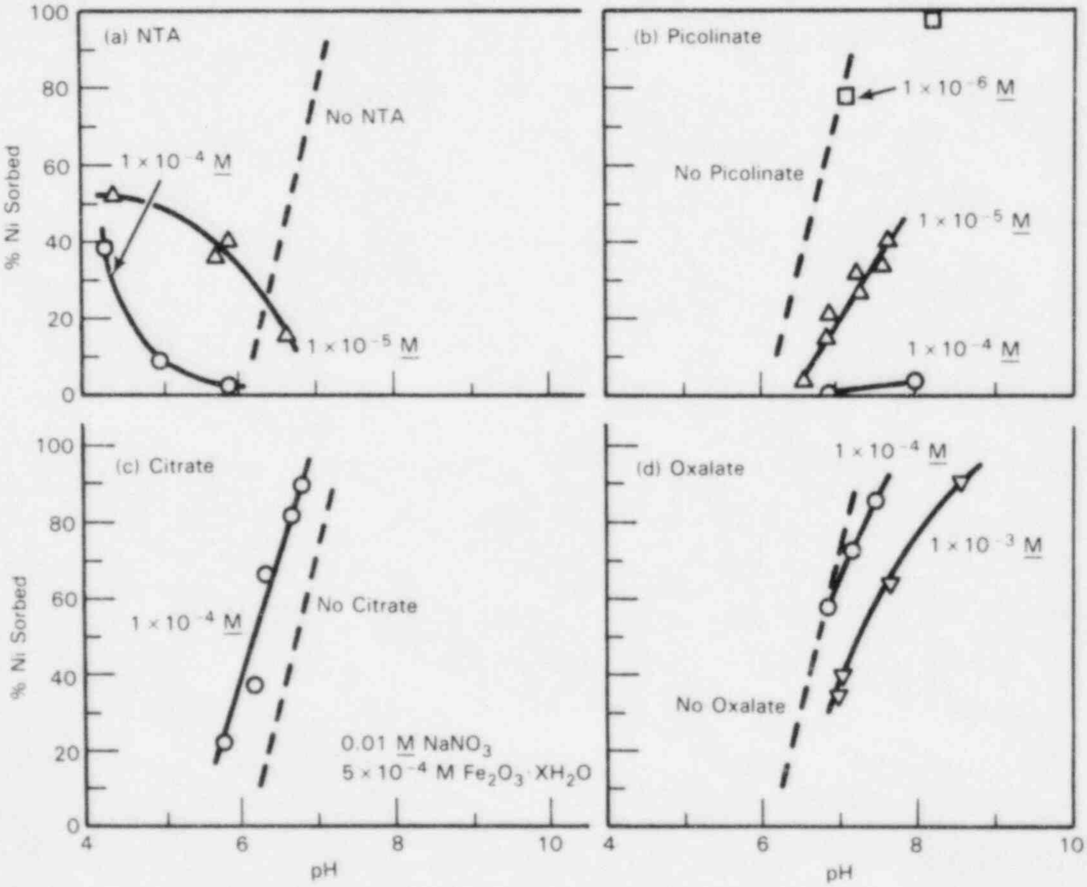


FIGURE 8. Nickel Sorption by $Fe_2O_3 \cdot xH_2O$ in the Presence of Other Complexants

A different type of effect was observed with picolinate complexant (Figure 8b). The observed effect is typical of that expected when nonsorbable complexes are formed; when sufficient complexant is present, it reduces the sorption of the metal ion. With $5x10^{-4}$ M $Fe_2O_3 \cdot xH_2O$, $1x10^{-6}$ M picolinate had no effect on Ni sorption, $1x10^{-4}$ M picolinate essentially prevented Ni sorption, and $1x10^{-5}$ M picolinate had an intermediate effect. The same Ni distribution was rapidly obtained when the Ni-picolinate complex was formed before exposure to the sorbent as when uncomplexed Ni was sorbed and picolinate was then added. This demonstrates that equilibrium is achieved rapidly in the Ni/picolinate/$Fe_2O_3 \cdot xH_2O$ system, as it was in the corresponding EDTA system.

Still another type of Ni sorption behavior was observed with citrate complexant (Figure 8c); citrate increased Ni sorption at all pH values. Increased sorption had also been observed with EDTA and NTA, but only at low pH values with those complexants. As with picolinate and EDTA, the same Ni sorption was obtained when equilibrium was approached from both the precomplexed and the presorbed directions. An experiment was also done at $1x10^{-3}$ M citrate to evaluate the effect of an increased citrate concentration on Ni distribution. The result was that most of the $Fe_2O_3 \cdot xH_2O$ sorbent dissolved, so that the desired comparison could not be made.

With oxalate (Figure 8d), a substantial effect on Ni sorption was observed only at a relatively high complexant concentration. The $Fe_2O_3 \cdot xH_2O$ sorbent was not dissolved by the high oxalate solution, contrary to the experience with the high citrate solution.

Figure 9 summarizes the effects of the five examined complexants on Ni sorption by $Fe_2O_3 \cdot xH_2O$. The differences between the percentage of Ni sorbed in the presence of complexant and the percentage of Ni sorbed in the absence of complexant are plotted against pH, for the conditions of $5x10^{-4}$ M $Fe_2O_3 \cdot xH_2O$ and $1x10^{-4}$ M complexant. This figure illustrates the variety of types of complexant behavior observed in this study. With EDTA and NTA, there is increased sorption (initially, at least, as discussed elsewhere) at low pH and decreased sorption at high pH. Picolinate has no effect at low pH (where uncomplexed Ni is not sorbed anyway) but gives decreased sorption at high pH. Citrate gives increased Ni sorption that is relatively independent of pH and oxalate has relatively little effect on Ni sorption.

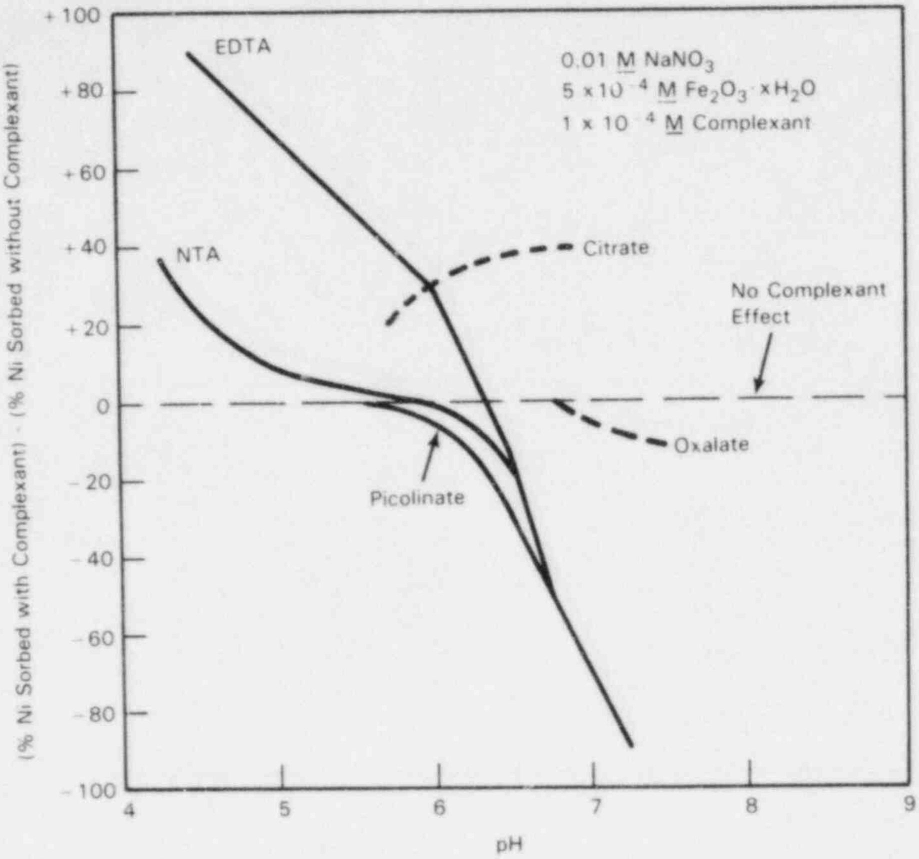


FIGURE 9. Comparison of Effects of Complexants on Ni Sorption by $Fe_2O_3 \cdot xH_2O$

Some of the differences in the effects of different complexants on the sorption of Ni by $Fe_2O_3 \cdot xH_2O$ are doubtless due to differences in the stabilities of the complexes they form with Ni and Fe. However, other effects appear to be more important in defining Ni sorption.

EFFECT OF COMPLEXANTS ON Ni SORPTION BY SiO_2

The effect of several complexants on Ni sorption was also examined with SiO_2 sorbent. The results obtained are shown in Figure 10. The two main features of these data in comparison to those obtained with $Fe_2O_3 \cdot xH_2O$ sorbent (Figures 8 and 9) are: 1) there is no Ni sorption behavior that suggests sorption of complexed species by SiO_2, and 2) a lower complexant concentration is effective in reducing Ni sorption by SiO_2.

The lack of apparent sorption of complexed species is in agreement with the observation that little, if any, EDTA was sorbed by SiO_2. This was observed in experiments at 1×10^{-6} and 1×10^{-5} M EDTA at pH values as high as 7.8.

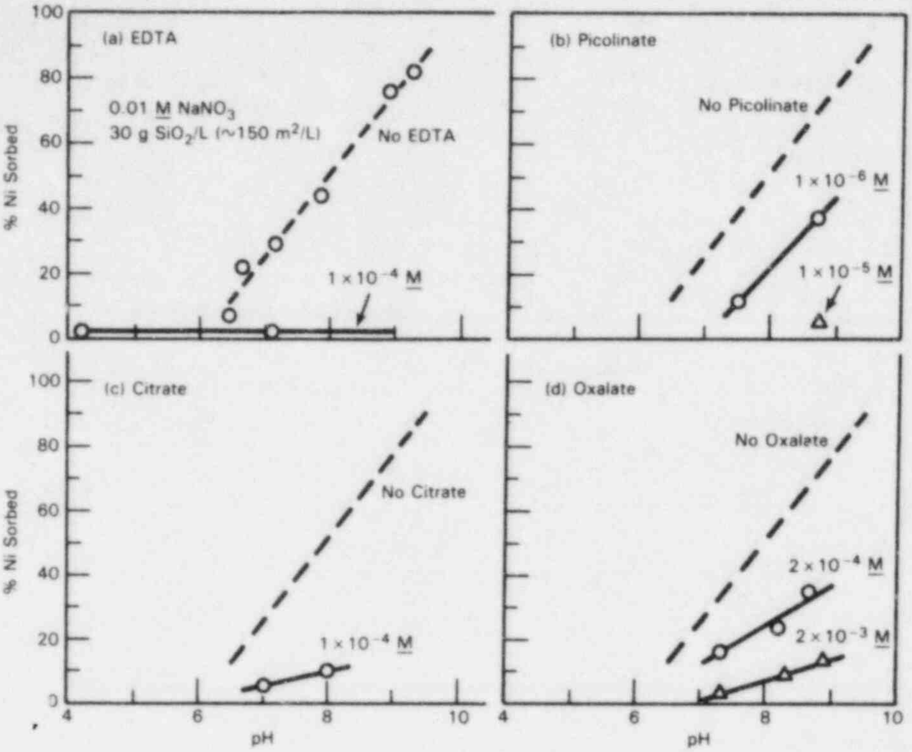


FIGURE 10. Effect of Complexants on Ni Sorption by SiO_2

The effectiveness of lower complexant concentrations in reducing Ni sorption by SiO_2 is probably related to the fact that uncomplexed Ni is sorbed less strongly by SiO_2 than it is by $Fe_2O_3 \cdot xH_2O$. Competition for the complexants by Fe dissolved from the $Fe_2O_3 \cdot xH_2O$ is probably also important in some cases.

With EDTA, identical Ni sorption results were obtained within one day when equilibrium was approached from both the presorbed and the precomplexed directions. This demonstrates that the Ni-EDTA complex is not kinetically inert with SiO_2 sorbent, either.

The Ni sorption data shown in the presence of citrate (Figure 10c) were those measured after 1 to 2 days. This sorption was not stable with time, as illustrated by Figure 11. The addition of citrate rapidly reduced the Ni sorption to a value that was stable for a few days, but then Ni sorption gradually returned to what it had been in the absence of citrate. Earlier work (Swanson 1982, 1983) showed similar short-lived citrate effects in different soil systems and determined that citrate was disappearing from

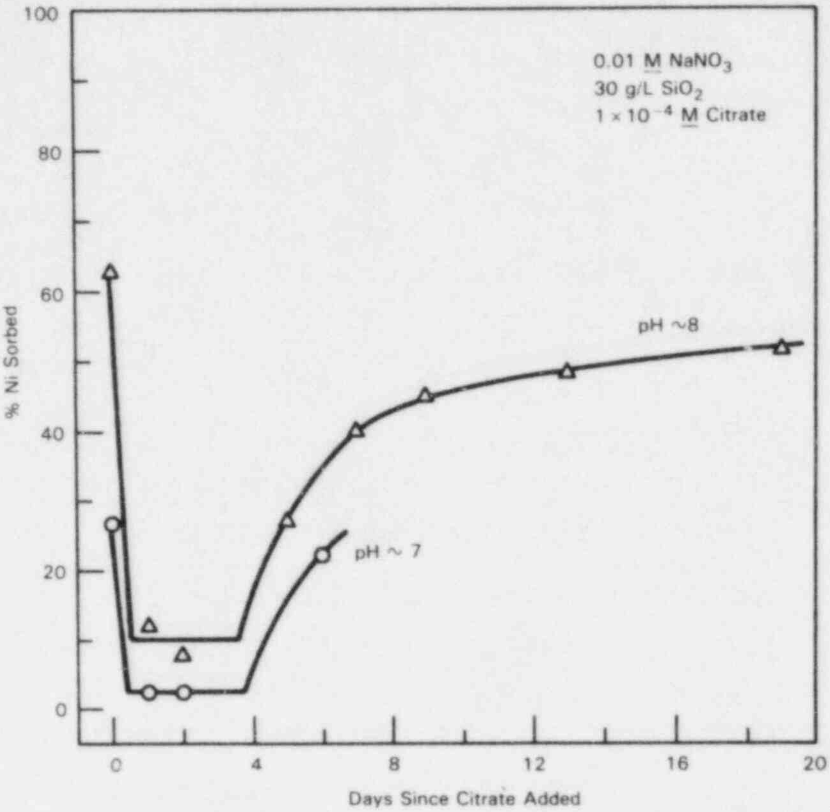


FIGURE 11. Changes with Time in Ni/Citrate/SiO_2 System

solution. It was noted that citrate would thus not be likely to cause excessive radionuclide migration problems.

Similar results were obtained in the presence or absence of light, indicating that the citrate disappearance is not a photolytic process. Such changes with time were not observed over a 19 day time period when the sorbent was $Fe_2O_3 \cdot xH_2O$ instead of SiO_2. The fact that citrate increases Ni sorption by $Fe_2O_3 \cdot xH_2O$ but decreases it by SiO_2 may help explain this difference in apparent stability with time.

The magnitude of Ni sorption by SiO_2 in the absence of complexant indicated in Figure 10 is not correct. Appreciable apparent sorption was observed at these high pH values even in the absence of SiO_2, so the portion due to sorption by SiO_2 is quite uncertain. However, this uncertainty should not affect the qualitative complexant effects discussed above. The apparent sorption may result from sorption by the polypropylene containers or by an impurity present in the solutions; published $Ni(OH)_2$ solubility data indicate that it could not be due to precipitation of that compound.

EFFECT OF EDTA ON Ni SORPTION BY TiO_2

A limited examination of the Ni/EDTA/TiO_2 system was performed to compare the behavior of this sorbent with the others. TiO_2 is of special interest bvecause it is reported to be a strong sorbent and because it is a reported impurity in the clays that we are studying.

The results of this study are shown in Figure 12. A low concentration of EDTA is seen to markedly reduce Ni sorption. This effect occurred shortly after EDTA was added to a suspension containing sorbed, uncomplexed Ni. This indicates that equilibrium is achieved rapidly with this sorbent, too.

The Ni sorption pattern presents no evidence for the sorption of complexed Ni species. Other experiments were done to see if EDTA itself was sorbed by TiO_2; no sorption was found with either $1x10^{-6}$ or $1x10^{-5}$ M EDTA at pH values of 5.6 and 7.0.

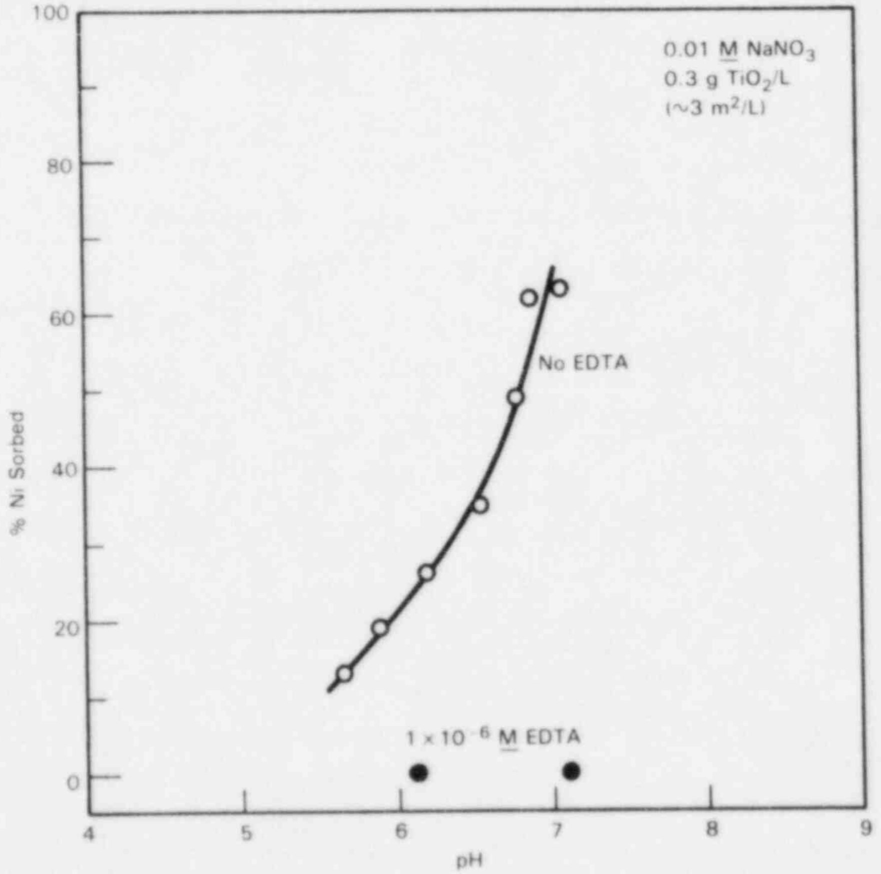


FIGURE 12. Nickel Sorption in the Ni/EDTA/TiO_2 System

Ti was not dissolved from TiO_2 sorbent by EDTA, as was Fe from $Fe_2O_3 \cdot xH_2O$ sorbent. Thus, there is no sorbent-derived ion competing for complexant in this case.

EFFECT OF EDTA ON Ni SORPTION BY KAOLINITE AND BY MONTMORILLONITE

Initial experiments have been performed with crude (unpurified) samples of kaolinite and montmorillonite in the Ni/EDTA system. The results of these preliminary measurements are presented in Figure 13.

With kaolinite (Figure 13a) and precomplexed Ni-EDTA, Ni sorption was high at low pH and low at high pH, and decreased at increasing EDTA concentration. This behavior is similar to that observed with $Fe_2O_3 \cdot xH_2O$ sorbent, where evidence was obtained to indicate that sorbed EDTA was complexing Ni and thereby removing it from solution. Moderate sorption of EDTA by kaolinite was observed in a separate experiment; with 1×10^{-5} <u>M</u> EDTA and 1 g/L kaolinite, 9% of the EDTA was sorbed at pH=6.9 and 25% was sorbed at pH=4.7.

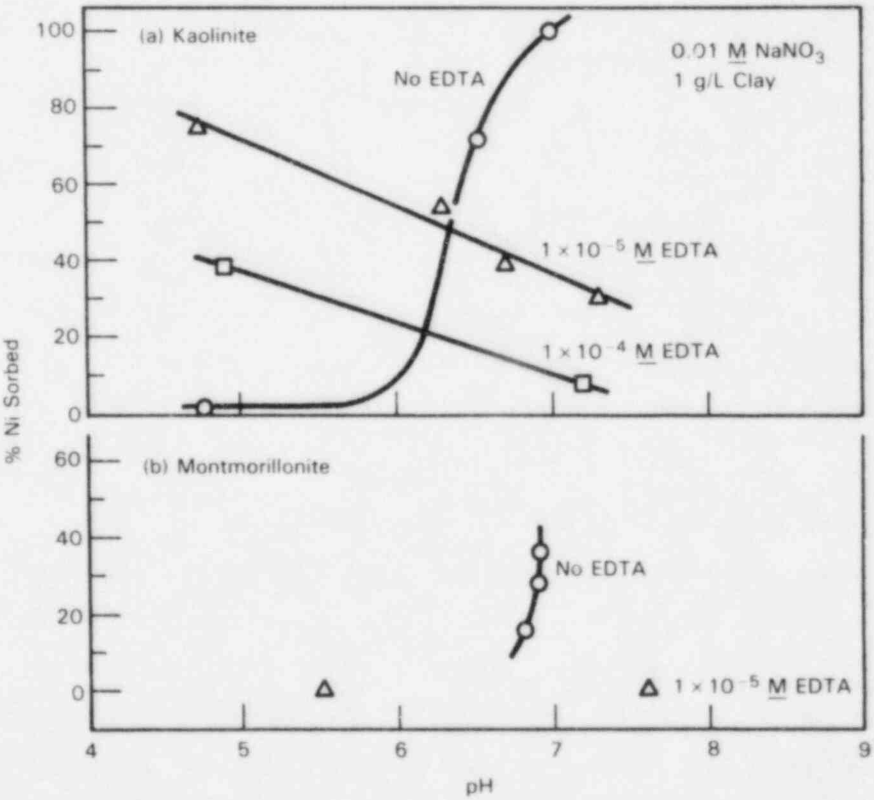


FIGURE 13. Nickel Sorption by Clays in Presence and Absence of EDTA

Of potentially great importance is the observation that slow kinetics are apparent in the Ni/EDTA/kaolinite system. When uncomplexed Ni was first sorbed by kaolinite and the solution was then made 1 x 10^{-5} M in EDTA at pH=7, the Ni sorption remained near 100% for a period of 5 days. This is in marked contrast to the ~35% Ni sorption observed at this pH when Ni was complexed with EDTA before it was exposed to the kaolinite. At steady state, the Ni sorption for a given set of conditions should be the same regardless of the direction of approach to steady state. Lack of such agreement is an indication that slow kinetics are important.

This is the first evidence of kinetically inert complexes obtained in the current work. Such complexes played an important role in our earlier studies with actual soils (Swanson 1981, 1982, 1983). When they exist and are not sorbed by the soil, the Ni (or other toxic element) can migrate through the soil at essentially the same rate as groundwater.

Even fewer data are available with montmorillonite (Figure 13b). In contrast to kaolinite, the Ni sorption behavior in the presence of EDTA does not indicate that sorption of complexed species occurred. However, some EDTA sorption was observed in a separate experiment; with 1x10^{-5} M EDTA and 1 g/L montmorillonite, ~2% of the EDTA was sorbed at pH=7.5 and 8% was sorbed at pH=6.5.

Also in contrast to kaolinite, rapid kinetics were observed with montmorillonite. When the montmorillonite suspension in which 30% of the (uncomplexed) Ni was sorbed was adjusted to 1x10^{-5} M EDTA, rapid desorption of Ni was observed. Only ~8% of the Ni was sorbed after ~3 hours and 3% was sorbed after 2 days.

SORPTION OF Ni-EDTA AND Ni-PICOLINATE COMPLEXES BY ION EXCHANGE RESINS

An important trend in reactor decontamination operations is toward the use of dilute complexant solutions, with subsequent sorption of both nuclides and complexants onto ion exchange resins for disposal. We are especially interested in whether resins sorb radionuclide complexes, which are a major concern in radionuclide migration, and have performed some preliminary investigations in this regard.

In a typical reactor decontamination operation using a dilute complexant solution, the solution is recirculated around a loop containing a cation exchange resin to sorb the metal ions removed from the contaminated surfaces. At the completion of the decontamination, the solution is discharged through both cation and anion exchange resins to sorb the complexants as well as the dissolved metal ions. We have done experiments with both a strong acid cation exchange resin (Bio-Rad AG-50W) and a strong base anion exchange resin (Bio-Rad AG-1); results with Ni and EDTA are presented in Table 2.

Ni sorption by the cation resin was quite high in the absence of EDTA but was decreased as the EDTA concentration was increased. However, it was still quite high at 1×10^{-3} M EDTA, which is in the range of complexant concentrations likely used in dilute decontamination operations. To learn whether Ni-EDTA complexes were being sorbed, the sorption of ^{14}C-labeled EDTA was measured in the presence and the absence of Ni. Essentially identical EDTA sorptions were measured with 0.01 M $NaNO_3$ solutions containing either only 1×10^{-4} M EDTA or 5×10^{-5} M Ni in addition to 1×10^{-4} M EDTA, indicating that Ni-EDTA complexes were not sorbed by the cation resin. The EDTA sorption was surprisingly high in these experiments, giving Kd values of about 100 mL/g.

With the anion resin, no sorption of Ni occurred in the absence of complexants. However, Ni was strongly sorbed when as little as 10^{-6} M EDTA was present, indicating that Ni-EDTA complexes were sorbed by the anion resin. The data shown in Table 2 indicate that the Ni-EDTA complex is sorbed more strongly than is EDTA itself.

Evidence was also obtained for the sorption of a nickel picolinate complex by the anion resin. About 97% of the Ni was sorbed from a 1×10^{-3} M picolinate solution; this is comparable to the results obtained with EDTA (Table 2).

In some reactor decontamination procedures employing dilute complexants, the final solution treatment involves cation and anion exchange colums in sequence, and in others the two resins are mixed together. The latter procedure would be much more likely to result in the presence of sorbed Ni-EDTA complexes since, as shown in Table 2, the sorption of Ni from EDTA solutions was stronger by the anion resin (which sorbs the Ni-EDTA complex).

TABLE 2. Effect of EDTA on the Sorption of Ni by Cation and Anion Exchange Resins

Initial Molarity		Percent Sorbed by Resin(a)			
Ni	EDTA	Ni	EDTA	pH	Ni Kd, mL/g
With Cation Resin					
3×10^{-8}	--	100	--	2.1	$>10^4$
3×10^{-8}	9×10^{-5}	86	N.M.(b)	2.1	610
3×10^{-8}	1×10^{-4}	89	N.M.	2.1	810
3×10^{-8}	1×10^{-3}	38	N.M.	2.1	61
5×10^{-5}	1×10^{-4}	N.M.	50	2.2	
--	1×10^{-4}	--	49	2.1	
With Anion Resin					
3×10^{-8}	--	0	--	3.8	0
3×10^{-8}	1.5×10^{-6}	100	N.M.	4.0	$>10^4$
3×10^{-8}	1.5×10^{-5}	100	N.M.	3.7	$>10^4$
3×10^{-8}	1.4×10^{-4}	99	N.M.	3.3	10^4
3×10^{-8}	1.5×10^{-3}	96	N.M.	2.6	2400
3×10^{-8}	1.6×10^{-3}	98	N.M.	2.6	4900
--	1.5×10^{-3}	--	82	2.6	

(a) After a 1-day contact with 0.01 g air dried resin/mL solution.

(b) Not measured.

How severe a problem would result from the presence of a sorbed Ni-EDTA complex in disposed ion exchange resins depends on a number of factors that have not been quantified. In the worst case, which results in soil systems where the complexes are kinetically inert and not sorbed by the soil, the complexed Ni released by the resin could migrate as rapidly as the groundwater. In other cases there could be little, if any, enhanced mobility resulting from the presence of a sorbed complex on the resin. However, in the absence of other contraints, it would appear prudent from a waste disposal standpoint to separate the toxic element and the complexant by first sorbing uncomplexed Ni on a cation resin and then sorbing the EDTA on an anion resin.

EFFECT OF EDTA ON Pu(IV) SORPTION BY $Fe_2O_3 \cdot xH_2O$

Initial experiments in the Pu/EDTA/$Fe_2O_3 \cdot xH_2O$ system compared the concentration of Pu remaining in solution when an EDTA solution containing preformed Pu(IV)-EDTA complex was contacted with $Fe_2O_3 \cdot xH_2O$ with that remaining in solution when an uncomplexed Pu(IV) solution was contacted with $Fe_2O_3 \cdot xH_2O$. Contrary to expectations, the Pu concentration was found to be lower in the presence of the EDTA. This observation is an indication that the Pu-EDTA complex itself is sorbed by the $Fe_2O_3 \cdot xH_2O$. This indication is not in agreement with the common hypothesis that the importance of Fe in minimizing the EDTA-enhanced mobility of Pu in soils lies in Fe displacing Pu from the complex and leaving ionic Pu bonded with the soil (Polzer 1983).

In both the presence and absence of EDTA, contacting the solution with $Fe_2O_3 \cdot xH_2O$ resulted in the disappearance of most of the Pu from solution within 3 hours, and a small amount of additional Pu disappeared over the next several days. However, the concentrations were markedly lower in the experiment containing EDTA, as shown in Table 3. As mentioned earlier, this effect is attributed to the sorption of the Pu-EDTA complex by $Fe_2O_3 \cdot xH_2O$.

Table 3. Effect of EDTA on the Sorption of Pu by $Fe_2O_3 \cdot xH_2O$(a)

Total Added, M		Time,		Pu in
Pu(IV)	EDTA	Days	pH	Solution, M(b)
1.3×10^{-6}	1.0×10^{-4}	0.1	7.7	$(1.7 \pm 1.1) \times 10^{-9}$
		4	6.0	$(0.2 \pm 0.2) \times 10^{-9}$
1.5×10^{-6}	--	0.1	5.8	$(11.7 \pm 1.3) \times 10^{-9}$
		3	5.9	$(3.0 \pm 0.3) \times 10^{-9}$ (c)

(a) 5.0×10^{-4} M $Fe_2O_3 \cdot xH_2O$ in 0.1 M $NaNO_3$.

(b) Listed uncertainty limits reflect only counting statistics.

(c) A value of $(5.6 \pm 1.5) \times 10^{-9}$ M Pu was found in a similar experiment in the absence of $Fe_2O_3 \cdot xH_2O$, indicating that appreciable sorption by the container had occurred.

Experiments were also conducted under similar conditions except that $Fe_2O_3 \cdot xH_2O$ was absent. With 1.3×10^{-6} M Pu(IV)-EDTA and 1.0×10^{-4} M EDTA at pH = 5.9, about 9×10^{-7} M Pu remained in solution after 1 day. Comparison of this result with that in the presence of $Fe_2O_3 \cdot xH_2O$ shows that the $Fe_2O_3 \cdot xH_2O$ must have been responsible for the rapid and nearly complete disappearance of Pu from solution in that experiment. This is an important observation; whether or not the postulated mechanism for this disappearance is correct, the data indicate that Pu would not be highly mobile in soils containing $Fe_2O_3 \cdot xH_2O$ even if EDTA were present.

Another experiment involved Pu(IV) without either EDTA or $Fe_2O_3 \cdot xH_2O$. Most of the Pu rapidly disappeared from solution in this case also. Since the resultant Pu concentration ($\sim1\times10^{-8}$ M) was much lower than the $\sim1\times10^{-6}$ M value expected from the solubility of amorphous hydrous plutonium dioxide (Rai, Serne, and Moore 1980) or the $\sim2\times10^{-7}$ M value expected from the solubility of plutonium polymer (Rai and Swanson 1981) at pH = 6, it was concluded that the polypropylene container must have sorbed the Pu.

The sorption of uncomplexed Pu by the containers used in these experiments may affect the values obtained, but the conclusion that the Pu-EDTA complex is sorbed by $Fe_2O_3 \cdot xH_2O$ would not be affected by this phenomenon.

Corroborative evidence for the sorption of a Pu-EDTA complex by $Fe_2O_3 \cdot xH_2O$ was obtained by measuring the effect of Pu on the sorption of EDTA by $Fe_2O_3 \cdot xH_2O$. Table 4 presents the results of these experiments. In three experiments in the absence of Pu, ~17% of the EDTA was sorbed by 1.5×10^{-4} M $Fe_2O_3 \cdot xH_2O$ at pH ~7.4. When part of the EDTA was complex by Pu(IV) before exposure to $Fe_2O_3 \cdot xH_2O$, a much larger portion of the EDTA was sorbed. This indicates that a preformed Pu(IV)-EDTA complex is indeed sorbed by $Fe_2O_3 \cdot xH_2O$. This sorption mechanism is a different than that in the Ni/EDTA/$Fe_2O_3 \cdot xH_2O$ system, where EDTA sorption was the same in the presence or absence of Ni and it appeared that sorbed EDTA complexes Ni and thereby removes it from solution.

Calculation of the EDTA:Pu ratio in the sorbed complex gave values ranging from 0.25 to 0.5 (Table 4), assuming that all of the sorbed Pu was present as a complex. Because we don't know whether this assumption is correct, we apply no significance to these ratios. However, we do feel that the data clearly show that sorption of a Pu(IV)-EDTA complex by $Fe_2O_3 \cdot xH_2O$ does indeed occur.

Table 4. Evidence for Sorption of Pu(IV)-EDTA Complex by $Fe_2O_3 \cdot xH_2O$(a)

Tube No.	Initial Composition, M		Initial	Time		% of Total Sorbed		EDTA Sorbed as(b)	EDTA/Pu in(c)
	EDTA	Pu	EDTA/Pu	Days	pH	EDTA	Pu	Pu Complex, M	Sorbed Complex
130	3.8×10^{-6}	--	∞	1	7.4	19	--	--	--
				2	7.3	19	--	--	--
118	5.8×10^{-6}	--	∞	1	7.4	16	--	--	--
				2	7.5	13	--	--	--
121	5.8×10^{-6}	--	∞	1	7.4	17	--	--	--
129	3.5×10^{-6}	4.5×10^{-6}	0.8	1	7.3	49	100	1.1×10^{-6}	0.25
				2	7.2	46	100	1.0×10^{-6}	0.23
117	5.4×10^{-6}	4.5×10^{-6}	1.2	1	7.2	61	100	2.4×10^{-6}	0.53
				2	7.2	58	100	2.2×10^{-6}	0.49
120	5.4×10^{-6}	2.3×10^{-6}	2.4	1	7.2	38	100	1.1×10^{-6}	0.49

(a) 1.5×10^{-4} M $Fe_2O_3 \cdot xH_2O$.

(b) [(Fraction of EDTA sorbed in presence of Pu)-0.17] (initial EDTA concentration).

(c) (Molarity of EDTA sorbed as Pu complex)/(molarity of Pu sorbed).

Pu(V)/$Fe_2O_3 \cdot xH_2O$ System

In the absence of complexants which may stabilize Pu(IV), Pu(V) is the predominant valence state of soluble Pu under environmental conditions (Rai, Serne, and Swanson 1980). Before examining the effects of organic complexants on the behavior of this species, an experiment was done in the absence of any such complexant.

A suspension containing 5×10^{-5} M $Fe_2O_3 \cdot xH_2O$ and 0.01 M $NaNO_3$ was aged for a day at pH=7 and then was spiked with a Pu(V) solution. Samples of the suspension were periodically removed and analyzed for Pu valence states both before and after filtration. The valence state analyses were performed by TTA extraction of acidified samples, with only a few minutes elapsing between acidification to 0.3 M and extraction. The analyses of the unfiltered suspension thus include the Pu that was present in solution plus that which was present on the $Fe_2O_3 \cdot xH_2O$, and which was readily converted to nonpolymeric species when the sample was acidified. The filtrate analyses include only the Pu that was present in solution.

The results of this test (Table 5) clearly show that Pu(V) was reduced to Pu(IV) and/or Pu(III), which was then sorbed by the $Fe_2O_3 \cdot xH_2O$. While no

TABLE 5. Reduction of Pu(V) in $Fe_2O_3 \cdot xH_2O$ Suspension

$Pu=5x10^{-8}$ M, $Fe_2O_3=5x10^{-5}$ M, $NaNO_3=0.01$ M, pH=6.9

Time,	In Unfiltered Suspension, % of Total Added			In Filtrate, % of Total Added		
Hr	Pu(III+IV)	Pu(V)[(a)]	Total Pu	Pu(III+IV)	Pu(V)[(a)]	Total Pu
0.1	3	97	100		Not analyzed	
3.0	18	44	62	1	46	47
26	17	2	19	0	2	2

(a) The analytical method actually determined Pu(V) and (VI). Other considerations indicate that Pu(VI) would not be important under these conditions.

Pu(IV) was present in the Pu(V) solution spiked into the suspension, the unfiltered suspension showed a small amount of Pu(IV) and/or Pu(III) after 0.1 hours, and markedly more after 3 hours. Little or no Pu(IV) and/or Pu(III) was found in the filtrate, showing that that present in the suspension was associated with the solid phase. The concentration of Pu(V), on the other hand, was the same in the suspension as in the filtrate, indicating that little, if any, of the Pu(V) was associated with the solid.

As time progressed, the Pu(V) concentration decreased to near zero, and the total Pu found in the suspension also decreased. The decrease in the amount of total Pu found indicates that either 1) much of the Pu(IV) and/or Pu(III) was sorbed in a form (e.g., plutonium polymer) not readily converted to monomeric species (which could be determined in the extraction analyses) or 2) much of the Pu(IV) and/or Pu(III) was sorbed by the container instead of by the suspended $Fe_2O_3 \cdot xH_2O$.

The reduction of Pu(V) during contact with Fe_2O_3 was not expected. The Eh of the suspension was measured to be 342 mV. The validity of the measurement is questionable because of the low concentration of electroactive ions. However, if the measurement was valid, the potential was low enough that reduction would be expected. The low potential indicates that Fe(II) was the predominant valence state in solution. Lindsay (1979) comments that the activity of Fe(II) in soils is most often greater than that of Fe(III), which is consistent with the reduction that was observed here.

Another mechanism proposed to explain the reduction of Pu(V) is the disproportionation of Pu(V) to Pu(IV) and Pu(VI). However, published data (Cleveland 1970) indicate that this reaction is much too slow to account for the observed data; a 5×10^{-8} $\underline{M}$ Pu(V) solution at pH=7 is calculated to disproportionate at a rate of $\sim 10^{-20}$ $\underline{M}$/hr ($\sim 10^{-11}$ %/hr).

Because of the reduction of Pu(V) by the $Fe_2O_3 \cdot xH_2O$ suspension, the effect of complexing agents in this system was not examined. The results obtained in the Pu(IV)/$Fe_2O_3 \cdot xH_2O$ system would apply here as well.

EFFECT OF EDTA ON Cd SORPTION BY $Fe_2O_3 \cdot xH_2O$

One objective of this project is to address the question of organic complexant-enhanced mobility of nonradioactive toxic elements, as well as radioactive elements, that might be present in commercially generated low-level wastes. The literature regarding the presence of such elements was surveyed to identify candidate elements to be included in this study. Of special interest were those whose mobility would be expected to be affected by organic complexants.

There appears to be very little valid information on the identities and the quantities of nonradioactive toxic elements in low-level wastes. A study of the chemical toxicity of low-level wastes was performed several years ago by General Research Corporation (1980), but that study emphasized toxic organic compounds. The report did say "...selected inorganics that are representative of metals found in LLW burial sites include barium, cadmium, chromium, copper, lead, and zinc," (p. 105) and "The three elements of greatest concern (in rank order) appear to be cadmium, copper, and chromium." (p. 140). It is to be stressed that the report did <u>not</u> say that these elements are present in LLW in sufficient quantities to be of concern; it said that <u>if</u> these elements are present in sufficient quantities, they could be of concern.

The question of chemical toxicity of low-level wastes has also been addressed by Wickham (1983), who is attempting to develop a waste classification system that evaluates the relative total hazard of chemical and radiological waste mixtures. Wickham provides evaluation of the total hazard of two types of low-level wastes; evaporator bottom concentrates, and reactor control rods containing 80% silver, 15% indium, and 5% cadmium. The chemical hazard was judged to be insignificant relative to the radiological hazard with the evaporator concentrates, but the chemical hazard of the silver and the cadmium was judged to outweigh the radiological hazard with the control rods.

Because of the lack of appropriate information on the presence of nonradioactive toxic elements in low-level wastes, the selection of elements to be studied in this project was difficult. Cadmium appeared to be the most reasonable choice and was selected for initial study.

The results of the initial experiments in the Cd/EDTA/$Fe_2O_3 \cdot xH_2O$ system are compared with those in the Ni/EDTA/$Fe_2O_3 \cdot xH_2O$ system in Figure 14. The behavior of the two toxic elements is seen to be qualitatively the same. However, the sorption of Cd is greater than that of Ni both in the presence and absence of EDTA.

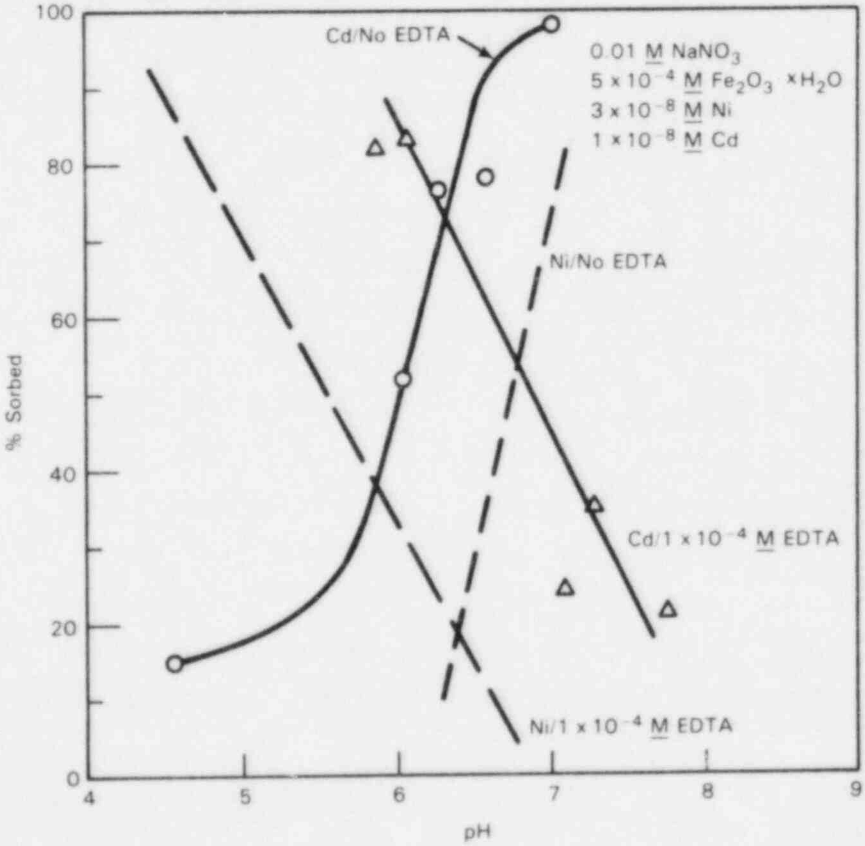


FIGURE 14. Cadmium and Ni Sorption by $Fe_2O_3 \cdot xH_2O$ in Presence and Absence of EDTA

CONCLUSIONS

A wide diversity of effects of organic complexants on toxic element sorption by generic soil components has been demonstrated in the experimental work of this project. The effects vary not only among complexants, but also among toxic elements and among soil components. In some toxic element/complexant/soil component systems, the complexant results in increased toxic element sorption (decreased mobility) while in other systems the complexant results in decreased toxic element sorption (increased mobility).

These results expand on those obtained earlier (Swanson 1981, 1982, 1983) and substantiate the conclusion that disposal requirements should not be the same for all organic complexants, since different complexants have markedly different effects on toxic element mobilities. These results also suggest that the effect of complexants on toxic element sorption should be examined with soils from specific proposed commercial low-level waste disposal sites.

With one soil component, $Fe_2O_3 \cdot xH_2O$, sorption of EDTA complexes of both Ni and Pu(IV) appears to be important. However, the data obtained so far indicate that this apparent complex sorption occurs by different mechanisms with the two elements. The sorption of Ni in the presence of EDTA apears to involve complexing of Ni by EDTA that is sorbed by the $Fe_2O_3 \cdot xH_2O$, while that of Pu(IV) appears to involve sorption of a preformed Pu(IV)-EDTA complex in addition to sorption of EDTA.

While changes with time were observed in the Ni/EDTA/$Fe_2O_3 \cdot xH_2O$ system, they were not changes like those observed earlier (Swanson 1981, 1982, 1983) with Ni/EDTA and specific soils. The kinetically inert behavior observed earlier is especially important since kinetically inert complexes that are not sorbed by the soil can migrate at the same rate as groundwater. The results of the preliminary experiments in the Ni/EDTA/kaolinite system indicate that kinetically inert complexes are important in that system.

Of the complexants studied, citrate and oxalate would provide the least chance of enhancing Ni (and presumably other toxic elements) mobility. Their complexes are weaker than the others, so that a higher concentration is required to have an effect. With $Fe_2O_3 \cdot xH_2O$ sorbent, low concentrations of citrate decrease Ni mobility while low concentrations of oxalate have little effect on Ni mobility. However, high concentrations of citrate dissolve

$Fe_2O_3 \cdot xH_2O$, and thus greatly increase Ni mobility in that sorbent system. With SiO_2 sorbent, low concentrations of citrate initially increase Ni mobility but the effect is short-lived.

Ni-EDTA and Ni-picolinate complexes are sorbed by anion ion exchange resins, which are often used to clean up reactor decontamination solutions. Sorption of such complexes would not occur if such clean up operations employed cation and anion resins in sequence rather than together.

Plutonium should not be highly mobile in soils containing $Fe_2O_3 \cdot xH_2O$. Uncomplexed Pu(IV) is very highly sorbed, and the presence of EDTA results in even lower mobility because of the sorption of a Pu(IV)-EDTA complex. Plutonium (V), which might be highly mobile in the environment, is reduced by $Fe_2O_3 \cdot xH_2O$ suspensions,thereby markedly decreasing its mobility.

ANTICIPATED RESULTS IN FOURTH QUARTER OF FY 1984

Unanswered questions remain in all of the systems discussed in this report. Additional work is planned in all of the systems to address these questions, but some will be given higher priority than others.

Highest priority will be given to the effect of the various complexants on Ni sorption by the clays (kaolinite and montmorillonite). Of special interest here will be the determination of which complexes exhibit kinetic inertness and which don't, since this property is so important in toxic element migration considerations.

Additional investigation into the reason for the changes with time that occur when Ni-EDTA is sorbed by $Fe_2O_3 \cdot xH_2O$ will also be given priority. The hypothesis that EDTA degradation products may be responsible for this effect will be tested by obtaining additional analyses, hopefully of sorbed complexants as well as those that remain in solution.

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13. ABSTRACT (200 words or less)

This report describes the initial results obtained in a project whose objective is to determine how and to what extent organic complexants affect the mobility of toxic elements in subsurface groundwaters at commercial low-level waste disposal sites. Generic soil components (e.g., hydrous oxides, silica, clays) are being employed so that the results will be broadly applicable. Organic complexants used in the nuclear industry are being emphasized.

Data have been obtained with two radioactive (Ni and Pu) and one nonradioactive toxic element (Cd). Work with Ni has been emphasized; it was studied with five different generic soil components (hydrous ferric oxide, silica, titania, kaolinite, and montmorillonite) and five different complexants (EDTA, NTA, picolinate, citrate, and oxalate). EDTA was the complexant studied most extensively and hydrous ferric oxide was the most studied soil component.

A wide diversity of effects of organic complexants on toxic elements sorption was observed. The effects vary not only among complexants, but also among toxic elements and among soil components. In some systems the complexant results in increased toxic element sorption (decreased mobility) while in other systems the complexant results in decreased toxic element sorption (increased mobility).

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