

STUDIES OF THE INFLUENCE OF COMPLEXING AGENTS ON COBALT AND URANIUM LEACHING FROM SIMULATED LOW AND INTERMEDIATE-LEVEL CEMENTED WASTE FORMS

Peter Vejmelka and Rainer Koester
Kernforschungszentrum Karlsruhe GmbH
75 Karlsruhe 1, FRG

Daro Ferrara and Morton E. Wacks
University of Arizona
Tucson, Arizona 85721

ABSTRACT

Leach studies were carried out to determine the effects of several complexing agents on the equilibrium concentrations of cobalt and uranium in a system cemented waste form/aqueous solution. The complexants examined were ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid, oxalic acid, tartaric acid, tributyl phosphate (TBP) and dibutyl phosphate (DBP). Solutions used as leachants were deionized water, saturated sodium chloride solution and Q-brine, which is a solution with magnesium chloride as the main constituent. In addition to determining the effects of the complexants and leachants, the role of the cement matrix in establishing the equilibrium concentrations was also examined. Uranium was chosen for the investigations because it is one of the important radionuclides for long term safety considerations, and it is contained in the low and intermediate level cemented waste forms in amounts up to 1 kg/200 L drum. Cobalt forms strong complexes with some of the complexants mentioned and can be measured at low concentration levels when cobalt-60 is used as a radioactive tracer. For this reason, it was used as a model to study the effects of the complexants in the different systems.

The results indicate that the equilibrium concentrations of cobalt and uranium in the systems cemented waste form/water and cemented waste form/sodium chloride solution at the equilibrium pH value of 12.5 are independent of the complexants present and are determined only by the solubility of metal hydroxides. In the system cemented waste form/Q-brine with an equilibrium pH value of 6.5, tartaric acid, EDTA and NTA increase the cobalt equilibrium concentration by two orders of magnitude. Citric acid has a smaller effect, and all the other complexants show no effect. The uranium equilibrium concentration is slightly increased by EDTA, tartaric acid and citric acid, but the amount of uranium in solution corresponds to less than 5% of the total amount of uranium added to the system.

INTRODUCTION

Safety considerations for a repository of radioactive waste include the scenario of a water ingress into the storage area in the post operative phase. This requires assessments of the release rate of radionuclides from waste forms in contact with aqueous solutions.

Low and medium level evaporator concentrates, which are solidified by embedding into cement, may contain varying amounts of organic complexing agents added at different points of the nuclear fuel cycle for decontamination purposes or from active laundries. The materials found most frequently include ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid, tartaric acid and oxalic acid. Tributyl phosphate (TBP) is among the constituents of the waste stream from extractant purification in the PUREX process, and dibutyl phosphate (DBP) may be formed by hydrolysis of TBP during the waste treatment process or by the alkaline conditions in the cemented waste form.

As these complexing agents may influence decisively the release and the migration behavior of the radionuclides, it is necessary to investigate the impact of these substances

on the radionuclide release in the cemented waste form/aqueous solution system.

To study the release of radionuclides from waste forms, two approaches have traditionally been taken. One method has been to study a closed system of the waste form and leachant. At the desired leach times, samples are either taken of the leachant, or the leachant is changed by removing the waste form and immersing it in fresh leachant. Examples of these static leach tests are ANS 16.1 (1) and MCC-1 (2).

Another approach to leachability studies has been to run fresh leachant continuously into the container holding the waste form and to take leachant continuously from the container at the same rate. Samples can be taken of the leachant as it leaves the sample compartment. MCC-4 is one example of these dynamic or flow tests (3).

More recently, efforts have been made to study the amount of radionuclides in leachants at equilibrium with the waste forms (4, 5). Since the flow rate of water in a repository is very low, radionuclide concentrations can be predicted on the assumption that an equilibrium concentration

will be reached and that any subsequent release from the near-field is by escape of the equilibrated solution only.

While other leach tests provide results such as leachability indexes which are difficult to relate to real systems, or cumulative release fractions which are very dependent on such experimental parameters as leachant flow rates, equilibrium leach studies provide concentrations and release fractions which require much less interpretation.

Equilibrium source term data can be modelled using any one of several chemical equilibrium codes (6-8). These codes have been used in several diverse applications. The results of such models are solution concentrations which are very dependent on the equilibrium coefficients used. A number of reports have compared experimental results to results predicted by the chemical equilibrium models with various degrees of success (9-11).

The goal of this study is threefold. First, the effect of the complexants on the leachability of the radionuclides from the waste form was determined. The effect of the cement on the radionuclide release was also studied. Finally, an attempt was made to model the system using the available chemical equilibrium code.

For the studies performed, cobalt and uranium were used. Uranium is one of the important radionuclides for long term safety considerations and is contained in the low and intermediate level cemented waste forms in amounts up to 1 kg/200L drum. Cobalt forms complexes with relatively high stability and can be measured at low concentration levels when cobalt-60 is used as a radioactive tracer. Therefore, it was used as a model to study the effects of the complexants. For comparison some stability constants of organometallic complexes are summarized in Table I (12).

With Co the effect of TBP, DBP, oxalic acid and tartaric acid was investigated. The effect of EDTA, NTA and citric acid on the Co equilibrium concentration and the influence of cement on the system deionized water/complexant has already been reported (13). Unpublished results for the effects of EDTA, NTA, and citric acid in the system Q-brine/cemented waste form were also already available. In

TABLE I

Stability Constants (log K) for Selected Organometallic Complexes

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

the experiments with uranium all the complexants mentioned above were used.

The long term goal of this and similar studies is to provide information on the source term for low and intermediate level cemented waste forms in a repository.

EXPERIMENTAL

The procedure used in order to determine the concentration of Co and U in equilibrium with cementitious products was as follows: For each test, 30 mL of leachant were added to 2 g of crushed cementitious product and 0.02 g of complexing agent. This ratio is much larger than expected in real waste forms, but was chosen to permit reasonable measurements. Actual specimens contain only about 3 E-4 g of complexant per gram; an increased amount was used in these experiments in order to enhance the effects. The simulated waste form was prepared by mixing 1.0 kg of ordinary portland cement (OPC) with 150 g of sodium nitrate and 400 mL of deionized water. The mixture was then poured into several fifty mL cylindrical plastic jars and allowed to set for ten to fifteen days. After the set time, four of the samples were crushed. As leachants, deionized water, saturated sodium chloride solution and Q-brine (1.9% sodium chloride, 2.3% potassium chloride, 3.3% magnesium sulfate and 24% magnesium chloride) were used. To study the effect of the cemented waste form, samples containing no cemented waste form were prepared, and the pH's were adjusted to the same values as that of the samples containing cement (pH of 12.5 for samples with deionized water and sodium chloride solution, pH 6.5 for samples with Q-brine) using 1 M sodium hydroxide. For the Co samples, 0.1 g of inactive Co(II) nitrate hexahydrate and 0.64 uCi of Co-60 were added to the samples. For the U samples, 0.08 g of uranium as uranyl nitrate was used in each sample.

After a storage time sufficient to attain equilibrium (normally 90 days(14)), samples were drawn from the solutions. The amount of Co-60 was measured by filtering a 10.0 mL aliquot of the sample using an Amicon filter system (1.8 nm). The filtered aliquots were counted for one minute with a NaI detector and a single channel analyzer. In addition, counts were taken of two standards and a blank. Once the measurements had been made, the aliquots were returned to the samples.

For the uranium measurements, aliquots of the samples were filtered, and 1.0 mL of the filtrate was added to 15.0 mL of a liquid scintillation cocktail. The mixture was counted using a liquid scintillation detector in series with a multichannel analyzer (Beckmann LS 7800). Two standards and a blank were also counted.

RESULTS

Table II shows the results obtained in Q-brine and Table III the results in deionized water for cobalt and

TABLE II

Equilibrium Concentrations of Cobalt and Uranium in the System Q Brine/Complexant and Q Brine/Complexant/Cemented Waste Form (pH 6.5, 30 mL Solution, Room Temperature)

<u>Complexant</u>	<u>Co Concentration (M)</u>		<u>U Concentration (M)</u>	
	<u>Without Cement</u>	<u>With Cement</u>	<u>Without Cement</u>	<u>With Cement</u>
No Complexant	9.2 E-3	1.9 E-5	1.0 E-4	7.4 E-5
EDTA	-----	6.9 E-3*	1.8 E-4	1.5 E-4
NTA	-----	3.5 E-3*	8.4 E-5	5.0 E-5
Citric Acid	-----	2.1 E-4*	4.3 E-4	1.3 E-4
Tartaric Acid	8.2 E-3	3.0 E-3	1.2 E-4	1.9 E-4
Oxalic Acid	7.9 E-3	3.9 E-5	3.4 E-5	3.6 E-5
TBP	9.4 E-3	2.6 E-5	7.9 E-5	4.3 E-5
DBP	1.1 E-2	4.9 E-5	7.2 E-5	4.6 E-5

*unpublished results

TABLE III

Equilibrium Concentrations of Cobalt and Uranium in the System Deionized Water/Complexant and Deionized Water/Cemented Waste Form/Complexant (pH 12.5, 30 mL Solution, Room Temperature)

<u>Complexant</u>	<u>Co Concentration (M)</u>		<u>U Concentration (M)</u>	
	<u>Without Cement</u>	<u>With Cement</u>	<u>Without Cement</u>	<u>With Cement</u>
No Complexant	1.6 E-4	< 1.0 E-5	< 1.0 E-5	< 1.0 E-5
EDTA	2.8 E-2*	4 E-5*	4.0 E-5	< 1.0 E-5
NTA	3.0 E-2*	4 E-5*	< 1.0 E-5	< 1.0 E-5
Citric Acid	1.8 E-2*	4 E-5*	< 1.0 E-5	< 1.0 E-5
Tartaric Acid	< 1.0 E-5	< 1.0 E-5	< 1.0 E-5	< 1.0 E-5
Oxalic Acid	< 1.0 E-5	< 1.0 E-5	< 1.0 E-5	< 1.0 E-5
TBP	1.5 E-4	< 1.0 E-5	< 1.0 E-5	< 1.0 E-5
DBP	6.4 E-5	< 1.0 E-5	< 1.0 E-5	< 1.0 E-5

* Reference 13.

uranium for the different complexants without and with the addition of the cemented waste form. The results obtained for saturated sodium chloride solution are comparable with the results in water with the exception of the uranium samples containing EDTA in water.

Cobalt

The data in Table II, which is also shown in Fig. 1, indicates that in Q-brine without the addition of the cemented waste form all of the cobalt is in solution indepen-

dent of whether there is a complexant in solution. This indicates that the cobalt concentration under the experimental conditions (pH value 6.5) is lower than the solubility limit, and therefore, it is not possible to observe an effect of the complexants on the cobalt concentration. If the cemented waste form is present in the system, the cobalt concentration is decreased by two orders of magnitude for all samples with exception of those containing tartaric acid. Tartaric acid causes a distinct increase in the cobalt equilibrium concentration, and about 30-40% of the cobalt

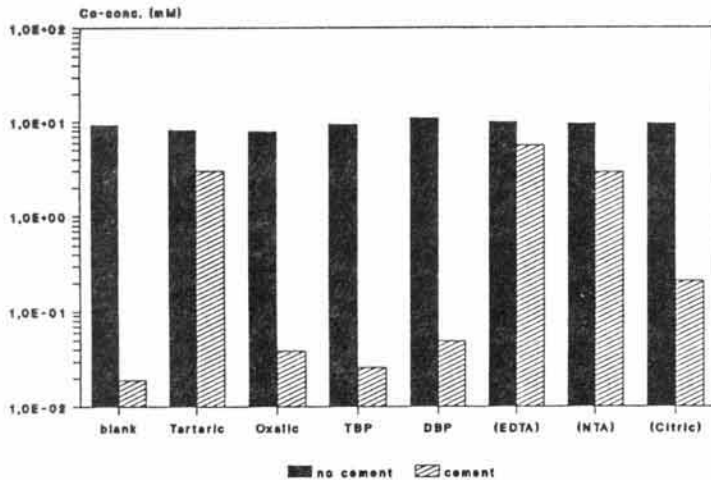


Fig. 1. Co equilibrium concentrations in Q brine in presence of complexants without and with cemented waste form (room temperature, pH = 6.5, 30 ml Q brine).

added to the system is found in solution. A comparable increase in the cobalt concentration was also observed in former experiments using EDTA and NTA as complexants whereas citric acid produced only a very slight increase in the cobalt concentration.

The results obtained in deionized water and saturated sodium chloride solutions indicate that the cobalt concentrations in both systems are comparably low and are determined by the solubility of cobalt hydroxide. Without and with the cemented waste form in the systems at the equilibrium pH of 12.5, no complexant increases the equilibrium concentration of cobalt.

The results for the system deionized water/complexant/cemented waste form are consistent with the results from former experiments using EDTA, NTA and citric acid as complexants (13). The only difference is, that in the system without cemented waste at pH 12.0 strong complex formation takes place with the three complexants and nearly 100% of the cobalt added is found in solution. By addition of the cemented waste form, the cobalt concentration is reduced to the low values determined by the solubility of cobalt hydroxide as in the experiments described here. The effect of the cement is explained by the interaction of the calcium contained in the cement with the cobalt complex, which causes the cobalt to be replaced by calcium, and the cobalt is then precipitated as hydroxide. This statement is confirmed by the results of thermodynamic calculations performed using the computer code MINEQL (6). The results of the calculations are shown in Fig. 2 and Fig. 3. In the system without calcium (Fig. 2), the Co-EDTA complex is stable over the entire pH range from 2 to 12 and no hydrolysis takes place. If Ca ions compete with the cobalt

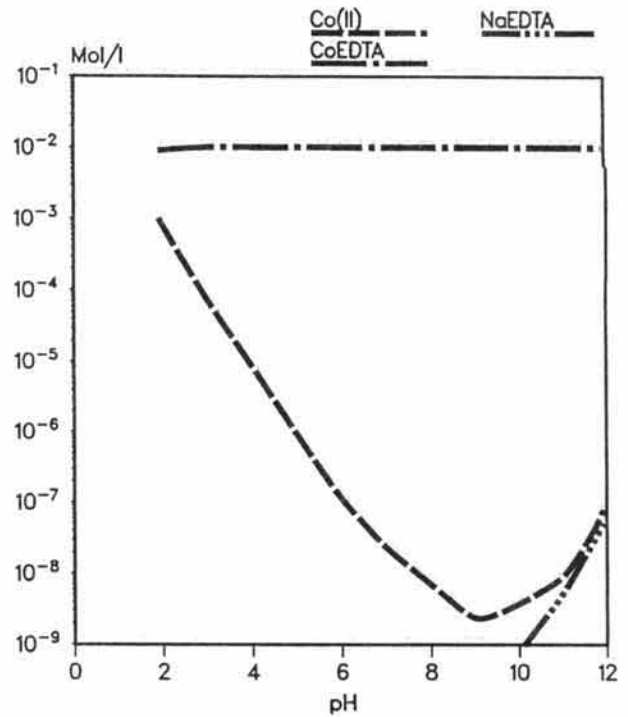


Fig. 2. Calculated cobalt concentration as a function of pH with EDTA (0.01 M) and Na (0.02 M) added.

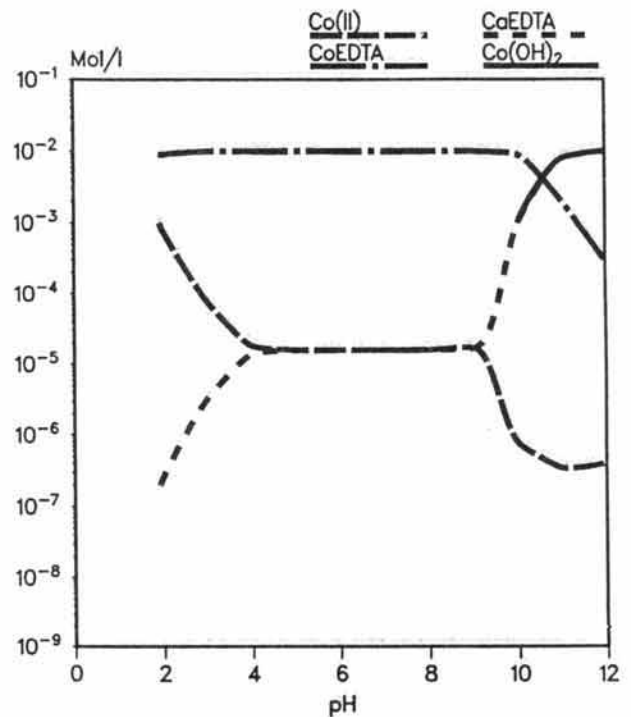


Fig. 3. Calculated cobalt concentration as a function of pH with EDTA (0.01 M) and Ca (0.02 M) added.

for the EDTA (Fig. 3), the limit of the stability region of the cobalt complex is lowered to pH 10.

Uranium

The data for uranium in Table II and given in Fig. 4 shows that complexation does not play an important role in establishing the uranium equilibrium concentration in Q-brine. Without the cemented waste form, in all samples with the exception of citric acid and EDTA, the uranium concentration amounts to 1 E-4 M or less, and no influence of the complexants is observed. In all cases a yellow precipitate is observed. In the presence of citric acid the uranium concentration amounts to 4.3 E-4 M and in presence of EDTA to 1.8 E-4 M but these values are only slightly higher than the value of 1.0 E-4 M for the samples containing no complexant. In presence of the cemented waste form a slight increase of the uranium concentration is also observed for the samples containing EDTA, tartaric acid and citric acid. The largest effect of the cemented waste form is seen for the samples containing tartaric acid.

The results obtained in deionized water and saturated sodium chloride solutions and summarized in Table III show that in deionized water without the cemented waste form only EDTA increases the uranium concentration above the detection limit to 4.0 E-5 M , and this value decreases with time. In sodium chloride, no effect of the complexants at the pH value of 12.5 can be observed. In the presence of the cemented waste form, the uranium concentration for all samples amounts to or less than 1.0 E-5 M , which is the detection limit under the experimental conditions. Therefore, no influence of any of the complexants on the uranium equilibrium concentration can be seen. The

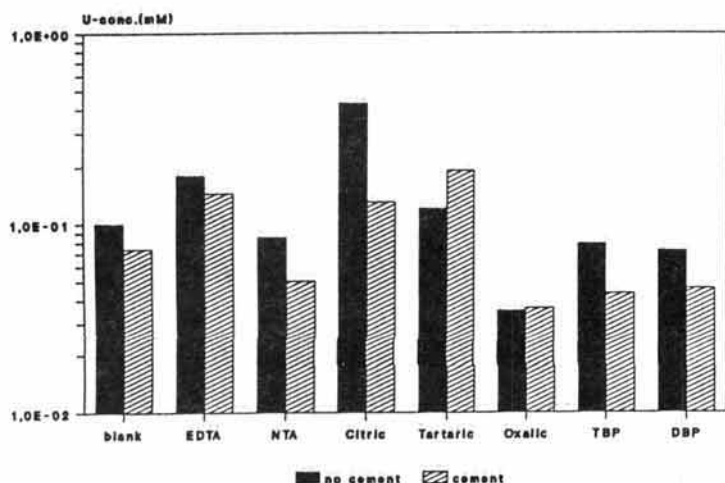


Fig. 4. U equilibrium concentrations in Q brine in presence of complexants without and with cemented waste form (room temperature, pH = 6.5, 30 ml Q brine).

fraction of uranium in solution calculated from the detection limit and the total amount of uranium added, amounts to 0.001. The results for uranium are in good agreement with the results obtained for cobalt and are also comparable to the results of former experiments using plutonium, americium and neptunium under similar conditions (14).

SUMMARY

The results show that the cobalt and uranium equilibrium concentrations in the systems aqueous solution/cemented waste form/complexant are influenced by the cement matrix. In case of Q-brine containing only complexants and no cement all of the cobalt added is found in solution. By addition of the cemented waste form the radionuclide concentration is decreased, but the equilibrium concentration depends on the complexant added. An increase of the cobalt concentration compared with samples containing no complexant is observed when EDTA, NTA and tartaric acid are added to the system.

In the case of uranium, only citric acid and EDTA have a small effect on the uranium concentration in Q-brine if the system contains no cemented waste form. By addition of the cemented waste form a slight increase of the uranium concentration is also observed in presence of citric acid, tartaric acid and EDTA.

The results for the systems sodium chloride solution/cemented waste form/complexant and deionized water/cemented waste form/complexants are comparable. The radionuclide concentrations in these systems are determined by the solubility of the hydroxides at the equilibrium pH value of 12.5 and are relatively low. In no case, was an influence of any of the complexants on the radionuclide concentration observed when the cemented waste form was present. In contrast, for samples containing no cemented waste form the cobalt concentration is increased by EDTA, NTA and citric acid when the equilibrium pH value of 12.5 is adjusted with sodium hydroxide and for uranium, but only in deionized water, if EDTA is present. The reason for the influence of the cemented waste form on the cobalt and uranium concentration is the replacement of the complexed radionuclides by the calcium released from the cement and the precipitation of the hydroxides at the high pH value of 12.5. This statement is confirmed by the results of thermodynamic calculations using the computer code MINEQL.

ACKNOWLEDGEMENT

The authors would like to thank Mrs. I. Kahl for performing a large part of the experimental work, for providing the methodology for determining the concentrations of the radionuclides, and for overseeing these measurements and Mr. G. Rudolph for performing the calculations with the computer code MINEQL.

REFERENCES

1. American Nuclear Society Standards Committee. "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Procedure", ANSI/ANS-16.1 (1986).
2. Material Characterization Center. "MCC1P Static Leach Test Method" Nuclear Waste Materials Handbook: Test Methods (1984).
3. Material Characterization Center. "MCC4S Low-Flow Leach Test Method" Nuclear Waste Materials Handbook: Test Methods (1981).
4. RUDOLPH, G. VEJMEKKA, P. KOESTER, R. "Equilibrium Concept for the Assessment of the Actinide Release from Waste Forms into Salt Brines", Mat. Res. Soc. Proc. 127 (1989).
5. PRATOPO, M. I. MORIYAMA, H. HIGASHI, K. "The Behavior of Neptunium under Reducing Conditions", Proceedings of the 1989 Joint International Waste Management Conference, Kyoto, Japan, 2, 309 (1989).
6. WESTALL, J. C. ZACHARY, J. L. MOREL, F. M. M. "MINEQL-A Computer Program for the Calculation of Chemical Equilibrium Compositions of Aqueous Systems", MIT Technical Note, 18, 91p (1976).
7. JACKSON, K. J. WOLERY, T. J. "Extension of the EQ 3/6 Computer Codes to Geochemical Modelling of Brines", MRS 44, 507 (1984).
8. PARKHURST, D. L. THORSTENSON, D. C. PLUMMER, L. N. "PHREEQE - A Computer Program for Geochemical Calculations", U.S. Geological Survey Water-Resources Investigations 80-96, 210p (1982).
9. WOLERY, T. J. DAVELER, S. A. EQ6 A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems: User's Guide and Documentation, 70 (1989).
10. WOLERY, T. J. EQ3NR A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation, UCRL-53414, 59 (1983).
11. PARKHURST, D. L. THORSTENSON, D. C.; PLUMMER, L. N. "PHREEQE - A Computer Program for Geochemical Calculations", U.S. Geological Survey Water-Resources Investigations 80-96, 54 (1982).
12. MEANS, J. L. ALEXANDER, C. A. "The Environmental Biochemistry of Chelating Agents and Recommendations for the Disposal of Chelated Radioactive Wastes", Nuclear and Chemical Waste Management, Vol. 2, 183-196, 1981.
13. VEJMEKKA, P. KOESTER, R. FERRARA, D. WACKS, M. E. "Leach Studies of Chelating Agents and Influence on Radionuclide Leaching from Simulated LLW/ILW Cemented Waste Forms", Proceedings of WM '90, 3, (1990).
14. VEJMEKKA, P. RUDOLPH, G. KOESTER, R. "Source Term Evaluation for Actinide Elements in the System Cemented Waste Form/Salt Brines-Influence of Organic Complexants", Migration 89, International Conference on Geochemistry and Migration of Actinides and Fission Products, (1989).