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Studies of the effects of chelates on the leaching of radionuclides from cement

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The University of Arizona, 1991

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Ann Arbor, MI 48106

STUDIES OF THE EFFECTS OF CHELATES ON THE

LEACHING OF RADIONUCLIDES FROM CEMENT

by

Daro Mitchell Ferrara

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A Dissertation Submitted to the Faculty of the

DEPARTMENT OF NUCLEAR AND ENERGY ENGINEERING

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY
WITH A MAJOR IN NUCLEAR ENGINEERING

In the Graduate College

THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read

the dissertation prepared by __Daro Mitchell Ferrara__

entitled __Studies of the Effects of Chelates on the Leaching of Radionuclides__

__from Cement__

and recommend that it be accepted as fulfilling the dissertation requirement

for the Degree of __Doctor of Philosophy__.

Signature	Date
	May 10, 1991
	May 10, 1991
	May 29, 1991
	5/28/91
	5/28/91

Final approval and acceptance of this dissertation is contingent upon the
candidate's submission of the final copy of the dissertation to the Graduate
College.

I hereby certify that I have read this dissertation prepared under my
direction and recommend that it be accepted as fulfilling the dissertation
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Dissertation Director   Date   May 10, 1991

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SIGNED: _Dario Ferrara_

Dedicated to Jodi, J.J., Mom and Dad. Their love, support, encouragement, patience and interest in this work has made this as much theirs as it is mine.

ACKNOWLEDGMENTS

I would like to thank Dr. Morton E. Wacks for his guidance and friendship, and for the opportunities he has made available to me. In addition, the advice and insight provided by the faculty, staff and students of the University of Arizona Nuclear and Energy Engineering Department has been invaluable.

I am also indebted to Dr. Henry Freiser of the University of Arizona Chemistry Department for his advice and encouragement.

This work could not even have been started without the oversight of the people at the Institut für Nukleare Entsorgungstechnik, at the Kernforshungszentrum Karlsruhe, in Karlsruhe, Germany. Special thanks are in order to Dr. R. Köster, Dr. P. Vejmelka, Mrs. I. Kahl, Mr. W. Kluger and Dr. G. Rudolph.

Of course, without the love of God none of this would have been possible, nor would it have been important. I thank Jesus for all He has given and shown me and for the many people He has brought into my life.

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ABSTRACT

To evaluate the release of some important radionuclides from cement waste forms, a variety of studies have been completed. Leach rates and equilibrium concentrations of some complexing agents and radionuclides were measured, and the effect of a simulated waste form on these values was determined.

Complexing agent concentrations were evaluated. Tests in deionized water showed ethylenediaminetetraacetic acid (EDTA) was leached from a simulated waste form more rapidly than nitrilotriacetic acid (NTA) which was released more rapidly than citric acid. Equilibrium concentrations were measured in deionized water, saturated sodium chloride, 24% magnesium chloride and Q-brine which is a simulated groundwater based on magnesium chloride. At equilibrium, the EDTA release fraction was independent of the amount of EDTA in the cement. The citric acid concentration was constant at less than 10^{-5} M. Finally, NTA concentrations and release fractions were both dependent on the cement loading.

To evaluate the effect of complexing agents on some radionuclides, leach rates of cesium and cobalt and equilibrium concentrations of cobalt and uranium were studied. The effects of EDTA, NTA and citric acid on release rates of

cesium and cobalt were studied, and the effects of several complexing agents on the equilibrium concentrations of cobalt and uranium were examined. Complexing agents had no effect on cesium leach rates. In water and in sodium chloride, cobalt and uranium concentrations in the presence of cement did not vary with any complexing agent. In Q-brine in the presence of cement, tartaric acid, EDTA and NTA increased the soluble cobalt concentration two orders of magnitude, and citric acid had a much smaller effect. Uranium concentrations in Q-brine were increased by EDTA, tartaric acid and citric acid when cement was in the system.

CHAPTER 1

INTRODUCTION

The most likely pathways for release of
radionuclides from a waste repository are usually considered
to be through an intruder or through intrusion of water to
the waste form followed by release of the radionuclide to
the water and movement of the solution from the repository.
The latter of these two scenarios and the effects that
complexing agents would have on it were examined in these
studies.

In this scenario, several species would be leached
from the waste form as it equilibrates with the groundwater.
Several characteristics of the solution, e.g. pH and calcium
concentration, would then be dependent on the waste form.
For low-level (LLW) and intermediate-level (ILW) waste,
cement-based waste forms have been used most often for
immobilization. This in itself would be motivation enough
for studying simulated cement waste forms. In addition,
while high-level waste, HLW, is immobilized in glass, the
repositories will be cement. The effects of the repository
on the solution chemistry will, therefore, be similar to the
effects of the LLW and ILW waste form on the solution.

Evaluation of the Source Term

The scenario of interest can be divided into the intrusion of water, movement of the radionuclide from the waste form into the water, transport of the solution through the near-field, through the far-field and into the accessible environment. The second step is called the source term since this process supplies the radionuclide for the release. Studies of radionuclide source terms from radioactive waste can generally be grouped into one of three categories. The traditional approaches have been the static tests and dynamic (also called flow) tests. More recently, another approach has gained popularity. This has been the equilibrium study.

The first type of study, static leach tests, is run by immersing a waste form in a leachant and allowing it to equilibrate undisturbed until a sample is taken. At appropriate times, samples are either taken of the leachant, or the waste form is removed from the system and immersed in a fresh solution. Examples of standard static leach test procedures are ANS 16.1[1] and MCC-1[2].

The other traditional leach tests, dynamic tests, are run by immersing a waste form in a leachant and running fresh leachant into the container at the same rate as leachant is being removed from the system. Samples are

taken from the leachant as it leaves the container. An example of dynamic tests is MCC-4[3].

The more recent approach, equilibrium studies, is to determine the concentrations of species in a leachant at equilibrium with a waste form[4,5]. In repositories, groundwater flow rates are very low. Therefore, species should have sufficient time to equilibrate with waste forms. Source term concentrations should be very close to equilibrium values.

Static and dynamic leach test results are usually expressed in terms of leachability indexes, and cumulative release fractions. These results are usually very dependent on a number of experimental parameters such as leachant flow rates.

On the other hand, equilibrium studies provide equilibrium concentrations and release fractions which are less sensitive to variations in experimental fluxuations. Another advantage of equilibrium studies is that results are susceptible to modelling through one of the chemical equilibrium codes available[6,7,8]. While the results of these models are dependent on the equilibrium coefficients used, they have been applied to a variety of cases with varying degrees of success[9,10,11].

Source terms are decreased by a number of parameters. The matrix of the waste form has a large effect. In cement, for example, use has been made of such additives as fly ash[12] and blast furnace slag[13], and such materials as polymer modified cements have been developed[14] to reduce the source term. In addition, disposal of waste in a dry environment reduces the release rates. Finally, preferential leaching of species other than the radionuclides may also account for decreases in the radionuclide release rates. In cement, calcium is present in large abundances and may act to inhibit the releases.

On the other hand, many factors can increase the release rates of radionuclides. Ingression of groundwater into a repository can provide an opportunity for increases in release rates. In addition, loading of the waste form often degrades the physical properties[15,16] which are responsible for retaining radionuclides. The presence of liquids in the waste form can also increase the release rate of radionuclides[17]. Finally, complexation with other species in the waste stream or with soluble species in the waste form itself can provide for more rapid releases of the radionuclides.

Complexing Agents in Radioactive Waste

Low and intermediate-level radioactive wastes often contain a number of compounds which may alter the behavior of the waste form. One group frequently in the waste streams is complexing agents. Since these compounds are often soluble in aqueous solutions and can form complexes with metal ions, they have the potential to increase the radionuclide concentrations in solutions around a waste form[18].

Many complexing agents come into the waste stream through decontamination processes. Some of those most commonly used for decontamination have been citric acid[19,20,21], ethylenediaminetetraacetic acid[19,20,21], oxalic acid[19,20,21] and tartaric acid[19,20].

Although many of the decontamination solutions used are proprietary, probably the most widely accepted decontamination methods are based on a permanganate solution wash followed by an ammonium citrate rinse. The citrate attacks much of the contamination not removed in the initial wash and strips the residual permanganate from the surface. Typically, concentrations of about 100 g of ammonium citrate per liter have been used[19].

Ethylenendiaminetetraacetic acid, EDTA, has also been added to the ammonium citrate rinses to reduce precipitation. EDTA binds to the ions increasing their solubility. Concentrations of about 1 g of EDTA per liter have been typical.

In addition, oxalic acid has played several roles in decontamination solutions. It has been used alone or in conjunction with other decontamination species[22], such as in the citrate solution described above. Some applications have been keeping iron in solution, removing rust from iron and in cleanup of uranium and fission products from fuel failures. Typical oxalic acid concentrations range from 1 to 100 g/l.

Tartaric acid has also been used in more specific applications. Although in recent years, it has not been as widely used, the effectiveness of tartaric acid was proven in a number of early radionuclide decontaminations[19].

Like these other complexing agents, nitrilotriacetic acid, NTA, has also been used in typical decontamination applications[20], but has been used more often as a laundry detergent in cleaning active and inactive clothing[23].

Complexing agents also enter the radioactive waste stream through reprocessing. By far, the greatest amount is of tributyl phosphate, TBP, which has been extensively used in the PUREX process[24,25].

Hydrolysis of TBP produces dibutyl phosphate, DBP,[26,27] which is also present in waste from the PUREX process. Hydrolysis of TBP to produce DBP may continue after the waste is immobilized in a cement waste form.

In addition to the complexing agents in the waste streams, species from the waste form may bond to the radionuclides and play an important role in establishing equilibrium concentrations of the radionuclides. Some species which may have significant effects in cement waste forms are phosphates and silicates. These species may form complexes with the radionuclides and alter their solubility in the leachant.

Once in the repository, complexing agents may eventually be released from a waste form[28]. They may then reach nearby waste forms. Therefore, these compounds may affect not only the waste form in which they are isolated, but they may also change the equilibrium solutions around neighboring waste forms.

Metal Ions of Interest

In choosing which ions to study, several considerations should be made. First, if the effect of interest occurs, the metal must exhibit this effect to the extent that it can be measured. Secondly, the behavior of the metal should be representative of other metals not

studied. In addition, species of practical interest are preferable. Finally, manipulation of the radionuclides should not be difficult. For these reasons, cesium, cobalt and uranium were studied.

For decades, leach tests have been used to study the radionuclide releases from radioactive waste forms. Cesium, cobalt and uranium have been used routinely in these studies. Each of these elements has been used to represent a group of elements. While cobalt and uranium are often used to simulate actinides, the actinides themselves have also been the subject of several studies. More recently, the nuclear industry has developed an interest in studying the effects of complexing agents on the release of radionuclides from waste[29]. Not surprisingly, a large number of these studies have been done on the elements mentioned above.

Cesium salts are very soluble in aqueous solutions. For this reason, cesium-137 is often used as a tracer for providing solution concentrations high enough to be measured using a Ge(Li) detector. The cesium ion acts as a good indicator of the behavior of soluble species. Because of its solubility and relatively high abundance in some waste streams, cesium is often of prime interest in safety analyses[30,31]. One disadvantage in using cesium is that it does not form complexes with most of the complexing agents

studied. Effects of the complexing agents, therefore, will not be measurable using cesium.

Cobalt, on the other hand, is not as soluble in aqueous solutions, however it forms strong complexes with many of the complexing agents studied. If the complexing agents have an effect on the solubility of a species, one would expect to see the effect on cobalt. Cobalt can also be easily measured using cobalt-60 as a tracer. In addition, cobalt has become a standard, useful for comparison of results from several different studies[30,31,32]. For these reasons, cobalt was used here in both the leach rate studies and equilibrium experiments.

One disadvantage in using cobalt is the ease in which it is oxidized from cobalt (II) to cobalt (III). The resulting ion forms stronger complexes with most complexing agents. If the goal of these studies were to evaluate the release rates in a controlled system, it would be necessary to control the Eh or to measure the oxidation state of the cobalt.

In addition to cobalt, uranium forms moderately strong complexes with many of the complexing agents used here. The long half-life of uranium has made it important for regulatory considerations. This element is often in low and intermediate level waste at levels up to 1 kg of uranium per 200 1 drum[33].

In addition to uranium, the other actinides are of interest in source term studies[34] because of the large amounts possibly present in the waste and the long half-lives some of these species have. However, these substances are more difficult to handle[35] requiring manipulations to be carried in a glove box. In addition, cobalt and uranium can be used as a models for the actinides. For these reasons, actinides other than uranium were not studied here.

Lanthanides have also been used to model the actinides. Lanthanides are much easier to handle than actinides, however they are more expensive than cobalt. In addition, they are not as commonly used in studies of radionuclide releases. For this reason, cobalt and uranium were used instead of the lanthanides as models for fission product and actinide leaching behavior.

Chemical Equilibrium Codes

Several different chemical equilibrium codes have been developed for geochemical applications[36]. The basic equilibrium calculations are the same, but differences exist in such areas as flexibility of input data, activity coefficient corrections, ability of codes to be extended, the data base used and the ease with which codes can be transported to other computers. While several of the codes have been applied to radioactive waste forms, three have

been used far more than the others. These are MINEQL,
PHREEQE and EQ3/6.

MINEQL was developed at Massachuessets Institute of
Technology[6]. It can be easily transported to different
computers. The code works well for very dilute solutions
when the pH and total concentrations of species are known.
Calculations cannot be made when the input data is in a
different format, and even slightly concentrated solutions
cannot be reliably handled by the code.

Another chemical equilibrium code, PHREEQE, was
created by the U. S. Geological Survey and has become very
popular for modelling radioactive waste form releases[8].
This code has the ability to accept input data in a variety
of formats and can be used with some degree of reliability
in solutions with ionic strengths as high as 0.1 to 1 molal.
PHREEQE has a very extensive, well-documented data base,
however it cannot be conveniently altered to fit individual
needs, especially for further corrections in ionic strength.

Perhaps the most versatile of the codes is EQ3/6[9].
In its present form, calculations can be made from a variety
of input data formats with some degree of reliability for
solutions with ionic strengths as high as 0.1 to 1 molal.
In addition, the code can easily be modified. One notable
feature is the incorporation of an option for activity
corrections using Pitzer's equation. While much of the

necessary coefficients are not yet available, this code has the ability to use the information as it is developed. Finally, EQ3/6 can be transported easily to several different types of computers.

Waste Form Regulations

While this is not the appropriate forum for a rigorous review of the regulations governing the disposal of radioactive waste, two groups of regulations were among the motivations for these studies.

First of all, the potential for increased radionuclide release by the presence of chelates has prompted one of the three currently active low-level waste, LLW, disposal sites to reject waste containing these species above a specified concentration. While this may seem somewhat extreme, uranium and cobalt[37] releases have been reported from waste containing EDTA which was buried without being immobilized.

Additional motivation for studies of solutions in equilibrium with waste forms comes from HLW disposal regulations. Immobilization of high-level waste, HLW, by vitrification is scheduled to begin at Savannah River, SC within two years and then at Hanford, WA. Regulations which are to govern the disposal of this waste form are to be based on the EQ3/6 chemical equilibrium codes. Application

of EQ3/6 to real world groundwaters is of questionable value, since these solutions will undoubtably have ionic strengths which are too high for the code in its current form.

Scope of the Studies

Several approaches were taken in these studies of the radionuclide release from a simulated cement waste form. Evaluations included determinations of leach rates and equilibrium concentrations of both the complexing agents and metal ions. Results from the equilibrium studies were compared to predictions from the chemical equilibrium codes.

Leach rates were studied. The purposes of these were to compare the release rates of cesium and cobalt ions to those of some complexing agents and to determine whether the complexing agents had an effect on the radionuclide release rates. The leach rate studies were limited in their scope. Only the most soluble element, cesium, and the element which forms the strongest complexes, cobalt, were examined. In addition, the studies were not an exhaustive examination of all the complexing agents. Three complexing agents were chosen based on the likelihood of having a measurable effect on the radionuclide leach rates.

Equilibrium concentrations of some chelating agents were also measured. The amounts of the chelating agent in solution were compared to the amount of soluble radionuclide to get information on the possible nature of the soluble species.

The most extensive portion of these studies was the evaluation of the metal ion equilibrium concentrations. Of specific interest was the effect of the cement, the leachant and the complexing agents on the concentrations of cobalt and uranium at equilibrium.

While these studies were extensive, the goal was to determine the effects of the complexing agents on the radionuclides and to evaluate the feasibility of interpreting these results with very limited knowledge of the system. For this reason, very little effort was made toward careful characterization of precipitates or other parameters in the solution, e.g. Eh was not determined.

In addition, only the analysis of the cement provided from the manufacturer was used. The results were interpreted on the basis of compounds that were reported as being present. When results were inconsistent with the behavior of the known components, possible explanations were then given based on the possible behavior of other compounds, e.g., from the cement. This approach was taken since detailed information of the cement is often not given.

CHAPTER 2

THEORY

Because of the concentrations and variety of species
involved, a rigorous evaluation of the equilibrium
concentrations in a cement waste form/groundwater system
would be very complex. Even determining the order of
magnitude would require consideration of activity
coefficients and reduction-oxidation potentials in the
chemical equilibrium calculations for the species in the
groundwater and the waste form. In addition, modelling of
the cement itself would be difficult.

Chemical Equilibrium Calculations

Determining the concentrations of n species in a
dilute solution requires n independent equations. These
equations are based on the equilibrium concentrations from
the relevant chemical reactions and mass balance equations
for the species. Combining these equations, one can handle
several different interactions in dilute solutions.

Basic Chemical Equilibria Calculations

Consider first the case where a known amount of two
species, A and B, are added to a solution and the reaction,
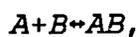
$$A + B \leftrightarrow AB,$$

(1)

is allowed to reach equilibrium. The equilibrium concentrations of the solution follow the simple relationship,

$$\frac{[AB]}{[A][B]} = K,$$

(2)

where

[A] is the equilibrium concentration of A,

[B] is the equilibrium concentration of B,

[AB] is the equilibrium concentration of AB, and

K is the formation coefficient of AB from A and B.

If the amount of A initially added to the solution was C_A, a mass balance of A would be

$$C_A = [A] + [AB].$$

(3)

Solving Eq. 2 for [AB] and substituting this into Eq. 3,

$$C_A = [A] + K[A][B],$$

(4)

or

$$\frac{C_A}{1+K[B]} = [A] .$$

(5)

Repeating this thought process for the analytical concentration of the species of B, C_B, produces the equation,

$$\frac{C_B}{1+K[A]} = [B] .$$

(6)

Eq. 2, Eq. 5 and Eq. 6 are the three equations which can be solved to determine the concentration of A, B and AB in the solution at equilibrium. The procedure used to derive these equations from the reaction in Eq. 1 is often applied to many types of reactions. Of interest to this study are distributions, solubilities, acid-base interactions, reduction-oxidation reactions and complexations.

Distribution Equilibrium Calculations

A sample is known to have a concentration, C_A, of some species, A. Assume the sample is allowed to equilibrate with a solution with which it is immiscible. This may be an organic solution being brought in contact with an aqueous solution or an insoluble solid being immersed in a solution. If A is soluble in both phases, it

will distribute itself between the two phases according to

$$A_1 \leftrightarrow A_2,$$

(7)

where

A$_1$ is a species in the original phase,

and A$_2$ is a species in the second phase.

The equilibrium concentration of A in the first phase, $[A]_1$, can be related to the equilibrium concentration in the second phase, $[A]_2$, using the distribution coefficient, K_D, and the equation,

$$K_D = \frac{[A]_2}{[A]_1}.$$

(8)

In the previous example, a mass balance equation was written directly in terms of concentrations. This was possible only because all species were assumed to be homogeneously mixed in the solution.

Here, since the volume, V_1, of the first and the volume, V_2, of the second phases are not necessarily the same, the mass balance equation must first be written in terms of the number of moles of A in each. The mass balance equation would be

$$C_A V_1 - [A]_1 V_1 + [A]_2 V_2,$$

(9)

or

$$C_A - [A]_1 + [A]_2 \frac{V_2}{V_1}.$$

(10)

Solving Eq. 8 for $[A]_2$, substituting this into Eq. 10 and solving for $[A]_1$, one can get the equation

$$[A]_1 - \frac{C_A}{1 + K_D \dfrac{V_2}{V_1}}.$$

(11)

Eq. 8 and Eq. 11 are the two equations commonly used to determine the concentrations of a species in two phases at equilibrium.

Solubility Calculations

Eq. 1 was written as a formation of the species AB. Consider the equilibria between the soluble species, A and B, and the insoluble compound, $A_a B_b$. This equilibrium is usually consider as the dissociation,

$$A_a B_b \rightleftharpoons aA + bB.$$

(12)

The preceding examples have been limited to concentrations in dilute solutions. For this case, one species, A_aB_b, is a solid. The assumption that it is in a dilute solution is obviously no longer valid. In dealing with anything except very dilute solutions, activities must be used instead of concentrations. The basic equations for dealing with activities are discussed in the next section of this chapter. For the present case, however, the activity of a solid is needed to continue. For a solid, the activity is set at unity.

If the solution is very dilute and the species A and B are at equilibrium with A_aB_b, the concentrations of A and B, [A] and [B] respectively, can be related to the solubility product, K_{sp}, through the equation,

$$K_{sp} = [A]^a [B]^b.$$

(13)

The precipitate, A_aB_b, will not be distributed homogeneously throughout the solution. A mass balance equation cannot be written in terms of the concentration, $[A_aB_b]$, of the compound for a homogeneous solution. Instead, the number of moles, $n(A_aB_b)$, and the volume, V, of the solution are used to create an effective concentration. The mass balance for the analytical concentration, C_A, of A is

$$C_A = [A] + a\frac{n(A_a B_b)}{V}.$$

(14)

Similarly, for the analytical concentration, C_B, the mass balance equation would be

$$C_B = [B] + b\frac{n(A_a B_b)}{V}.$$

(15)

Eq. 13, Eq. 14 and Eq. 15 form a set of three equations which can be solved for the three unknowns [A], [B] and $n(A_a B_b)$.

Acid-Base Equilibrium Calculations

Equilibrium calculations for Bronsted-Lowry acid-base reactions have also been based on dissociation reactions. For this case consider the multiple-step dissociation,

$$H_n A \leftrightarrow H_{n-1} A^- + H^+ \leftrightarrow H_{n-2} A^{2-} + 2H^+ \leftrightarrow \ldots \leftrightarrow A^{n-} + nH^+.$$

(16)
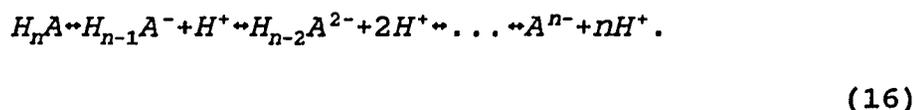
Each of the steps in Eq. 16 has associated with it an acid dissociation coefficient, K_{a1}, K_{a2}, $\ldots K_{an}$, related to the concentrations, $[H_n A]$, $[H_{n-1} A^-]$, $[H_{n-2} A^{2-}]$, $\ldots, [A^{n-}]$, through such equations as

$$K_{a1} = \frac{[H_{n-1}A^-]\,[H^+]}{[H_nA]},$$

(17)

$$K_{a2} = \frac{[H_{n-2}A^{2-}]\,[H^+]}{[H_{n-1}A^-]},$$

(18)

.

.

.

$$K_{an} = \frac{[A^{n-}]\,[H^+]}{[HA^{1-n}]}.$$

(19)

The above expressions provide n equations for the n+1 variables, $[H_nA]$, $[H_{n-1}A^-]$, $[H_{n-2}A^{2-}]$,...and $[A^{n-}]$. For the final equation, a mass balance equations for the analytical concentration, C_A, of A is used. This equation is

$$C_A = [H_nA] + [H_{n-1}A^-] + [H_{n-2}A^{2-}] +\ldots+ [A^{n-}].$$

(20)

Using Eq. 20 and the n equations above, a series of equations can be derived for the unknown concentrations. These equations are of the form

$$[H_nA] =$$

$$\frac{[H^+]^n}{[H^+]^n + K_1[H^+]^{n-1} + \ldots + K_nK_{n-1}\ldots K_1} C_A,$$

$$\text{(21)}$$

$$[H_{n-1}A] =$$

$$\frac{K_1[H^+]^{n-1}}{[H^+]^n + K_1[H^+]^{n-1} + \ldots + K_nK_{n-1}\ldots K_1} C_A,$$

$$\text{(22)}$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$[A^{n-}] =$$

$$\frac{K_nK_{n-1}\ldots K_1}{[H^+]^n + K_1[H^+]^{n-1} + \ldots + K_nK_{n-1}\ldots K_1} C_A.$$

$$\text{(23)}$$

These equations can be rewritten in terms of the ratio, α, of a species' concentration to the analytical concentration. Eq. 21, Eq. 22 and Eq. 23 then become

$$[H_nA] = \alpha_0 C_A,$$

$$\text{(24)}$$

$$[H_{n-1}A^-] = \alpha_1 C_A,$$

$$\text{(25)}$$

.

.

.

$$[A^{n-}] - \alpha_n C_A.$$

(26)

The set of n+1 equations can be used to determine
the concentrations of the n+1 different compounds of A if
the pH and the analytical concentration of A is known. For
this study, this is the case. In other cases, calculations
may be set up to determine the pH or the analytical
concentration of the acid necessary to make a solution of a
desired pH. To make these calculations, the set of
equations above and the "proton balance equation" can be
used. The proton balance equation is a mass balance
equation for protons. Since it was not used in this study,
no further details of the proton balance equation are given
here.

Complexation Equilibrium Calculations

Metal ions in solutions can form bonds with species
called ligands. Often, bonds are formed with more than one
ligand simultaneously. Such reactions can be treated in a
fashion similar to the acid-base equilibria discussed above,
but instead of using dissociations, these reactions are
usually considered as the formations reactions between the

metal, M, and some number, n, of the ligand, L,

$$M + nL \rightarrow ML + (n-1)L \rightarrow ML_2 + (n-2)L \rightarrow \ldots \rightarrow ML_n.$$

(27)

Using the same procedure followed for the acid-base equilibria, a series of equations can be found to relate the concentrations, [M], [ML], [ML$_2$], ..., [ML$_n$], of each species of Eq. 28 to the analytical concentration, C_M, of the metal. Ratios, β, of the actual concentrations to the analytical concentration are similar to the α's for the acids. The relationships between the concentrations and the ratios are

$$[M] = C_M \beta_0,$$

(28)

$$[ML] = C_M \beta_1,$$

(29)

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$[ML_n] = C_M \beta_n.$$

(30)

Using the equations for the formation coefficients, K_{f1}, K_{f2}, ..., K_{fn}, and the mass balance equation for the metal, one can find the equations for the ß's. These expressions are

$$\beta_0 = \frac{1}{1 + K_{f1}[L] + \ldots + K_{f1}K_{f2} \ldots K_{fn}[L]^n},$$

(31)

$$\beta_1 = \frac{K_{f1}[L]}{1 + K_{f1}[L] + \ldots + K_{f1}K_{f2} \ldots K_{fn}[L]^n},$$

(32)

.

.

.

$$\beta_n = \frac{K_{f1}K_{f2} \ldots K_{fn}[L]^n}{1 + K_{f1}[L] + \ldots + K_{f1}K_{f2} \ldots K_{fn}[L]^n}.$$

(33)

Using the ß's, the concentrations of the different compounds of the metal ion, M, can be calculated from the analytical concentration of the metal and the concentration of the ligand. The ligand is usually a base, and its concentration is usually calculated using the equations given above for acid-base equilibria.

For these studies, the complexes of interest interact with the metal ions as ligands. Some typical values of the formation constants for these complexing agents are given in Table I.

Table I: Formation Constants ($\log K_f$) for Some Complexes[38]

COMPLEXANT	Co^{2+}	UO_2^{2+}	Pu^{4+}	Am^{3+}
EDTA	16.28	7.40	25.60	18.16
NTA	10.38	9.50		11.5
Citric Acid	5.0	7.4	15.54	7.74
Oxalic Acid	3.84	6.36		5.25

Equilibria Calculations of Complex Solutions

In many cases, several of the above processes must be considered simultaneously. In addition, reduction-oxidation reactions must often also be considered. These reactions will be considered later. For now, consider the processes discussed above.

For an example, consider the distribution of cobalt (II) from a solid phase into a solution in the presence of EDTA. The relevant reactions and equations have been summarized in Table II.

Table II: Some Processes Occurring in a Typical Solution

PROCESS	REACTION	EQUATIONS
Distribute between Phases	$Co_{(s)}^{2+} \leftrightarrow Co_{(l)}^{2+}$	$K_D = \dfrac{[Co_{(s)}^{2+}]}{[Co_{(l)}^{2+}]}$ (34)
Solubility	$Co(OH)_2 \leftrightarrow$ $Co^{2+} + 2OH^-$	$K_{sp} =$ $[Co^{2+}][OH^-]^2$ (35)
Oxidation	$Co^{2+} + Fe^{3+} \leftrightarrow$ $Co^{3+} + Fe^{2+}$	$K = $ $\dfrac{[Co^{3+}][Fe^{2+}]}{[Co^{2+}][Fe^{3+}]}$ (36)
Acid-Base	$[H_4EDTA] \leftrightarrow$ $[EDTA^{4-}]$ $+4H^+$	$K_a = $ $\dfrac{[EDTA^{4-}][H^+]^4}{[H_4EDTA]}$ (37)
Complex Formation	$EDTA^{4-} + Co^{2+}$ $\leftrightarrow CoEDTA^{2-}$	$K_f = $ $\dfrac{[CoEDTA^{2-}]}{[EDTA^{4-}][Co^{2+}]}$ (38)

Considering the different forms of cobalt in Table II, the volumes if the two phases, V_s and V_l, and the analytical concentration, C_{Co}, of cobalt a mass balance

gives

$$C_{Co} =$$
$$[Co_{(l)}^{2+}] + [Co_{(s)}^{2+}] \frac{V_{(s)}}{V_{(l)}} + [Co^{3+}] + [CoEDTA^{2-}] .$$

<div align="right">(39)</div>

The solubility terms have not been included in Eq. 39. The solubility of the cobalt hydroxide sets an upper limit to the concentration of Co^{2+} in solution. If the calculated concentration of the ion in solution exceeds the concentration predicted by Eq. 35, enough cobalt hydroxide will precipitate to bring the concentration down to the limit.

Using the equations in Table II, the mass balance equation can be rewritten as

$$C_{Co} = [Co_{(l)}^{2+}] + K_D [Co_{(l)}^{2+}] \frac{V_{(s)}}{V_{(l)}} +$$
$$K[Co_{(l)}^{2+}] \frac{[Fe^{3+}]}{[Fe^{2+}]} + K_f [EDTA^{4-}] [Co^{2+}] ,$$

<div align="right">(40)</div>

or

$$C_{Co} = [Co_{(l)}^{2+}] \left\{ 1 + K_D \frac{V_{(s)}}{V_{(l)}} + K \frac{[Fe^{3+}]}{[Fe^{2+}]} + K_f [EDTA^{4-}] \right\} .$$

<div align="right">(41)</div>

To run the analysis, the pH and the analytical concentrations of the cobalt and other species such as the iron and EDTA are usually known. Concentrations of species such as the iron ions are calculated by deriving equations similar to Eq. 41. The concentration of $EDTA^{4-}$ is calculated from the analytical concentration using an equation of the form of Eq. 23. Once all the necessary concentrations are known, the concentration of the species of interest can be calculated. If this concentration is below the solubility limit set by Eq. 35, this result can be used to calculate the concentrations of other species. If not, the solution is saturated, and the saturation concentration can be used to calculate the other species' concentrations.

For most applications, the scenario above is an extreme simplification. First of all, several interactions have not been considered, e.g. complexation from other species like $HEDTA^-$, phosphates or silicates. When all interactions are considered, the problem becomes one which must be handled by one of the available computer codes.

In addition, the discussion above is only valid for very dilute solutions. At concentrations where interactions of the ions in a solution are no longer negligible, effective concentrations must be used in place of the

concentrations discussed above. These effective concentrations are called activities.

Activity Corrections

In the previous section, all calculations were based on concentrations. This is only valid when the solution is dilute enough so that interactions between dissolved species are negligible. At higher concentrations the equilibrium coefficients are no longer constant. Two approaches can be used in conjunction with the chemical equilibrium models to compensate for this change. These two approaches are the use of activities and use of equilibrium coefficients for the solution of interest.

Activities

Although the equilibrium coefficients are not constant since they are based on concentrations, the equilibrium constant, K, is independent of the concentrations. The equilibrium constant can be defined using the generic reaction

$$aA+bB \leftrightarrow cC+dD.$$

<div align="right">(42)</div>

Rather than defining the equilibrium constant with the concentrations, [A], [B], [C] and [D], the equilibrium constant is based on the activities, a_A, a_B, a_C and a_D of these species. The activities are ratios of the effective molal concentration of the species in the solution and the effective molal concentration of a standard. In solutions the standard is taken to be a one molal solution. For this reaction the equilibrium constant is

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b}.$$

(43)

To determine the activities, the ionic strength, μ, of the solution must first be calculated. The ionic strength of a solution with n dissolved species is

$$\mu = 0.5 \sum_{s=1}^{n} [X_s] z_s,$$

(44)

where

   [X_s] is the concentration of the sth species,

   and z_s is the charge on the sth species.

   Once the ionic strength is known, an activity coefficient, γ_s, must be calculated. Several different methods have been used to determine the appropriate activity coefficient. Two of the most poplar approaches are based on

the Davies equation and on extended Debye-Hückel equations. In addition, a technique for extending the Debye-Hückel equation to more concentrated solutions has been gaining popularity. These three approaches represent the most significant methods used in most chemical equilibrium codes[39,40,41] for getting the activity coefficients.

The first method for determining values for the activity coefficients is the Davies equation[42],

$$\log\gamma_s = -Az_s^2 \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - d\mu \right) ,$$

(45)

where

A is a constant usually taken to be 0.51,

and d is a constant usually taken to 0.3.

This equation is usually reliable to ionic strengths as high as 1 molal, however in more concentrated solutions different species act differently, and the corrections become more dependent on the specific species present. The Davies equation is one option in the PHREEQE chemical equilibrium code for determining the activity coefficients.

The extended Debye-Hückel equation[43] is very similar to the Davies equation in both form and applicability. It is

$$\log\gamma_s = -Az_s^2\left(\frac{\sqrt{\mu}}{1+Ba_s\sqrt{\mu}}\right)+b_s\mu,$$

(45)

where

B is a constant usually taken to be 3.3×10^7,

and b_s is a constant dependent on the species, s. As with the Davies equation, the extended Debye-Hückel equation can be used to produce reasonable results in solutions with ionic strengths up to one molal. This form of the Debye-Hückel equation is used in the PHREEQE and the EQ3/6 chemical equilibrium codes.

For more concentrated solutions, a method has been described for accounting for the dependence of b_s on the ionic strength[44]. Instead of a constant, b_s is determined by fitting experimental data to a power series of the ionic strength. Use of such an approach has been shown to be successful[45]. Its major disadvantage is that the values of the coefficients in the power series are only currently available for some very specific cases, however work is currently under way to determine these coefficients[7,46,47]. Once these coefficients become available, the EQ3/6 code has been written to utilize this technique for determination of the activity coefficients.

Once the activity coefficients have been determined, the activities can easily be determined using

$$a_s = \gamma_s [s] .$$

<div align="right">(46)</div>

For the calculations to be applicable to anything but a very dilute solution, the concentrations in equations from the previous section must be replaced by the activities. Only then can the equilibrium constants be used in place of the equilibrium coefficients.

Equilibrium Coefficients

Another approach to working with concentrated solutions is to use equilibrium coefficients which have been determined in solutions of a composition similar to the solution of interest. This is perhaps the easiest solution to the problem of high ionic strength, however it is not without its limitations. First, the data must be found. In many cases this is very difficult. Secondly, once the data has been found, the user must be certain that the solution used was similar in composition and ionic strength to the solution of interest.

This approach to concentrated solutions can be used with any of the chemical equilibrium codes. To use new equilibrium coefficients, one needs only put the new value in the data base of the code.

Reduction-Oxidation Reactions

Reduction-oxidation reactions were described briefly in the first section of this chapter. While one of the goals of this study was to evaluate the possibility of using a very simple model, it was realized that the processes involved were not simple. To keep the system simple, no attempt was made to buffer or monitor the reduction-oxidation reactions. While it was recognized that such reactions could greatly affect the results of the experiments, monitoring them would have complicated the analytical procedure, and buffering the system may have artificially altered the system.

The Nernst Equation

Reduction-oxidation reactions can be written in terms of hypothetical half-reactions of the form

$$Ox + ne^- \rightarrow Red.$$

(47)

where n electrons are being removed from some species, Red to produce a species, Ox. Although the half reaction cannot occur alone in a real system, it can be used to develop an expression for the potential for the reaction to occur. This potential is the electromotive force, E, of the reaction.

The electromotive force can be related to the activities, a_{Ox} and a_{Red}, of the species in the solution and to the standard electrode potential, E^o, through the Nernst equation,

$$E = E^o - \frac{RT}{n\mathscr{F}} \ln \frac{a_{Red}}{a_{Ox}} .$$

(48)

where

R is the universal gas constant,

$\mathscr{F}$ is the Faraday constant,

and T is the temperature.

The electromotive forces for these half-reactions are the potential for the half reaction to occur relative to some standard. The standard has been taken to be the oxidation of hydrogen gas in the presence of distilled water to produce a solution of H^+ with an activity of 1.

As mentioned, a half-reaction cannot proceed alone. When one species is oxidized, another must be reduced. Therefore, the concentration of a specific ion is dependent not only on the concentration of that element, but also on what other species are in the solution.

Reduction-Oxidation in the Lab

Although laboratory solutions are not as complicated as solutions in a repository, solutions in equilibrium with cement will have a wide variety of species present at a range of concentrations. These species may have a noticeable effect on the reduction-oxidation behavior of a solution.

Consider, for example, the study of equilibrium concentrations of cobalt (II). In a solution with a high enough pH, one may expect to see reactions of the sort

$$Co(OH)_3 + e^- \leftrightarrow Co(OH)_2 + OH^-.$$
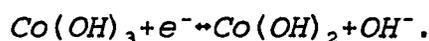
(49)

The standard potential for this reaction is fairly low, $E^\circ = 0.17$[48]. If, in addition, the concentration of hydroxyl ions is significant, the potential for the cobalt (II) to be oxidized to cobalt (III) can be large. In the presence of a species which can be reduced (accept an electron), a large majority of the cobalt may be cobalt (III). This species may be a component of the cement.

Reduction-Oxidation in a Repository

In addition to slightly more complicated groundwaters in a repository, the reduction-oxidation considerations may be governed by the iron (II)-(III) equilibrium. Iron present as structural material and as

barrels for the waste can easily undergo a series of reduction-oxidation reactions based on species such as $Fe(III)$, $Fe(II)$, $Fe(OH)_2$ and $Fe(OH)_3$.

The Chemistry of Cement

To understand the nature of a solution at equilibrium with cement, one must consider the composition of the cement, the hydration process, the nature of the hardened cement and the processes by which the solution interacts with the cement.

Composition of Portland Cement

Portland cement is made by heating a mixture of clay materials with lime, CaO, at high temperatures. The resulting material is then mixed with gypsum, $CaSO_4 \cdot 2H_2O$ and crushed. By varying the amount and the nature of the clay minerals, one can change the nature of the resulting cement. This is done intentionally in many cases to produce a cement which has a desired property. To a lesser extent, the composition of a cement will vary as a function of the manufacturer or even as a function of time at the same manufacturer.

Portland cement is sixty percent calcium oxide, lime, and twenty percent silica, from the clay minerals. When these compounds are mixed and heated they interact with each other and with other oxides present in lesser

quantities to form the four major compounds of cement. These compounds are dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium silicate ($3CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$) and tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). It is the relative amounts of these compounds which govern a majority of the characteristics of the resulting cement.

Less abundant species in Portland cement are alumina (2-8% Al_2O_3), magnesia (0.6 to 4% MgO) and sulfur trioxide (1-3% SO_3). While the alumina and magnesia are in the clay minerals, the sulfur trioxide is from the gypsum. As mentioned the alumina is an important part of the major components of cement. Magnesia is also integrated into the cement matrix as part of a much larger oxide. The sulfur trioxide is part of the gypsum which is important in the hydration process.

At still lower concentrations are such oxides as ferric oxide (Fe_2O_3), potassium oxide (K_2O) and sodium oxide (NaO). These too are part of the clay minerals and are part of larger oxides after being heated with the lime. As noted above, the ferric oxide is part of one of the major constituents of the cement.

To further complicate the mixture, several additives are commonly added to cement to improve such properties as porosity, leachability and improve resistance to sulfate attack. Typical additives have included fly ash[49] and blast furnace slag[50].

The Hydration Process

The silicates, aluminate and ferrite compounds which make up a majority of the cement are anhydrides. As such, they are not stable in the presence of water. Initially, they form a supersaturated solution of the anhydrides. From this solution, calcium hydroxide crystals and the hydrated products of the silicates, aluminate and ferrite compounds are deposited.

The most predominate species is the calcium silicate hydride. This compound precipitates from the solution in very small particles or "grains". Because of the nondescript nature of the particles, this phase of calcium silicates is often called the calcium silicate hydrate gel or the C-S-H gel. It is in this phase and in the pore that most of the radionuclides in the waste will concentrate. The C-S-H gel accounts for approximately half to one third of the cement volume.

The second most abundant phase is calcium hydroxide. The calcium hydroxide takes the form of well defined crystals which grow in the vacancies of the C-S-H gel. This phase is also formed as the calcium hydroxide comes out of a supersaturated solution.

A much less abundant phase comes from the hydration of tricalcium aluminate in the presence of gypsum to form ettlingite. This phase is also much more crystalline than the C-S-H gel. These crystals usually appear in pores of the gel and are the location of attack by sulfates.

Solutions at Equilibrium with Cement

Most of the less abundant components of the cement and any additives are usually found as isolated species as described above for the ettlingite, as part of the C-S-H gel or in the pore water. This also true of the components in the radioactive waste stream.

The pore water in the cement is a very concentrated, high pH (12.5) solution of the soluble species from the cement. The solution is saturated with calcium hydroxide, and one would expect to find much smaller concentrations of such species as phosphates, silicates, and in radioactive waste forms one would also expect some of the radionuclides. Species in the pore solution would equilibrate with any leachants which come into contact with the cement much more

rapidly than species in the C-S-H gel. The high
concentration of calcium hydroxide will be released to the
leachant, and unless some species, e.g. magnesium, is
present at high levels to moderate the pH, the leachant will
rapidly become saturated with calcium hydroxide.

Impurities, additives and other species bound in the
C-S-H gel are immobilized by surrounding layers of calcium
silicate hydrate. For these species to be released, water
must diffuse to the species, dissolve it and diffuse from
the gel. This process is much slower than the interaction
of the leachant with the pore solution. It is this process
which limits the speed at which the cement will reach
equilibrium in the solution of interest.

Models of Cement

Because of the widespread use of cement, models have
been developed to describe several aspects of applications
and behavior. Models are available for describing the C-S-H
gel of cement[51,52,53], the leaching of cement-based
radioactive waste forms[54,55,56] and the rate at which
cement in a repository decomposes[57,58].

For use of the chemical equilibrium codes with
cement waste forms, a model had to be developed for
describing cement in equilibrium with solutions. Such a
code has been developed for the EQ 3/6 code and is based on

the rate at which the calcium hydroxide in the cement is dissolved by the leachant. The model is simplified in that it is used only to determine the amounts of calcium hydroxide and calcium silicate in the cement. Once this information is known, it can be used as input information for the equilibrium calculations to predict the concentrations of such species as the silicates of a species of interest.

CHAPTER 3

EXPERIMENTAL

The goal of this study was to evaluate the concentrations of species released from a low or intermediate-level waste form using a simple experimental approach. To do this a number of concentration measurements were made on solutions in contact with a simulated cement waste form.

Three groups of concentration measurements were made. These were measurements for determining concentrations of the metal ions of interest, of other inorganic cations and of the complexing agents.

Metal Ion Concentrations

Simulated waste forms were prepared and equilibrated with various solutions to determine the concentrations of the metal ions. Initially, leach rate and equilibrium experiments were run on the waste forms, however the equilibrium studies proved to be more fruitful. The leach rate experiments were eventually discontinued.

Sample Preparation

Inactive simulated cement waste forms were used in all equilibrium tests and all experiments for determining leach rates of complexing agents. Active waste forms were used only in studies of the metal ion leach rates.

Availability required two types of cement to be used. Initially, simulated waste forms were made from type I/II Arizona Portland cement supplied by the Arizona Portland Cement Company. A description of the cement has been included in Table III. In latter studies, a German Portland cement was used. Its composition has also been included in Table III.

Table III: Composition of Cements Used in the Waste Forms

	Composition (%)	
Species	Arizona Cement	German Cement
CaO	63.68	63.20
SiO_2	21.99	18.40
Al_2O_3	3.46	3.94
Fe_2O_3	2.88	3.91
SO_3	2.56	3.08
MgO	4.36	2.40
Na_2O	0.13	0.29
K_2O	0.64	1.61
Mn_2O_3	Not Available	0.39

The composition of the cement could obviously have had a large effect on the equilibrium concentrations. Although the major components of these cements seem to have been fairly similar, the differences in the less abundant species, such as the iron and magnesium oxides, could theoretically have had a significant effect on the resulting equilibrium concentrations. No attempt was made to compensate for these differences. Such compensations or evaluations would have changed the nature of the studies from a simplistic to a more controlled approach. Simple studies follow procedures which are more attractive and widely available.

Inactive Simulated Waste Forms. The first batch of inactive simulated waste forms was made with the Arizona Portland cement. The samples were prepared by mixing 310 g cement, 140 ml water, 50 g sodium nitrate, and the appropriate amounts of the complexing agents. Each mixture was divided among 6 fifty ml cylindrical plastic jars, and the resulting simulated cement waste forms were allowed to cure for two to three months. The amounts of complexants used have been listed in Table IV.

The German Portland cement was used to prepare a second batch of inactive simulated waste forms. These samples were made from a mixture of 1 kg cement, 400 ml water and 150 g sodium nitrate. The mixture was again

poured into several fifty ml cylindrical plastic jars, and 10 to 15 days was allowed for curing. No complexing agent was included in these waste forms.

Table IV: Cement and Complexants in Inactive Waste Forms

Waste Forms	Type of Cement	Complexant
1-6	Arizona Portland	None Added
7-12	Arizona Portland	0.3 g NaEDTA
13-18	Arizona Portland	1.5 g NaEDTA
19-24	Arizona Portland	0.2 g NaNTA
25-30	Arizona Portland	0.2 g NaCitrate
31-36	Arizona Portland	1.5 g NaCitrate
37-42	Arizona Portland	1.5 g NaNTA
Batch 2	German Portland	None Added

Although the two batches of simulated waste forms varied in preparation, results were standardized through the use of blanks. It is possible, however, that some observed effects could be due to a component of the cement. While some small differences were observed in the results from the two batches of cement, the use of blank waste forms provided a means for standardizing the results. No unique behavior could be seen for either of the two batches.

Active Simulated Waste Forms. The active simulated
waste forms were made using the same quantities as in the
first batch of inactive simulated waste forms, i.e. 310 g of
the Arizona Portland cement, 140 ml deionized water, 50 g
sodium nitrate and the appropriate amount of the complexing
agent. With these components, 40 μCi of cesium-137 and 11.6
μCi of cobalt-60 were mixed. Five waste forms were then
made from each mixture, and these were allowed to cure for
two to three months in plastic jars as described above.

The radionuclides had been dissolved in aqueous
solution. One mL of an aqueous 40 μCi Cs-137 solution and
one mL of an aqueous 11.6 μCi Co-60 solution were used.
Since the half-life of Co-60 is over five years and of Cs-
137 is thirty years, no correction was made for the decay of
these radionuclides. In the worst cases, the error
introduced through neglecting such a correction would have
been less than six percent.

Equilibrium Studies

These experiments were run to determine the
concentrations of the metal ions in solution at equilibrium
with the waste form. Equilibrium concentrations of cobalt
and uranium were studied extensively. Cesium equilibrium
concentrations were not studied because it was not expected
to form complexes with the complexing agents[59], and the

leach tests showed this to be true. To study the effects of the cement on the concentrations, experiments were run both with and without cement immersed in the solutions.

Metal Ion Concentrations in the Presence of Cement.

Once the simulated waste forms had cured, they were removed from the plastic jars. To do this, the jar was first sprayed with freon. This made the plastic brittle enough to be broken removing the waste form from the jar. Compressive strength tests were then run to crush the waste forms. Finally, two grams of the fine powder from the crushed waste forms were immersed in 30.0 ml of each solution.

Four solutions were initially used in the studies, deionized water, saturated sodium chloride, 24% magnesium chloride and Q-brine. Q-brine is a synthetic groundwater made up of 24% magnesium chloride, 3.3% magnesium sulfate, 2.3% potassium chloride and 1.9% sodium chloride. Because the results for the sodium chloride were the same as the water and the 24% magnesium chloride results mimiced the Q-brine results, saturated sodium chloride and magnesium chloride solutions were used more rarely than the other solutions.

The second batch of simulated waste forms had no complexing agents. To study this batch, 0.02 g of the appropriate complexing agent was added to the leachant solutions. In studies with the first batch of waste forms, adding the complexing agents to the solution was not necessary since they were already in the waste forms.

Finally, the appropriate amount of the metal ion of interest was added to the solution. Some studies were run using only trace amounts of the cobalt, however in most cobalt studies, 0.1 g of inactive Co(II) nitrate hexahydrate was used as a carrier. In the uranium studies, 0.08 g of uranium was added to the solutions in the form of uranyl nitrate.

Once all the components were added to the solution, the tests were allowed to run long enough to reach equilibrium. Samples were taken after three different time intervals to ensure equilibrium had been reached. Because different procedures were used in the tests, reliable comparison of results from the first and second batches depended on the assurance that all tests had reached equilibrium.

Chemicals used were analytic grade with the following exceptions. The cement used has been described in Table III. Technical grade sodium nitrate was used. The TBP had been purified in another laboratory. The same was

true with the DBP, and this solution was known to have a small unknown amount of monobutyl phosphate (MBP) in it.

Metal Ion Concentrations in the Absence of Cement.
To determine the soluble metal ion concentrations in the absence of cement, 30.0 ml of each leachant was mixed with 0.02 g of the complexing agent and 0.3 g of sodium nitrate.

In addition, the solution pH's were set. In the magnesium based solutions, 24% magnesium chloride and Q-brine, in the presence of the waste form, the pH was buffered by the precipitation of magnesium hydroxide. The magnesium hydroxide buffered the pH at 6.5. Since no magnesium was present in the sodium chloride and water solutions, the pH would rise to the point where calcium hydroxide was no longer soluble. This buffered these solutions at a pH of 12.5.

In the absence of cement, the pH's had to be set to these values. The pH's were adjusted by adding the appropriate amount of 1 M sodium hydroxide.

While the pH in the magnesium chloride and Q-brine solutions were once again buffered by the precipitation of magnesium hydroxide, the pH's of the other solutions drifted somewhat because no calcium hydroxide was present to buffer them. Recent studies have shown that these pH's should be monitored and held at 12.5[60].

On the other hand, since cobalt hydroxide precipitates just above a pH of 6.5, care was also necessary in setting the pH of the magnesium based solutions. If too much sodium hydroxide was added, some of the cobalt could precipitate, and the cobalt concentration would be artificially low. In fact, it is possible that at 6.5 some of the cobalt is coprecipitating with the magnesium hydroxide. The uncertainty in the pH of the solutions offers perhaps the largest source of error in these experiments. pH's were set using pH paper. The uncertainty associated with such a procedure was approximately ± 0.3 pH units. A change in the pH of 0.3 represents a doubling in the hydroxide concentration.

As described above, the solutions were sampled at several different time intervals to ensure that the results reported were equilibrium concentrations. The usual sampling schedule was to sample the experiments after three, four and five weeks. Equilibration was expedited by using only 2 g of finely crushed cement and only leaching with thirty milliliters of solution.

Analyses. The concentrations of cobalt and uranium were determined by different methods. To find the cobalt concentrations, gammas from cobalt-60 decays were counted using a NaI detector. The uranium concentration was

determined by counting alphas from uranium-238 decay using a liquid scintillation detector.

Before the samples were counted, particulates were removed through filtration with the Amicon filter system. To use the Amicon system, a sample of the test solution was pipetted into a Centricon 30 Microcentrator. These filters were designed to remove particulates with diameters of 1.8 nm or greater. Once the sample was inside the Microcentrator, the assembly was centrifuged. The water and sodium chloride solutions could be completed after one hour of centrifugation. The Q-brine solutions required two hours because the magnesium hydroxide precipitate impeded the filtration. Magnesium chloride solutions were not used in these experiments.

The cobalt concentrations were determined by taking a 10.0 ml sample from the test solution and filtering it as described. Once filtered, the samples were counted for one minute with a NaI detector using a single channel analyzer. One minute counts were also taken of two standards and a blank. Upon completion of the counting, the samples were returned to the test solutions. Measurements of the samples were made in triplicate, averaged and corrected for background.

A slightly different procedure was used for measuring the uranium concentrations. From each uranium test solution, only 1.0 ml was removed and filtered using the Amicon filter system. The filtrate was mixed with 15 ml of liquid scintillation cocktail. This mixture was then counted for ten minutes using a Beckmann LS 7800 liquid scintillation detector and a multichannel analyzer. Ten minute counts were also taken of two standards and a blank. Results were then corrected for background. Because uranium samples were mixed with the scintillation cocktail, they could not be returned to the test solutions.

Using the detection methods described above, the determination limits were 2×10^{-5} M for cobalt and 5×10^{-5} M for uranium. These were based on typical background counts of four in one minute for the NaI detector and one hundred in ten minutes for the liquid scintillation counter. Fluctuations in the background were considered to be one standard deviation, and the minimum determination was set at ten times the fluctuation level above background.

Leach Rate Studies

The goal of these experiments was to examine the rates at which the metals were leached from the waste forms into the solutions. Leach rates were studied for cesium and cobalt. Because information obtained from the equilibrium

studies was generally of greater significance, the leach rate experiments were discontinued after results had been obtained for the metal ions in the presence of EDTA, NTA and citrate in deionized water.

In these tests the active simulated waste forms were removed from the fifty ml plastic jars and immersed in 300.0 ml of water. These samples were not crushed as were the samples used in the equilibrium studies. After 1, 2, 4, 8 and 22 weeks, each experiment was analyzed.

To analyze the tests, 10.0 ml samples were taken from each. The samples were then counted for 2000 seconds each using a Ge(Li) detector equiped with a multichannel analyzer and an automatic sampler. Samples were then returned to the experiment solutions. Using the same requirements described above for the NaI and liquid scintillation detectors, the minimum determination limit for this system was 1 x 10^{-12} M.

Complexing Agent Concentrations

The goal of these equilibrium and leach rate studies was to determine the complexing agent concentrations in the leachants. The experiments were very similar to those used for the metal ion studies, but the analysis of samples was substantially different. Instead of gamma or alpha spectrometry, a complexometric titration was used.

Equilibrium and Leach Rate Studies

These experiments were limited to EDTA, NTA, and citric acid. Because of time restraints and the lack of a convenient, widely applicable method for analysis, this work was abandoned in favor of the metal ion concentration studies.

These experiments were similar to equilibrium and leach rate studies described in the preceding pages.

The materials used were the first batch of simulated inactive waste forms described in the first section of this chapter, deionized water, saturated sodium chloride, 24% magnesium chloride and Q-brine.

The equilibrium studies were run to determine the concentrations of the complexing agents when the solutions were at equilibrium with the simulated waste form. To run these experiments, the waste forms were removed from the plastic jars, crushed, and 2.0 grams of the resulting fine cement powder were immersed in 30.0 mL of each solution. Each experiment was analyzed at three, four and five weeks to ensure that equilibrium had been reached. All tests were run in duplicate.

The leach rate studies were run to determine the rate at which the EDTA, NTA, and citric acid were leached into deionized water in contact with the simulated waste forms. Since this is dependent on such factors as surface

area and volume, the waste forms were used without being crushed. The simulated waste form of interest was removed from the plastic jar and immersed in 300.0 ml of deionized water. Samples were analyzed after 1, 2, 4, 8 and 22 weeks using the complexometric titration described below. Duplicate studies were made of each experiment.

Analysis of Complexing Agents

Determination of the complexing agent concentrations was made with a complexometric titration. The method was a well-established but somewhat limited procedure using a copper(II) solution and a copper(II) ion-selective electrode[61]. Complexing agents could be measured to about 1 E-5 M. At lower concentrations, end point potential jumps were too small to be of use, especially for citric acid.

Methods such as high pressure liquid chromatography (HPLC), gas chromatography and total organic carbon determinations may extend the detection limits. At the time of these experiments, the available instrumentation was in high demand by other groups. In addition, nitrate in the solutions may have caused interference problems with detection of the organics using HPLC.

Instrumentation and Materials. To hold the pH of the samples constant during titrations, a pH 5.0 acetate buffer was used. To make the buffer, equal volumes of 0.20 M sodium acetate and 0.20 M acetic acid were mixed, and the pH was adjusted with 1 M sodium hydroxide. All reagents were analytical grade.

The standard solutions were also made from analytical grade chemicals. A 1×10^{-3} M copper solution was used in the analysis. It was made from copper(II) nitrate. To run feasibility studies on the analytical method, solutions ranging from 1.00×10^{-3} to 1.0×10^{-5} in either EDTA or citric acid were made using sodium citrate or disodium EDTA. The 1.00×10^{-3} M EDTA solution was also used daily to standardize the copper standard solution.

For the titrations, a copper(II) ion selective electrode and a silver-silver chloride double junction reference electrode were used. The electrolyte in the reference electrode was 3.0 M potassium chloride.

The titration was automatically controlled by a Mettler DL 40 RC automatic titrator. Once the parameters were input to the titrator, the titration was run automatically, printing the results at the end of the titration.

Analytical Method. Daily, before any analysis was run, the 1×10^{-3} M copper solution was standardized with the 1.00×10^{-3} M EDTA solution. To standardize the copper solution, the automatic titrator was used to disperse 1.0, 2.0 and 3.0 ml samples to three different thirty ml plastic beakers.

To each sample, 10.0 ml of the acetate buffer was added. The titrator was then loaded with the 1.00×10^{-3} M EDTA standard solution. The samples were titrated. Before the titration, the titrator stirred the solutions for one minute. The maximum titration rate was set at 1 ml/min. The rate slowed substantially when the cell potential started to change. Upon completion of each standardization, the copper concentration was determined. The results of the three determinations were then averaged to get the concentration of the copper solution.

To determine the amount of the chelates in the solutions, 5.0 ml of the leachant from the experiment was pipetted from the experiments. No trouble was encountered in sampling water and sodium chloride solutions, however the magnesium hydroxide precipitate in the magnesium chloride and Q-brine solutions had a tendency to plug the pipet. With these solutions it was essential to pipet the samples slowly. These samples were not filtered before the analysis.

Once the samples had been pipetted into a thirty ml beaker, 10.0 ml of the acetate buffer was added to the beaker, and it was put in place for the titration. The titrator was loaded with the 1 x 10^{-3} M copper standard, and the titration was carried out as described above except now, the chelate was titrated with copper instead of the copper with the chelate. Once again, the solutions were stirred for one minute before the titration, and the maximum titration rate was still set at one mL/min.

Results were converted from moles to concentration and then to the release fraction.

Because the method was destructive, samples could not be returned to the test solutions. Therefore, the volume of solution in the experiments was not constant. The 25.0 ml total removed from the 300 ml of the leach studies may have had some effect on the results, however the error introduced would have been much less than ten percent. Since blank studies were run and the change in the volume was the same in all the experiments, the loss in volume should not effect the conclusions of the studies.

For the equilibrium experiments, 15.0 of the 30.0 ml were taken from each of the samples, but the loss of volume did not change the results because the tests had reached equilibrium before the first analysis had been run. Once

the solutions had reached equilibrium, removal of the
solution should not have changed the concentrations.

Equilibrium Solution Composition

Chemical equilibrium calculations are commonly run
in conjunction with experiments. The reliability of these
calculations is heavily dependent upon the nature of the
solution considered. Increasing the amount of information
on the solution improves the predictive and interpretive
value of the calculations.

To further characterize the equilibrium solutions,
sodium and calcium concentrations and pH's were measured.

pH Measurements

pH's measurements were made with the DL 40 RC
automatic titrator, a Mettler DG 111 pH electrode and the
silver-silver chloride double junction reference electrode.
Standard buffers with pH's of 2.0, 7.0 and 10.0 were used
for calibration of the system.

Once the system was calibrated, pH measurements were
made of the distilled water, saturated sodium chloride, 24%
magnesium chloride and Q-brine solutions at equilibrium with
the simulated waste form. Using this system, pH readings
drifted very little.

The pH values reported from these measurements are "measured" pH's. Ionic strengths of the solutions were very high. No attempt was made to correct the measurements for these high activities. Measurements were also made with pH paper. Since the paper could only be used to find pH's to within 0.3 of a pH unit, pH's determined potentiometrically were more useful for a comparison of the different equilibrium solutions. Differences in pH's measured potentiometrically and those measured with paper show the ionic strength did shift the readings significantly.

Elemental Analysis

Once the inactive equilibrium tests using distilled water had been completed, a 10.0 ml sample was taken and used for determination of the sodium and calcium concentrations in the solution. Analysis' were made by optical emission spectroscopy with an Inductively Coupled Plasma (ICP).

The saturated sodium chloride, 24% magnesium chloride and the Q-brine solutions were not analyzed because of their composition. It is possible the high ion concentrations could have made detection of the less prevalent ions difficult. In addition, the analysis was made in another group's laboratory. The ICP was in high demand.

In addition, the chemical equilibrium calculations are much more difficult to run on complicated solutions. In fact, it is generally accepted that solutions with ionic strengths of greater than 1 molal cannot be handled by simple activity corrections. Therefore, the results of calculating concentrations in the solutions other then water would be of limited use. In fact, the deionized water solutions in equilibrium with the simulated waste form may be difficult to model using these equilibrium codes because the ionic strengths of these solutions were even on the order of 0.1 molal.

Concentrations were reported for sodium in the Q-brine solution and magnesium in the 24% magnesium chloride and Q-brine solutions. These were calculated values determined by assuming all magnesium and sodium was in solution. While the values of the sodium concentrations were probably reliable, some magnesium had precipitated out of solution as magnesium hydroxide. The reported and actual magnesium concentrations should only be slightly different.

Error Analysis

Experiments were run in duplicate and triplicate. The uncertainties reported in the results were the standard deviations of these measurements. In some cases, it was not the reproducibility of these measurements which limited

their accuracies and precisions. In such cases, the uncertainties in the measurements were still reported, however the limiting processes were also discussed.

CHAPTER 4

RESULTS

The results of these studies fall conveniently into
three categories. First, equilibrium and nonequilibrium
concentrations of some complexing agents were studied.
Parallel to these tests, studies were made of cesium, cobalt
and uranium concentrations and the effect of the chelates on
them. For a better understanding of the solution chemistry,
measurements were also made of pH and magnesium and calcium
equilibrium concentrations.

Concentrations of EDTA, NTA, and Citrate

The leach rates, and equilibrium concentrations of
ethylenediaminetetraacetic acid (EDTA), nitrillotriacetic
acid (NTA) and citric acid were studied in deionized water.
As mentioned previously, similar experiments with the other
complexing agents were abandoned in favor of more cobalt and
uranium studies, however the results from these chelates can
be used as an indicator for the other complexing agents.

Leach Rate Studies

The goal of these studies was to examine the rate at
which the chelates were leached from the waste forms. The
three complexing agents studied behaved very differently.

In all cases, however the lightly loaded simulated waste forms seemed to be very close to equilibrium after about four weeks.

Ethylenediaminetetraacetic Acid (EDTA). The concentration of EDTA in solution as a function of time is shown in Fig. 1. These were concentrations found when deionized water was used as the leachant. These data represent measurements taken up to 155 days after the beginning of the experiments. Fig. 1 shows that the concentration of EDTA in solution was higher for the simulated waste form loaded with more EDTA. In addition, the waste forms with less of the chelate had almost reached equilibrium after about four weeks.

The values shown in Fig. 1 are averages of duplicate studies. In all cases, the standard deviation associated with the two measurements was less than $1x10^{-2}$ mM except for the readings taken at 55 days for the sample with 0.3 % EDTA. For this point, the standard deviation was 1.4×10^{-2} mM, however this represents less than a 10 % uncertainty in the concentration.

The determination limit for this technique was set by the limitation on the accuracy of the buret and the ability to determine the endpoint of the titration. Mettler had established 5 % of the buret volume as the lower limit for reliable quantitative measurements. Using a 1 ml buret
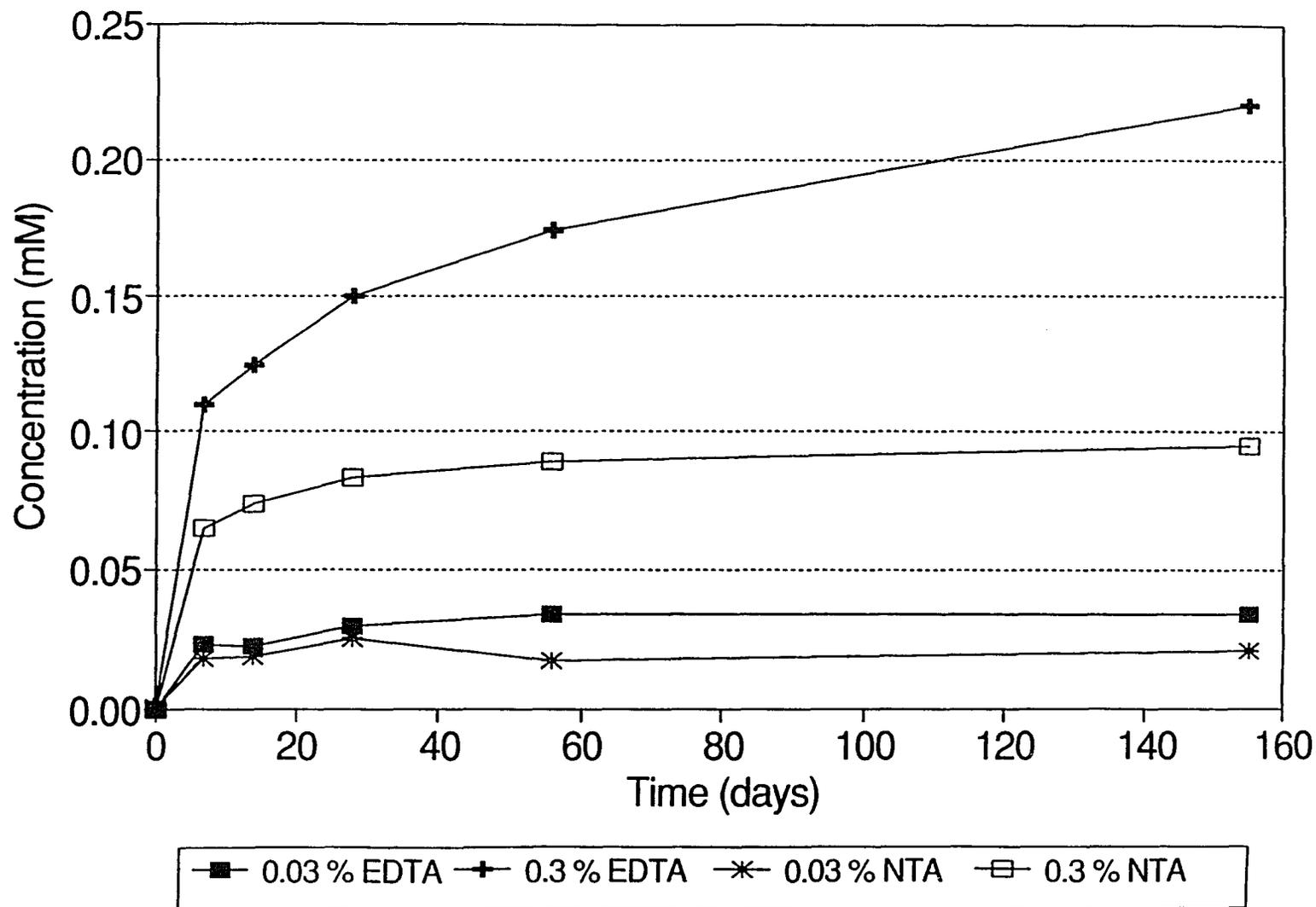
Figure 1. Time Dependence of Chelate Concentration in Deionized Water

with a 1.0×10^{-4} M standard solution to titrate a 10 ml
sample set the limit at 0.5×10^{-5} M. Although the baseline
in these titrations in most cases were very flat, at these
concentrations the endpoint became difficult to identify.
This was true whether it was determined automatically by the
titrator, or manually from the readout on the stripchart
recorder.

While the concentration of EDTA in solution was
dependent on the initial amount in the waste form, Fig. 2
indicates that the fraction released was not. This suggests
the solubility limit of EDTA was not reached. Since EDTA is
a soluble species, this was to be expected, however the
fraction of EDTA released was much lower than indicated for
a soluble species. This can be seen by comparing the EDTA
releases to the cesium releases which have also been
included in Fig. 2. Adsorption of the EDTA on the cement
may play an important role in the establishing the solution
concentration.

The values in Fig. 2 were also the averages of
duplicate experiments. As expected, the standard deviations
in the fractions released from the waste forms with the
higher inventory of EDTA were low, less than 0.01. For the
more lightly loaded waste forms, the standard deviations
were sometimes as high as 0.02. In all cases, the fraction
released from the waste form with 0.03 % EDTA was within a
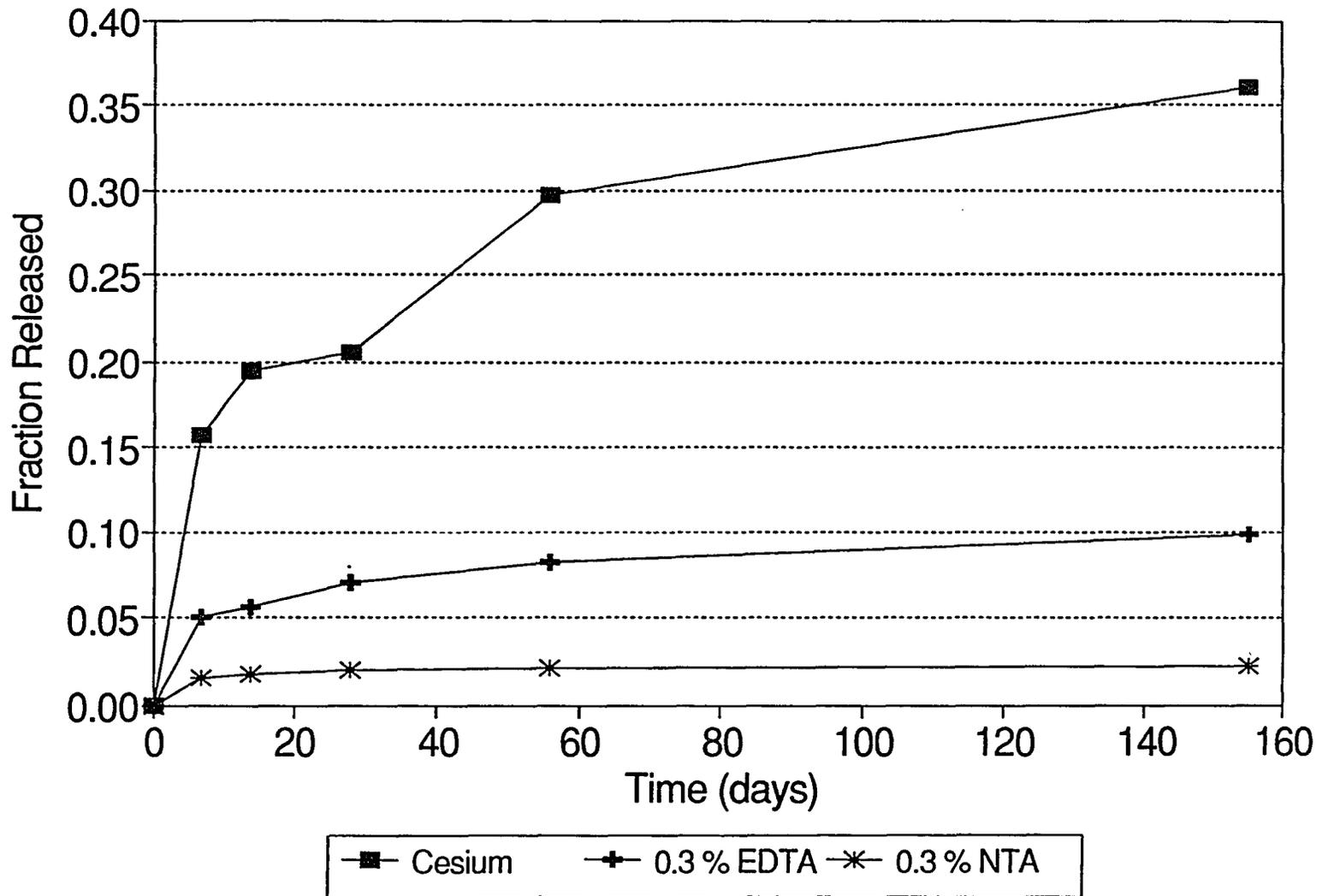
Figure 2. Cesium, EDTA, and NTA Fraction Released in Deionized Water
as a Function of Time

standard deviation of the fraction released from that with

0.3 % EDTA.

Citric Acid. Although citrate could be seen in

solutions of the leach studies, the voltage jump at the

endpoint of the titration was so small that the

concentrations were on the order of the method's

determination limit. For this reason, the data was not

included in Fig. 1 or Fig. 2.

The citrate concentrations were on the order of 1 x

10^{-5} M independent of the simulated waste form's loading. A

constant solution concentration suggests that the solubility

of some citrate species is controlling the system. Calcium

citrate is perhaps the limiting species. Since the

concentration of citrate in solution seems to be limited,

the release rate of citrate from a waste form will be more

dependent on the water flow rate than on the amount of

citrate in the waste form.

Nitrillotriacetic Acid. The concentration of NTA in

solution and the fraction of NTA released to the solution,

shown in Fig. 1 and Fig. 2 respectively, were both dependent

on the loading of the simulated waste form. As the loading

increased, so did the release rate. As in the case of the

EDTA studies, these results were determined by averaging two

duplicate experiments. The resulting standard deviations

were slightly lower, less than 0.015 for the fractions and

less than 0.007 mM for the concentrations, than the values
of the EDTA results.

The concentration of NTA in solution was
significantly less than the concentration of dissolved EDTA
for the more highly loaded simulated waste forms. When less
of the chelates was present, the difference was not so
obvious.

As in the case with the lower concentration samples
of EDTA, the lightly loaded NTA samples seemed to come very
close to equilibrium after about four weeks. In fact, the
equilibrium concentration was 3 x 10^{-5} M, the same as for
the EDTA samples.

The NTA samples behaved in a fashion intermediate to
the citrate and the EDTA samples. The solubility limit of
NTA seems to have been approached with the more highly
loaded waste forms, yet when less NTA was present, the
solution concentration was still below the solubility limit
of NTA.

For samples which are more highly loaded than these
samples, one would expect that the solution would start to
become saturated, and the concentration of NTA in solution
would become independent of the amount in the simulated
waste form. When less NTA is solidified in the cement, one
would expect that the fraction released would begin to
approach a constant value.

Based on the observed solubility of the other leachants, one would expect tributylphosphate and dibutylphosphate to behave in a fashion similar to the citric acid. Of the complexing agents studied, these were the least soluble in the aqueous solutions at the pH's of the cement. The oxalic acid was somewhat more soluble, but it too was noticeably less soluble than the citric acid. Finally, the tartaric acid was noticeably more soluble than oxalic acid, however it is probably not as soluble as NTA. Therefore, it too will probably act as the citric acid did. None of the complexing agents studied were more water soluble than the EDTA.

Equilibrium Studies

The equilibrium studies were run under conditions which would allow the tests to reach equilibrium much more quickly than the leach studies. In fact, the samples were not even analyzed until after three weeks. At this time the complexing agent had essentially reached equilibrium in all samples. The results from these studies were very consistent with the leach rate studies.

Ethylenediaminetetraacetic Acid. The fractions of EDTA released from the waste forms were independent of the loading, as was the case for the leach studies. The

solution concentrations and release fractions have been
presented in Table V.

Table V: Equilibrium EDTA Concentrations

Solution	Chelate (wt. %)	Concentration (M)	Fraction Released
Water	0.03	$4.50\pm0.094\text{x}10^{-5}$	0.4
	0.30	$2.4\pm0.31\text{x}10^{-4}$	0.39
Saturated NaCl	0.03	$7.0\pm0.10\text{x}10^{-5}$	0.5
	0.30	$3.30\pm0.094\text{x}10^{-4}$	0.49
Magnesium Chloride	0.03	$5.4\pm0.21\text{x}10^{-5}$	0.4
	0.30	$2.5\pm0.26\text{x}10^{-4}$	0.36
Q-Brine	0.03	$2.2\pm0.42\text{x}10^{-5}$	0.2
	0.30	$1.53\pm0.047\text{x}10^{-4}$	0.27

As in the leach rate studies, these values are the
averages of two parallel studies. The uncertainties in the
table are the standard deviations in these parallel studies.
They are perhaps somewhat misleading. Although the
precision in the studies seems to be high, the accuracy is
limited by the care that was used in measuring the mass of

the complexing agents. The mass measurements limit the accuracy in the results in some cases to ± twenty percent.

In all solutions except Q-brine the fraction of EDTA released from the cement was independent of the amount in the waste form. In the Q-brine study, the fraction released from the cement was greater in the case of the waste form with the higher initial loading. This is opposite to what would be expected if the solubility of the EDTA was approached. This inconsistency is most likely due to inhomogeneous mixing of the waste form. Even these values only deviate from each other by approximately fifty percent, and not a hundred percent or an order of magnitude.

The concentrations shown in Table V are all well below what would be expected based on terms of solubility alone. EDTA is a fairly soluble species. Therefore, one would expect that a majority of the EDTA would be found in solution.

Once again, the low EDTA concentrations seem to suggest that sorption of the EDTA on the cement has a significant effect on the equilibrium concentration. This sorption may cause some difficulties when attempting to model the releases using chemical equilibria considerations.

Citric Acid. While the fraction of EDTA released from the waste forms was independent of the loading, it was the concentration of citrate that seemed to be independent of the quantity of citrate in the waste form. The concentrations reached by the equilibrium studies were similar to those in the leach studies.

Once again, the concentrations of citrate were on the order of the determination limit of the titration. For this reason, the values have not been tabulated. It is of interest to note, however, that the equilibrium concentrations seemed to be insensitive to the simulated waste form loading.

Nitrillotriacetic Acid. As in the leach rate studies, the NTA concentrations and release fractions were both dependent on the amount of NTA initially in the simulated waste form. These results can be seen in Table VI. As discussed for the EDTA concentrations in Table V, the standard deviations for the duplicate values have been given, however the uncertainty in the values may not be as dependent on the precision as on the accuracy.

In the saturated NaCl solution, NTA seems to have approached its solubility limit even for the lightly loaded waste forms. This can be seen in Table VI. Perhaps the NTA is being salted out of the solution in this case, while in

the magnesium solutions, the chelate interacts with the magnesium keeping it in solution.

Table VI: Equilibrium NTA Concentrations

Solution	Chelate (wt. %)	Concentration (M)	Fraction Released
Water	0.03	$3.4\pm0.33\text{x}10^{-5}$	0.2
	0.30	$1.82\pm0.024\text{x}10^{-4}$	0.14
Saturated NaCl	0.03	$2.0\pm0.31\text{x}10^{-5}$	0.1
	0.30	$1.8\pm0.28\text{x}10^{-4}$	0.015
Magnesium Chloride	0.03	$7.5\pm0.66\text{x}10^{-5}$	0.4
	0.30	$2.3\pm0.15\text{x}10^{-4}$	0.17
Q-Brine	0.03	$3.1\pm0.31\text{x}10^{-5}$	0.1
	0.30	$8.55\pm0.071\text{x}10^{-4}$	0.056

As discussed at the end of the previous section of this chapter, the expected results for the complexing agents not studied would probably be closest to the results seen for citric acid.   Tartaric acid may be slightly more soluble but probably not noticeably,

Metal Ions

Perhaps the most important results of these studies were for the metal ions. After all, the leaching of the chelates is of relatively little consequence unless it affects the release of the radionuclides in the waste forms.

Three metals were studied. Cesium was chosen because of its high solubility in aqueous solutions, and relatively high abundance in some waste streams. Cobalt is important because it forms strong complexes with many of the complexing agents studied, has been shown to mimic the behavior of the actinides and can be detected down to 1 x 10^{-14} M using a sodium iodide detector. In addition, it has been used so often in other studies that it has become a convenient standard for comparisons. Uranium is present in waste at concentrations of up to 1 kg/200 l drum, and its large half-life makes it important in radiation hazard considerations. Therefore, uranium was also studied.

Cesium

The release rates of cesium from the simulated waste form was independent of the chelate present. This was expected since cesium does not form complexes with the complexing agents. The results for the cesium studies have been included in Fig. 3. The release fractions are all similar. As was the case with the EDTA and NTA release rate
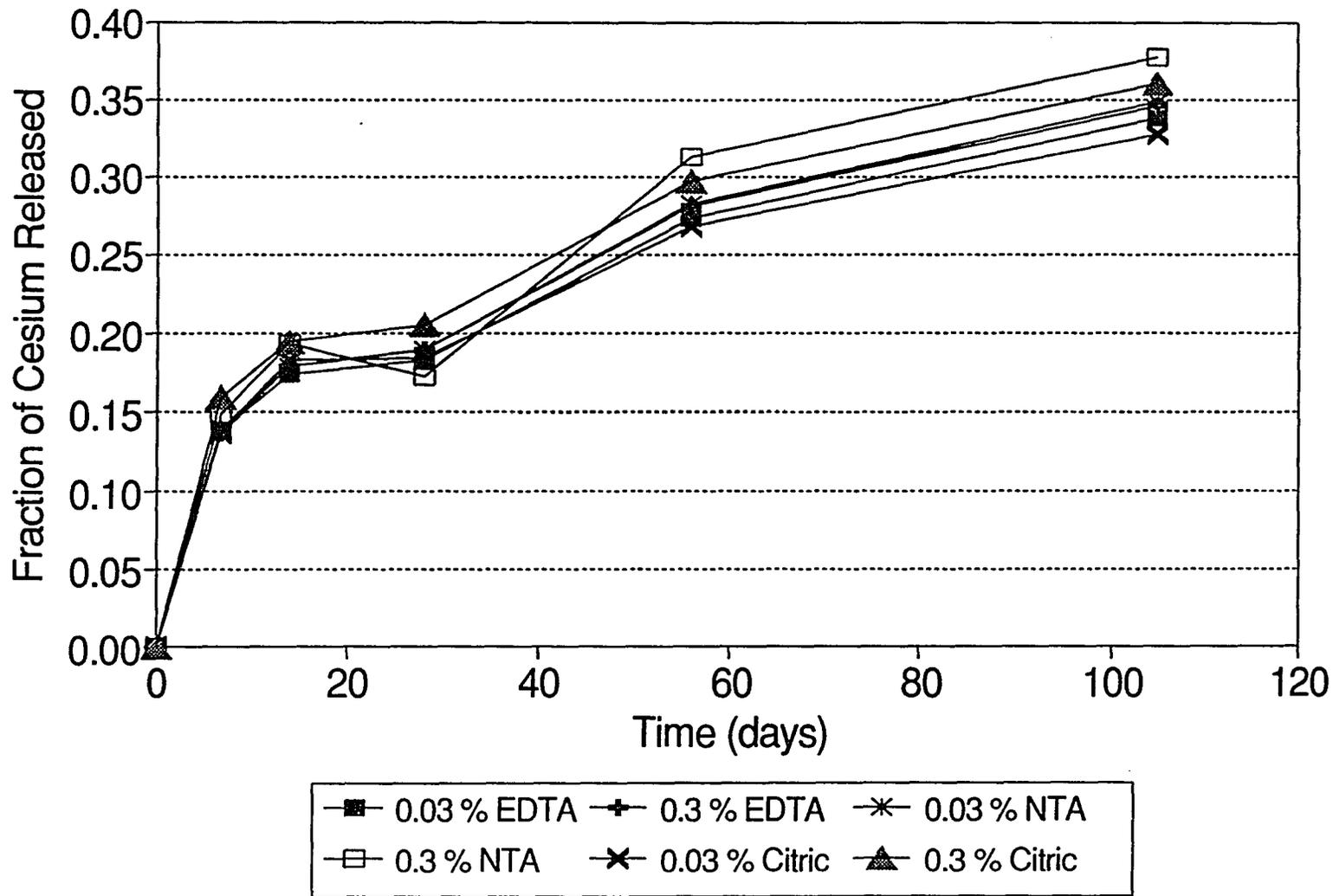
Figure 3. Time Dependence of Cesium Concentration in Deionized Water

studies, all experiments were run in duplicate. The values reported in Fig. 3 are averages of the duplicate studies. The standard deviations of these values are all less than or equal to ± 0.02. All samples were at least two orders of magnitude above the determination limits.

The release of cesium with respect to time is similar to that of EDTA. However, Fig. 2 shows that the fraction of cesium released is much higher than the fraction of EDTA released. As mentioned previously, this suggests that some process other than solubility limits is responsible for the low EDTA release rates. It is also of interest to note that after about 155 days, the cesium release fraction (Fig. 2) is approaching the equilibrium fraction of EDTA (Table V). While the equilibrium concentrations of these two species seem to be similar, the difference in the release rates indicate that the cesium is not being released as a complexed ion.

The release of cesium is similar to releases reported previously[59]. Leach rates from these studies are also similar. Since the behavior of cesium has been well documented and no unusual results were seen in the leach rate studies, no equilibrium studies were run on cesium. Because cesium does not form complexes with the chelating agents, there was no reason to believe that cesium studies

would produce any results which would not be more significant in the cobalt equilibrium studies.

While the results of these studies indicated that the presence of complexing agents did not increase the solubility of cesium, the solubility of cesium was in all cases very high. This and the high concentrations of cesium-137 in some waste forms indicate that cesium-137 is an important isotope in safety considerations of cemented waste forms.

Cobalt

Several different studies were run to determine the behavior of cobalt under different conditions. Leach rate studies were run on the active simulated waste forms to determine whether a measurement could be made of the rate at which cobalt was leached. Some work was also done to observe the effect of the chelates on trace amounts of cobalt at equilibrium. In addition, equilibrium studies were carried out with larger amounts of cobalt in the solutions described previously both with and without the simulated cement waste form.

Leach Rate Studies. In all the leach rate studies, the concentration of cobalt in solution was below the detection limit of the Ge(Li) detector. The low solubility

of cobalt in aqueous solutions is responsible for the very low concentrations.

It was necessary to use the Ge(Li) detector for these studies because the simulated waste form was loaded with both cesium-137 and cobalt-60. While the NaI detector could have been used, the resolution was not sufficient to distinguish between the cesium and cobalt peaks. In addition, the NaI detector was equipped with a single channel analyzer. Analysis of both the cesium and cobalt could not be carried out simultaneously. In the end, it was deemed unnecessary to run leach rate studies on the cobalt alone because the results of the equilibrium studies showed in most cases that even the equilibrium concentrations of cobalt in solution was very small in the presence of cement.

Effect of the Chelates on Trace Amounts of Cobalt. When the equilibrium studies were run using a cobalt-60 tracer without carrier cobalt, cobalt concentrations could be measured down to the range of 1×10^{-14} M. The results of these studies in water have been included in Table VII.

The values in Table VII for the studies using the simulated cemented waste form are from the more highly loaded samples. Even in these cases, no effect could be seen from the complexing agents. The studies without the cement were run using an equivalent amount of complexing

agent in each 30 ml sample. Once again, no effect could be seen from the complexing agents.

Table VII: Equilibrium Concentrations of Co at Trace Levels

Complexing Agent	Concentration of Cobalt (M)	
	With Cement	Without Cement
None	$2.6\pm0.35\times10^{-11}$	$6.7\pm0.11\times10^{-11}$
EDTA	$2.2\pm0.35\times10^{-11}$	$6.77\pm0.064\times10^{-11}$
Citric Acid	$2.4\pm0.21\times10^{-11}$	$6.9\pm0.11\times10^{-11}$
NTA	$2.7\pm0.49\times10^{-11}$	$7.2\pm0.16\times10^{-11}$

The uncertainties reported in Table VII are once again the standard deviations in the duplicate measurements. Considering the nature of the experiments, it is perhaps surprising that the results are as reproducible as indicated in theses studies. Of primary concern is the pH. Because of the high ionic strengths of some leachants, pH paper was used to set the solution pH's in the studies without cement. While less dependent on ionic strength than measurements made with a pH meter, the pH paper used could only give a resolution of $\pm$ 0.3 pH units. Since this corresponds to a difference in hydroxide concentration of two times, and

since the cobalt concentration depends on the square of the
hydroxide concentration, this could have a large effect on
the results.

Comparing the values from the studies without cement
to those with cement, one can see a marked decrease in the
soluble cobalt levels due to the presence of cement. This
is possibly due to sorption of the cobalt on the cement.
While an obvious difference in results with and without
cement is seen in Table VII, the order of magnitude of the
effect is important. In these studies, the cement seems to
reduce the soluble cobalt concentration approximately
threefold.

Equilibrium Cobalt Concentrations in Low pH
Solutions. The results from the equilibrium studies of
cobalt in Q-brine have been presented in Table VIII. These
values indicate that in the absence of the simulated
cemented waste form, essentially all of the cobalt is in
solution. This suggests that under these conditions, pH
6.5, the cobalt concentrations are below the solubility
limits. No effect can, therefore, be seen from the
complexing agents.

When the simulated cemented waste form was added to
the solutions, the concentration of the cobalt was reduced
by two orders of magnitude in all cases examined except in
the presence of tartaric acid. Tartaric acid was very

effective in moderating the effect of the cement. The cobalt-tartrate complex does not seem to be as sensitive to competition by the calcium from the cement as the other complexes do.

Table VIII: Equilibrium Concentrations of Co at Low pH's

Complexing Agent	Cobalt Concentration (M)	
	With Cement	Without Cement
None	$1.9 \pm 0.17 \times 10^{-5}$	$9.2 \pm 0.72 \times 10^{-3}$
EDTA[62]	6.9×10^{-3}	-----
NTA[62]	3.5×10^{-3}	-----
Citric Acid[62]	2.1×10^{-4}	-----
Tartaric Acid	$3.0 \pm 0.13 \times 10^{-3}$	$8 \pm 1.0 \times 10^{-3}$
Oxalic Acid	$3.9 \pm 0.69 \times 10^{-5}$	$8 \pm 2.3 \times 10^{-3}$
TBP	$2.6 \pm 0.79 \times 10^{-5}$	$9.4 \pm 0.68 \times 10^{-3}$
DBP	$4.9 \pm 0.37 \times 10^{-5}$	$1.096 \pm 0.0041 \times 10^{-2}$

Other studies have shown that EDTA and NTA also drastically reduce the effects of the cement at these pH's. Citric acid, on the other hand has been shown to only moderately increase the cobalt concentration in the presence

of the waste form. In Table VIII, the results for EDTA, NTA and citric acid in the presence of cement are from these previous studies[62]. The concentrations associated with no cemented waste forms in these cases are the values from these studies in the absence of any chelate. They have been presented in this fashion to offer a reference.

The concentrations and uncertainties in Table VIII are the averages and standard deviations of three parallel studies.

The uncertainty associated with the measurements in the absence of the cement is about 1×10^{-5} M. Therefore, even the oxalic acid and DBP show a significant effect on the cobalt concentration. However, these effects are orders of magnitude less than the effects from the tartaric acid, EDTA, NTA and citric acid.

In addition to the effects seen from the concentration measurements, the effect of the cement could be visually observed. The solutions without cement were turned light pink from the soluble cobalt. When cement was present, the pink solution was removed and a green precipitate caused the solution to be a murky green.

Equilibrium Cobalt Concentrations in High pH Solutions. Results from the equilibrium studies using water and saturated sodium chloride solutions were all within the experimental uncertainty of each other. For this reason,

only the results for the water studies have been presented. These results can be seen in Table IX.

The results in Table IX suggest that cobalt forms soluble complexes with EDTA, NTA, and citric acid in the absence of the simulated waste form. The other studies showed no measurable cobalt concentration in solution at pH's of 12.5.

Table IX: Equilibrium Concentrations of Co at High pH's

Complexing Agent	Cobalt Concentrations (M)	
	With Cement	Without Cement
None	$< 1 \times 10^{-5}$	$1.59 \pm 0.090 \times 10^{-4}$
EDTA	4×10^{-5}	$2.8 \pm 0.24 \times 10^{-2}$
NTA	4×10^{-5}	$3.0 \pm 0.26 \times 10^{-2}$
Citric Acid	4×10^{-5}	$1.8 \pm 0.26 \times 10^{-2}$
Tartaric Acid	$< 1 \times 10^{-5}$	$< 1 \times 10^{-5}$
Oxalic Acid	$< 1 \times 10^{-5}$	$< 1 \times 10^{-5}$
TBP	$< 1 \times 10^{-5}$	$< 1 \times 10^{-5}$
DBP	$< 1 \times 10^{-5}$	$< 1 \times 10^{-5}$

In these cases the addition of cement to the sample solutions brought the soluble cobalt concentration down several orders of magnitude. In fact, parallel to the EDTA, NTA and citric acid studies a test was run with no chelate. In this sample, the concentration of the soluble cobalt was seen to be 4 x 10^{-5} M. This indicates that in the presence of cement even EDTA, NTA and citric acid have no significant effect on the cobalt concentration. Once again, the reduction of the cobalt concentrations in the presence of cement may be due to the competition of calcium ions to form complexes with the complexing agents.

As above, the uncertainties in Table IX are standard deviations of triplicate studies. In three instances, no indication of the uncertainty was given. In these cases, only one study was made. The low count rates of these studies gave standard deviations of ± twenty percent.

In addition to the results shown in Table IX, the insolube cobalt could be seen as a brown precipitate at the bottom of all the samples except the EDTA, NTA, and citric acid studies without cement. The precipitate was probably cobalt hydroxide.

Other studies have indicated that the concentrations of some actinides are also reduced by the presence of cement even in the presence of EDTA, NTA and citric acid[63].

More recent studies have indicated the need to
continuously monitor the pH's of the solutions without
cement. Although the pH was set to 12.5 using sodium
hydroxide and the samples were stored in sealed containers,
the pH's have been seen to drift perhaps under the influence
of carbon dioxide. For this reason, the pH's of the latter
studies were constantly monitored. Although this drift was
noted, it should not have had an effect on the results of
these studies.

In all studies using cement, it was necessary to
filter the sample solutions to remove particulates which may
be suspended in the solution. When this was not done, the
resulting measurements were very inconsistent and almost
impossible to interpret. In our studies the Amicon
filtration system was used. The method involved using a
centrifuge to force the samples through the Amicon filters.
Each of the samples were centrifuged for an hour. The
maximum pore size of these filters were about 1.8 nm. This
procedure was also followed for the uranium studies.

Uranium[64]

The effect of the chelates on the equilibrium
concentration of uranium at was studied in the presence and
absence of the simulated cemented waste form. The studies
were run using Q-brine, water and saturated sodium chloride.

As in all other studies, the Q-brine solutions were kept at a pH of 6.5 either by the presence of the cement or by adjustment using sodium hydroxide. Likewise, the water and sodium chloride solutions were all at a pH of 12.5.

Equilibrium Uranium Concentrations in Low pH Solutions. The results of the studies to determine the equilibrium concentrations of uranium in Q-brine have been presented in Table VIII.

At these levels, one standard deviation corresponds to about 20% of the concentration. None of the complexing agents showed an order of magnitude or greater effect on the uranium concentration in Q-brine. Some of the studies did, however deviate from the blank solution by more than can be attributed to the experimental uncertainties.

Only the EDTA and the citrate increased the uranium solubility significantly in the absence of the simulated waste form. While the EDTA increased the cobalt concentration less than twofold, from 1.0×10^{-4} M to 1.8×10^{-4} M, the citrate increased the solubility more than four times to 4.3×10^{-4} M.

In addition to the above deviations, the concentration of soluble cobalt in the oxalic acid solutions was about one third of the blank sample concentration. Although oxalic acid was one of the least soluble of the

complexing agents used, a reduction in the soluble cobalt
was not expected.

Table X: Equilibrium Concentrations of U at Low pH's

Complexing Agent	Uranium Concentration (M)	
	With Cement	Without Cement
None	7.4×10^{-5}	1.0×10^{-4}
EDTA	1.5×10^{-4}	1.8×10^{-4}
NTA	5.0×10^{-5}	8.4×10^{-5}
Citric Acid	1.3×10^{-4}	4.3×10^{-4}
Tartaric Acid	1.9×10^{-4}	1.2×10^{-4}
Oxalic Acid	3.6×10^{-5}	3.4×10^{-5}
TBP	4.3×10^{-5}	7.9×10^{-5}
DBP	4.6×10^{-5}	7.2×10^{-5}

Studies done on the solutions with the simulated
cemented waste form showed the general trend described
previously.   In most cases, the presence of the cement
caused the uranium concentrations to drop somewhat.   These
changes were not as drastic as those seen in the cobalt
samples, however this is because the concentrations of

uranium in solution were much lower than the cobalt in
solution. In fact, no noticeable change was seen in the
already low uranium concentrations in the presence of
oxalate, and in tartrate solutions the uranium concentration
actually seemed to increase slightly.

In all samples regardless of whether cement was
present, a yellow uranium precipitate was seen at the bottom
of the test bottles.

Addition of tartaric acid had the largest effect on
the uranium concentration in the presence of cement. EDTA
and citric acid also acted to increase the uranium
concentration when the simulated waste form was present,
however the effect is not as large.

Equilibrium Uranium Concentrations in High pH
Solutions. Equilibrium concentrations of uranium in
saturated sodium chloride solutions were below the detection
limits of 1×10^{-5} M regardless of whether any of the
complexing agents were present and regardless of whether the
simulated waste form was present in the solutions.

The same was true for the studies using deionized
water except that in the absence of the simulated cement
waste form EDTA was seen to bring the concentration of the
uranium in solution up to 9.5×10^{-4} M, an increase of
almost two orders of magnitude. It is significant that
complexation of the uranium with EDTA increased the

concentration of uranium in the solution. EDTA has been shown to increase the uranium mobility in the field causing problems with containment. In addition, these cases have involved waste forms other than cement.

The results from the uranium studies were in good agreement with the cobalt studies except the effects of NTA and citric acid were not prominent on the uranium concentrations. In both cases, the effect of EDTA on the metal ion concentration was reduced by two or three orders of magnitude by the addition of the simulated cemented waste form. Also, the effects of oxalic acid, DBP and TBP were not sufficient enough to bring either of the metals to a high enough concentration to permit their detection. The fraction of uranium and cobalt in solution at the detection was below 0.001.

Results similar to these uranium results have been reported elsewhere for plutonium, americium and neptunium for similar studies[63].

Other Inorganic Species

To better understand the nature of the solutions used the concentrations of sodium, calcium and magnesium and the pH's were determined. This information will be important in modelling these systems in future work.

Other Metal Ions

Sodium, calcium and magnesium are all present at concentrations higher than the metal ions of interest in at least some of the solutions. Because of their high concentrations, the ions may have a large impact on the chemistry of the solutions. The concentrations determined for each of these species has been presented in Table XI.

Table XI: Equilibrium Concentrations of Inorganic Species

Solution	Concentration (M)		
	Calcium	Magnesium	Sodium
Water	1.4 E-2	-----	8 E-2
Sat. NaCl	(1.4 E-2)	-----	9
23.5% MgCl$_2$	-----	2.5	_____
Q-Brine	-----	2.5	0.33

() indicate values which were assumed from H$_2$O measurements.

Sodium. Optical emission spectroscopy using an inductively coupled plasma, ICP, was used to determine the equilibrium concentrations of sodium in water from samples of the studies of the EDTA, NTA, citric acid and from one

with no complexing agent. Deviations between results from samples with different complexing agents were insignificant.

Although the concentrations were not measured in the other solutions, they could be calculated from the composition of the Q-brine and the saturated sodium chloride solutions. These values and the measured values have been included in Table XI.

Calcium. The ICP was also used to determine the concentration of calcium in the solution. Once again, no significant deviation was observed between the solutions with different chelates.

The calcium concentration should be similar in the case of the water and sodium chloride solutions, however it may be somewhat different in the magnesium chloride and Q-brine solutions. In the former solutions, the pH is buffered by the precipitation of calcium hydroxide. In these solutions the calcium concentration is limited by the calcium hydroxide solubility. In the other solutions, the pH is buffered at a much lower value by the solubility of magnesium hydroxide. The calcium concentrations in these cases may have been somewhat higher.

Magnesium. The concentration of magnesium in solution was calculated for the magnesium chloride and Q-brine solutions. The actual values may be significantly

lower since some of the magnesium had precipitated from the sample solutions as magnesium hydroxide.

pH's

To compare the pH's of the different solutions, potentiometric measurements were made of the pH's. Previously, measurements had been made using pH paper, however the precision of the available paper was only half a pH unit. The results from the pH measurements are in Table XII.

Table XII: pH's of Equilibrium Solutions

Solution	pH	
	From pH Meter	From pH Paper
Deionized Water	12.6	12.5
Saturated NaCl	12.2	12.5
24 % MgCl$_2$	7.1	6.5
Q-Brine	6.9	6.5

The pH's were independent of the chelate in the solution to within three hundredths of a pH unit. This was to be expected since the complexing agents were in such low

concentrations in the solutions. The values reported in Table XII are the average of the readings.

Alkaline Solutions. The pH's of the water and sodium chloride solutions were controlled by the calcium hydroxide released from the cement. Although the values measured potentiometrically seemed to be different for the two solutions, sodium in the sodium chloride may be interfering with the pH readings. It is also possible that the higher activity of the sodium chloride solution has shifted the calcium hydroxide solubility slightly.

Neutral Solutions. Precipitation of magnesium hydroxide set the pH's of the magnesium chloride and Q-brine solutions. Once again, the values for these solutions in Table XII are slightly different. This may be due to interference from the other species in the Q-brine solution.

The magnesium hydroxide was seen in these solutions as a white flaky solid at the bottom of the samples. After a very short time, one day, the precipitate would form. The quantity of magnesium hydroxide formed was possibly great enough to alter the concentration of magnesium in solution significantly.

CHAPTER 5

CONCLUSIONS

This study has dealt with several parameters which affect the release of radionuclides from a radioactive waste form. Work has been done to determine the concentrations of complexing agents and their effects on the concentrations of metal ions in solutions around a simulated waste form. In so doing, the dependence of the equilibrium concentrations on the waste form itself has also been studied. Finally, some basic chemical equilibrium calculations have been in an attempt to model the more simple laboratory experiments.

As in most studies, for each question which was answered several others were asked. For this reason, work is currently under way on a number of projects.

Summary

Of the seven complexing agents examined, only the concentrations of EDTA, NTA and citrate were measured in these studies. Each of these complexing agents showed a different behavior as a function of the cement loading.

The fraction of EDTA released from the simulated waste form was independent of the amount of EDTA in the cement. This suggests that the concentration in solution was below the solubility limit of EDTA. If the solubility

limit were approached, the concentration of EDTA would be constant, but the fraction released would not. Concentrations of EDTA were well below the values expected based on the EDTA solubility. This suggests adsorption may play a significant role in establishing the equilibrium concentrations.

While the EDTA release fraction was independent of the loading in the simulated waste form, for citric acid, it was the concentration which was constant when the amount of citric acid in the waste was changed. This seems to indicate that the release of citrate to the solution was set by some solubility limit, possibly for calcium citrate. The release of citrate from a waste form in a repository should therefore be dependent on the flow rate of water to the waste form and fairly independent of the amount of citric acid in the waste form.

NTA releases behaved in a fashion intermediate to the EDTA and the citric acid samples. When much larger amounts of NTA are added to the waste, the solution should be saturated, and the NTA concentration should be constant as is the case for citric acid. When less NTA is put in the cement, the fraction released should be independent of the cement loading as was observed for EDTA.

Similar studies made on similar quantities of the remaining four complexing agents should produce results similar to those from the citric acid experiments since none of these compounds are as soluble as NTA in aqueous solutions.

Three different metals were studied, cesium, cobalt and uranium. While the cesium studies were restricted to leach rate observations, studies of the equilibrium concentrations of the cobalt and uranium were more thorough.

The leach rate of cesium was not affected noticeably by the presence of the complexing agents studied, i.e. EDTA, NTA and citric acid. This was expected since the cesium is very soluble in aqueous solutions even in the absence of the complexing agents and does not form strong complexes.

The leach rate of cobalt could not be determined because its concentration was well below the detection limit of the Ge(Li) detector.

The observed effects of the complexing agents on the equilibrium concentrations of the metals have been summarized in Table XIII.

The cobalt equilibrium concentration in solutions with pH's between 12.0 and 12.5 showed no dependence on the presence of any complexing agent when cement was added to the solution. In fact, most measurements were below the detection limit of 1×10^{-5} M.

Table XIII: Effect of Complexing Agents on Co Concentrations

	EFFECTS OF COMPLEXING AGENTS			
	WITH CEMENT		WITHOUT CEMENT	
COMPLEXANT	LOW pH	HIGH pH	LOW pH	HIGH pH
EDTA	INCREASE	NONE	NONE	INCREASE
NTA	INCREASE	NONE	NONE	INCREASE
Citric Acid	INCREASE	NONE	NONE	INCREASE
Tartaric Acid	INCREASE	NONE	NONE	NONE
Oxalic Acid	NONE	NONE	NONE	NONE
TBP	NONE	NONE	NONE	NONE
DBP	NONE	NONE	NONE	NONE

When no simulated cemented waste form was added, only EDTA, NTA and citric acid increased the solubility of the cobalt by several orders of magnitude. Concentrations in studies using the other complexing agents, and in tests without a complexing agent, were all below the 1 x 10^{-5} M detection limit.

In all cases, essentially all the cobalt was found
in solution when tests were run using Q-brine at a pH of 6.5
without the addition of the simulated cement waste form.
While studies were not made of EDTA, NTA and citric acid, it
is reasonable to believe that this would be the case in
these experiments.

When cement was added to the Q-brine solutions, the
presence of EDTA, NTA and tartaric acid caused the
concentration of the soluble cobalt to be increased by over
two orders of magnitude. Citric acid was seen to have a
smaller but still significant effect on the equilibrium
cobalt concentration, while oxalic acid and DBP studies
indicated these complexing agents may cause a very small
increase in the cobalt solubility. No concentration
increase could be seen in the TBP studies.

These results suggest that in a repository where the
pH of the groundwater is buffered at a fairly low value
(below 7) the presence of EDTA, NTA, citric acid and
tartaric acid may immobilize cobalt and similar elements
from cement waste forms. On the other hand, the solubility
of cobalt and similar elements in repositories at higher pH
environments is only significantly increased in the absence
of cement. In this case, only EDTA, NTA and citric acid
increase the solubility.

The results from the uranium studies were similar, however the concentrations of uranium in solution were far less than the cobalt in the solution. The results from the uranium studies have been included in Table XIV.

As was the case for the cobalt studies, no complexing agent significantly increased the uranium concentrations in the presence of cement at a pH of 12.5. Without exception, the equilibrium concentrations were below the detection limit of 1 x 10^{-5} M.

In the absence of cement, at the same pH, only EDTA raised the concentration of the uranium above the detection limit. In this case, however, EDTA brought the soluble uranium up two orders of magnitude above the detection limit.

In the Q-brine solutions, the uranium concentrations did seem to depend somewhat on the presence of the complexing agents when no cement was present, however, the concentration differences were all less than one order of magnitude. Citrate seems to have increased the uranium concentration about four times while EDTA almost doubled the concentration of soluble uranium. The presence of oxalic acid seems to have reduced the concentration of soluble uranium.

Table XIV: Effect of Complexing Agents on U Concentrations

	EFFECT OF COMPLEXING AGENTS			
	WITH CEMENT		WITHOUT CEMENT	
COMPLEXANT	LOW pH	HIGH pH	LOW pH	HIGH pH
EDTA	INCREASE	NONE	INCREASE	INCREASE
NTA	NONE	NONE	NONE	NONE
Citric Acid	INCREASE	NONE	INCREASE	NONE
Tartaric Acid	INCREASE	NONE	NONE	NONE
Oxalic Acid	DECREASE	NONE	DECREASE	NONE
TBP	NONE	NONE	NONE	NONE
DBP	NONE	NONE	NONE	NONE

In the presence of cement, the uranium concentrations are all within one order of magnitude of each other.   EDTA, citric acid and tartaric acid all increased the concentration by about two to two and a half times over the studies with no complexing agents.   Once again, the oxalic acid seems to have reduced the equilibrium concentration of uranium in solution.

The results for the water and the sodium chloride solutions were essentially the same. The only large difference in metal ion concentrations was seen for the uranium concentration in the presence of EDTA. Here, the sodium chloride solution had no measurable amount of uranium in solution while the EDTA was seen to raise the uranium concentration in the water to above the detection limit.

These results suggest that in a repository at a high pH environment, only when waste containing uranium is in the presence of EDTA will the solubility of uranium be increased. In repositories buffered at a low pH, uranium release from a cement waste form may be facilitated in the presence of EDTA, citric acid and tartaric acid. If the waste is not in the presence of cement, EDTA and citric acid alone may increase the uranium solubility. Oxalic acid seems to reduce the releases at low pH's.

The presence of magnesium in the solution was seen to have a large effect on the concentrations of both cobalt and uranium. Magnesium acts as a buffer by precipitating as magnesium hydroxide. This kept the pH of the solutions at a measured value of about 6.9.

In Q-brine, the cobalt was seen to precipitate as cobalt hydroxide at a measured pH of about 7.1. Therefore, in the presence of the magnesium the cobalt concentration

was substantially higher than in solutions without a substantial amount of magnesium.

Uranium, on the other hand, had already begun to precipitate at the pH of the Q-brine. Therefore, the concentrations of uranium were low regardless of the solution. The difference in the uranium solubilities were much less drastic than the cobalt solubilities.

These results suggest repositories located in a rock which is high in magnesium may be less desirable as sites for repositories.

The presence of cement reduced the concentration of cobalt in Q-brine by at least an order of magnitude in all studies except when tartaric acid was added. In this case, the cobalt concentration was only brought down threefold. In the water and sodium chloride solutions where the cobalt concentration was not already low, the concentrations were reduced by two to three orders of magnitude.

In general, cement was also seen to bring down the concentration of uranium in solution. Since the concentrations were already low, the effects of the cement on uranium were not as great as the effects on the cobalt. In some cases the concentrations were not noticeably affected, and in the case of the tartaric acid studies in Q-brine the concentrations even seemed to increase slightly.

Cement as a waste form and as structural material in a repository acts to reduce the release of radionuclides. It seems to do so not only physically, but also chemically through controlling the environment into which the radionuclide is being released. The presence of cement in solutions with substantial magnesium concentrations keeps the pH of the system at about 6.5 through the precipitation of magnesium hydroxide. In groundwater with no significant magnesium concentration, the solubility of calcium hydroxide buffers the pH at about 11.0. In addition, some additional process, perhaps adsorption, seems to moderate releases of such compounds as EDTA.

Recommendations

These studies have brought up a number of questions and problems. First, work is necessary in exploring different methods for detecting the complexing agents. The titration used in these studies was not applicable to all the complexing agents used at the levels of interest. Methods considered should be as widely applicable as possible. In addition, a great deal of motivation exists to considered only simple techniques which require as little expensive equipment as possible. Currently, work at the Institut fur Nukleare Entsorgungstechnik at

Kernforschungzentrum Karlsruhe has been geared toward
evaluating other types of titrations.

To avoid the necessity of running a destructive
analysis on the samples, the option of using coated-wire ion
selective electrodes has been suggested. If successful,
concentrations could be measured frequently without
requiring removal of an aliquot from the sample solution.

More work is also needed to evaluate the behavior of
the NTA in the waste forms. The concentrations of NTA
studied seemed to be close to the solubility limit. By
increasing the amount of NTA in the simulated waste form,
the solubility limit should be reached, and the
concentration should no longer be dependent on the amount of
NTA in the solution.

Measurements of cobalt and uranium could be improved
if the detection limits could be reduced. For cobalt, this
could be done by using a greater amount of cobalt-60 and
less of the inactive cobalt carrier. The measurements could
then be run as in these studies with a sodium iodide
detector.

Another approach would be to run the tests using
inactive solutions with a neutron activation analysis. This
would allow us to observe both the cobalt and uranium to
much greater detection limits. Before this could be done, a
feasible study would be necessary to determine the

activities produced by activation of other species, and to determine whether species such as sodium would cause too great an interference.

Studies such as these can be greatly complimented by such chemical equilibrium codes as MINEQL and EQ3/6. Use of such codes gives insight to the processes which might be responsible for observed phenomenon. In addition, models based on these codes are useful as predictive tools.

In addition to linking the chemical equilibrium codes with experimental results, work is necessary to make the available codes applicable to the high activity brine solutions which one might encounter in a waste repository. While all models have procedures for handling such solutions, the data necessary for such calculations is often lacking. Much of this data may be available in the literature. Some of it, however, may require interpretation of the literature information, and some may require measurements to be taken.

Finally, the results from such studies are only the source of the radionuclide release. To determine the release rates this information can be applied to models of radionuclide transport through the near and far-fields and into the accessible environment. Such an application has the potential for providing very pertinent information for safety analysis of repositories.

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64. The author is greatly indebted to Fr. I. Kahl for carrying out a great deal of the work on these equilibrium studies.