

LEACH STUDIES OF CHELATING AGENTS AND INFLUENCE ON RADIONUCLIDE LEACHING FROM SIMULATED LLW/ILW CEMENT 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 performed on cemented waste forms containing sodium nitrate, trace amounts of cesium-137, and cobalt-60, and a chelating agent (ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or citric acid). Leaching of the chelates was measured in water and the effect of the chelates on the release of the Cs-137 and Co-60 was studied. The time dependence of the release rate of the chelates is comparable but the chelate concentration in solution and therefore the released fractions are different. EDTA shows the highest release rate followed by NTA and citrate.

As expected, the release of the non complex forming cesium is not affected by the presence of the chelates. Independent from the strong complex formation of cobalt with EDTA, NTA, and citrate in the alkaline region, the cobalt release is also not affected by the presence of the chelates. This can be explained by the influence of the high calcium content of the system which decreases the stability of the Co complexes in the high pH region (12-13).

In addition, experiments were performed to determine the equilibrium concentration of the chelates between liquid and solid phases. The liquid phases were deionized water, saturated sodium chloride, 24 percent magnesium chloride and Q-brine. The equilibrium studies are based on the assumption that after a certain time a stable final condition is to be established in the near field of the waste form in which each compound is at chemical equilibrium between the dissolved phase and the various solid phases. The total release may be assessed from the concentration in solution and flow rate out of the near field.

The fraction of EDTA released from the cement ranged from 0.2 in the Q-brine to 0.5 in the saturated sodium chloride. The concentration of EDTA in solution was dependent on the amount originally present in the cement sample, but the released fraction was independent of the initial loading. These results indicate that the EDTA concentration is not affected by solubility limits. The concentration of citrate in solution was below 1 E-5 M in all cases. The citrate concentration may have been limited by solubility. NTA release fractions were between 0.015 and 0.4 for the saturated sodium chloride and magnesium chloride, respectively. Values varied greatly with the amount initially incorporated in the cement and the leachant. The concentration of NTA in solution also varied with the cement loading except in the saturated sodium chloride. Leaching of NTA seems to have been controlled by processes similar to those limiting EDTA and by solubility limits.

INTRODUCTION

Chelates disposed of with wastes may eventually be leached from the waste form and enter surrounding liquids. They may carry isotopes with them to the environment, or species in neighboring containers may be complexed and leached. The presence of the chelates may alter leaching characteristics in the repository. In addition, the properties of the cement itself may be affected by the complexing agents. Such scenarios are of great interest in cases where chemical wastes or low level radioactive waste containing such chelates are disposed of in the proximity of other radioactive waste, such as at Gorleben, Federal Republic of Germany, or possibly also when such wastes may be collocated as at the WIPP site in the USA. Also, to understand the processes involved in such systems, the effects of the chelates on release of isotopes, the transport of the species

through the near and far fields, and the characteristics of the cement as a function of time must all be examined.

When cement with a chelate is in equilibrium with a solution, several situations can be hypothesized. First, the chelate may be completely soluble in the liquid in which case virtually all will leave the waste form. If the cement itself has a high affinity for the chelate, the chelate released depends on the quantity present. If the complex is not very soluble in the solution, a precipitate may form or the species may stay in the cement phase. In either of the latter two cases, the concentration of chelate in solution at equilibrium will not be a function of the amount of complex in the cement. Of course, the system may also be controlled by more than one of the above effects.

The chelates may also change the behavior of the radioisotopes in many ways. If the chelate forms a stable complex

with the isotope, and is readily leached from the cement, the solubility of the radioisotope would increase. When the complex is less soluble than the free radioisotope, leaching of the species is retarded. If another ion is present which forms more stable complexes than the radioisotope, the chelate may increase the solubility of this ion and thereby increase the proportion of the radioisotope in the cement. In the case when the competing ion forms a complex which is less soluble, the isotope partitioning may shift in favor of the solution and result in more of the isotope being leached. If the chelate does not form complexes with any of the species present or if the complexes do not change the solubility of the ions present, no observable effect by the chelates may be seen.

For the assessment of the radionuclide release from a nuclear waste repository after an accidental water ingestion, a novel approach was proposed (1). After a certain period a stable final condition is assumed to be established in the near field of the waste form in which each radionuclide is at equilibrium between the dissolved phase and the various solid phases. The total release may be assessed from the concentration in solution and the flow rate out of the near field. Also, several models have been developed to calculate equilibrium concentrations in complex solution systems and to provide source term information (2,3). In addition, recent efforts have been made to predict the transport and chemical behavior of such systems using calculations based on diffusion models (4,5). A number of papers have also addressed cement aging (6,7). These models together with the effect of the chelates on the source term along with an evaluation of transport through near and far fields would enable an evaluation of the overall waste disposal system behavior to be made.

In this study, the equilibrium concentrations of ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and citric acid in solutions of deionized water, saturated sodium chloride, 24 % magnesium chloride, and Q-brine were determined for systems of the chelates in the presence of cement. Leach rates of the chelates were also studied in distilled water. This information was used to postulate the processes controlling the release of the chelates. The effect of the presence of chelates on the release of radioisotopes of cesium and cobalt was also studied.

Such studies will provide greater understanding of phenomena controlling the equilibrium composition of ground water around cemented waste forms and further the use of equilibrium models (2,3) in predicting movement of radioisotopes.

EXPERIMENTAL

Materials

Cement was mixed in 500 g batches. For the inactive samples, 310 g cement, 140 g water, and 50 g sodium nitrate

were combined. From this, six individual samples were made. Two batches were also mixed with 0.3 g and 1.5 g of sodium ethylene diamine tetra acetic acid (NaEDTA) in addition to the components listed above. Four other sets of samples were made each with 0.2 g and 1.5 g of sodium nitrilotriacetic acid (NaNTA) or sodium citrate. Each of these batches was used to make six samples. Cement used was Arizona Portland Cement Type I/II supplied by the Arizona Portland Cement Co.

In addition to the inactive cement, seven more batches were made as described except 40 uCi of cesium-137 and 11.6 uCi of cobalt-60 were added to the mixtures. In each case five samples were made of each composition instead of six as in the inactive cases.

Water used for the leach solutions was deionized using a mixed bed ion exchange. The saturated sodium chloride solution was made by adding sodium chloride to the solution until no more would dissolve. The 24% magnesium chloride solution was prepared by diluting 333.5 g of a magnesium chloride solution (449 g/l) to 500 ml. Q-brine was made from 9.5 g sodium chloride, 16.7 g potassium chloride, 23.7 g magnesium chloride, 23.7 g magnesium sulfate heptahydrate, 251.3 g magnesium chloride hexahydrate and enough water to make 500 ml of solution. This solution was 24% magnesium chloride, 2.3% magnesium sulfate, 1.9% sodium chloride, and 3.3% potassium chloride. The above are the compositions of the four leachants used.

Some studies were also made without cement. The four solutions used were deionized water, one percent NaEDTA, one percent NaNTA, and one percent sodium citrate. After addition of inactive cobalt nitrate and trace amounts of cobalt-60, the pH of each solution was adjusted to 12.5 using sodium hydroxide.

Leaching Studies

These tests were designed to examine the rates at which the chelates or radionuclides were leached from the cements. Cement samples were allowed to age for two to three months in fifty milliliter cylindrical plastic jars. To remove the cement samples, the jars were sprayed with freon. This made the plastic brittle enough so that it could be broken by hand and the cement cylinders removed.

The cement was then weighed and immersed in 300 ml of deionized water. At 1, 2, 4, 8 and 22 weeks after the start of the leach test, the leach solutions were stirred and aliquots were taken for analysis. For inactive samples, five milliliters were used. In these cases aliquots could not be returned to the leach solution. The leach solution was not changed during the experiments.

For analysis of cesium and cobalt, 10 ml were taken from the samples and filtered, using amicon filter systems

(1.8 nm). These aliquots were returned to the leach solutions after the analysis.

Equilibrium Studies

In order to determine equilibrium concentrations and fractions released, tests were made on smaller amounts of cement. In these cases, samples used for compressive strength tests (two samples of each inactive composition described in the Materials section) supplied the cement samples needed. From these cement pieces, two to three grams were immersed in thirty milliliters each of the deionized water, saturated sodium chloride, magnesium chloride, and Q-brine solutions.

Analyses of the chelating agents in solution were made after three, four, and five weeks. For inactive tests, five milliliter aliquots were taken for determination of the chelate concentrations. This volume could not be returned to the leach solutions.

The equilibrium concentration of cobalt was determined by adding 0.2 uCi of Co-60 to the deionized water used as leachant. For analysis, a ten milliliter sample was taken, filtered, and subsequently returned to the leach solutions after the analysis. Cesium batch tests were not made since the isotope was seen from leach studies to behave in a fashion similar to that observed in previous studies (8).

To observe the leaching of cobalt at higher concentrations, the batch tests were repeated in 8E-4 M solutions. The tests then proceeded as described above for the other cobalt studies.

Some analyses were performed with no cement present. In these tests, 0.1 g of inactive cobalt nitrate and 0.2 uCi of Co-60 was added to 30 milliliters of the one percent chelate solutions and the pH was adjusted to 12.5 using sodium hydroxide solution. Ten ml aliquots were taken, filtered, and returned after analysis as in the other cobalt studies.

Analysis

Determination of the chelate concentrations was made by titrating the aliquots from the inactive tests with 1 E-3 M copper nitrate (9). The pH was held constant at 5.0 using an acetate buffer. The endpoint was seen by potentiometric measurements using a copper selective electrode and a double junction silver-silver chloride reference electrode. The process was controlled by a Mettler DL 40 RC automatic titrator.

Cesium measurements were made using a Ge(Li) detector, a multichannel analyzer, and an automatic sampler. Measurements were taken for 2000 seconds. No cobalt was seen in any leach studies.

Cobalt concentrations in the equilibrium studies were measured with a NaI detector and a single channel analyzer. Counts were taken for one minute. Cobalt solutions of 0.12

uCi and 1.17 uCi were used as standards. A blank was measured for correction of the sample's activity.

Sodium and calcium concentrations were measured using optical emission spectroscopy with inductively coupled plasma (OES-ICP). For the analysis, 10 ml aliquots of the distilled water equilibrium tests were used.

Solution pH's were measured using the DL 40 RC automatic titrator and a Mettler DG 111 pH electrode. The system was calibrated with buffers at pH's of 2.0, 7.0, and 10.0. It is important to note that the pH's reported are measured pH's, and actual values may deviate significantly due to high ion concentrations.

RESULTS AND DISCUSSION

Chelates

Results of the leach tests carried out in the absence of cesium and cobalt can be seen in Fig. 1 and 2. From Fig. 1 it can be seen that the concentration of EDTA in solution was significantly higher when the initial amount of chelate in the cement was increased. The fraction released, however, was independent of the initial amount in the cement over the range examined and was lower than the cesium fraction released. The results in Fig. 1 indicate also, that for samples with lower loadings of EDTA (and NTA) after a leach period of about 4 weeks equilibrium concentrations of about 3 E-5 M were already reached. As mentioned in the analytical section, the leachant was not changed during the experiments and for this reason constant chelate concentrations were obtained. For the discussion of the results therefore more attention is given to the chelate concentrations and not to the fractions released.

For cement with citrate, the concentration of citrate in solution was not affected by the loading of the cement. The citrate concentration was always in the range of the detection limit of the analytical method used, which corresponds to about 1 E-5 M. For this reason, the results for citrate are not included in Fig. 1 and 2. It is necessary to improve the analytical method for determination of citrate concentrations lower than 1 E-5 M. This is part of ongoing work.

The concentration and fraction of NTA released were both dependent on the initial amount of NTA present. For the samples with higher loadings, the NTA concentration is lower than the EDTA concentration. For samples with lower loadings, after a short period a constant NTA concentration of about 3 E-5 M is observed. Leaching of NTA seems to have been controlled by processes similar to both that limiting EDTA and citrate leaching.

From the values of leached fractions, leach rates can be calculated and the values are 4.7 E-4 cm/d for EDTA and 1 E-4 cm/d for NTA respectively.

Data from the equilibrium tests are summarized in

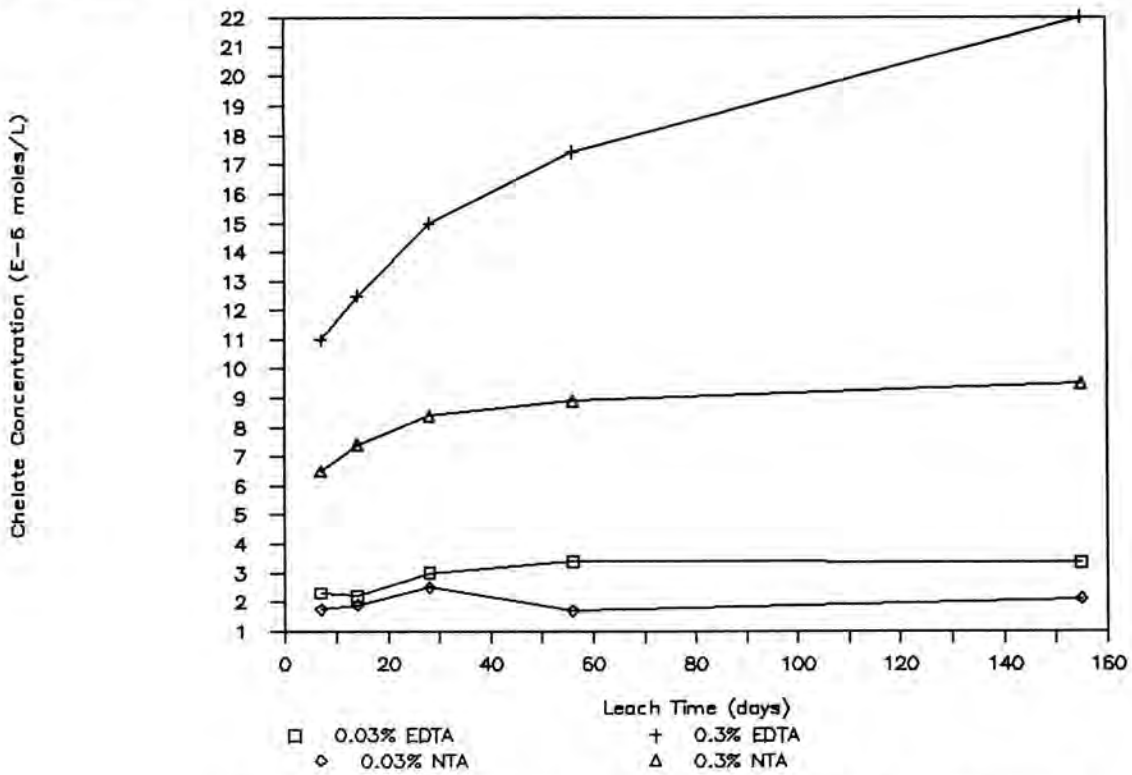


Fig. 1. Time Dependence of Chelate (Concentrations in Distilled Water).

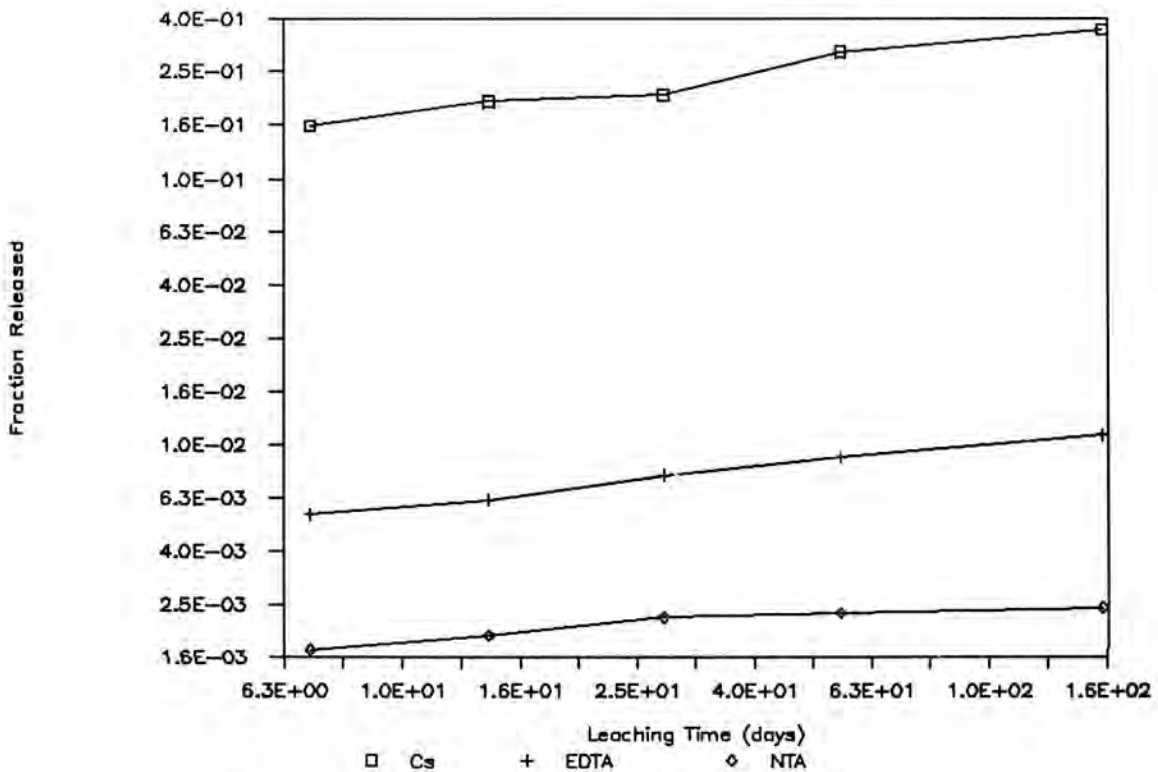


Fig. 2. Time Dependence of the Release of CS, EDTA, and NTA from Waste Form.

Table I. The samples used in the equilibrium batch tests had reached equilibrium within three weeks.

As in the leach test, the fraction of EDTA released was independent of the amount initially present in the cement. In addition, the concentration in solution is well below that expected on the basis of solubility of the EDTA ion alone. These results indicate that EDTA release is eventually affected by sorption on the cement.

The concentration of citrate in solution does not vary when the amount of citrate is increased in the cement. The

concentrations in these tests are similar to the concentrations reached in the leach studies, indicating that citrate release is determined by the solubility of calcium citrate.

As before, the NTA concentrations and release fractions were both dependent on the NTA initially present.

These observations are true in all solutions except that the NTA concentration is independent of the cement load-

TABLE I
Equilibrium Chelate Concentrations in Cement/Leachant Systems
(2g Cemented Waste Form, 30 mL Solution)

Solution	Chelate (moles)	Chelate Concentration (M)	Fraction Released
Distilled Water	EDTA 1	4.5 E-5	0.4
	2	2.4 E-4	0.4
	NTA 1	3.4 E-5	0.2
	2	3.8 E-5	0.14
	Citrate 1	<1.0 E-5	
NaCl Saturated	2	<1.0 E-5	
	EDTA 1	7.0 E-5	0.5
	2	3.3 E-4	0.5
	NTA 1	2.0 E-5	0.1
	2	1.8 E-5	0.01
Magnesium Chloride (23.5%)	Citrate 1	<1.0 E-5	
	2	<1.0 E-5	
	EDTA 1	5.4 E-5	0.4
	2	2.5 E-4	0.4
	NTA 1	7.5 E-5	0.4
Q-brine	2	2.3 E-4	0.2
	Citrate 1	<1.0 E-5	
	2	<1.0 E-5	
	EDTA 1	2.2 E-5	0.2
	2	1.5 E-4	0.3
Q-brine	NTA 1	3.1 E-5	0.15
	2	8.6 E-5	0.06
	Citrate 1	<1.0 E-5	
	2	<1.0 E-5	

Initial Chelate (wt. %): 1 = 0.03, 2 = 0.3

ing in saturated NaCl, and the fraction of EDTA released in Q-brine may be dependent on the initial amount present.

Sodium, Calcium, and pH

The concentration of sodium and calcium was measured by OES-ICP in the distilled water equilibrium studies. Deviations between cement samples of different chelates was insignificant. Although the concentrations of these ions in the other solutions were not measured, the concentration of sodium in the saturated sodium chloride and Q-brine solutions could be calculated. In addition, the calcium concentration should be comparable in the sodium chloride solution since it seems to be limited by the solubility of calcium hydroxide. Both the calculated and measured ion concentrations have been included in Table II.

The measured pH's are also presented in Table II. To within three hundredths of a pH unit, the values were independent of the chelates in the cement. The pH in the distilled water and saturated sodium chloride solutions seem to be controlled by the alkalinity of the cement. Although the solutions appear to be at different pH's this may be due to interference of sodium and chloride ions with the pH measurement.

The pH of the magnesium chloride and Q-brine solutions were buffered by the solubility of magnesium hydroxide. The small difference in the measured pH values may be due to interferences in the Q-brine solution. Magnesium hydroxide was observed in the magnesium chloride and Q-brine solutions as white flakes which precipitate from the solution. The precipitate often hindered sampling since the pipet was easily clogged.

Cesium

The leach rates of Cs were, as expected, independent of the presence of the chelates. For all samples without and with chelates present, the same Cs concentration and fraction released was measured. As can be seen from Fig. 2, the time dependence of the cesium release is comparable to the EDTA release, but the fraction released is higher for cesium

than for EDTA. This result again indicates that the release of EDTA is affected by sorption. The behavior of cesium here is similar to results previously observed (8). Therefore no equilibrium studies were performed on cesium. The leach rate for cesium, calculated from the fractions leached to be 1.6 E-3 cm/d , are in good agreement with values from other investigations.

Cobalt

In all leach studies of cobalt, independent from the presence of the chelates, the amount of cobalt in solution was too small to be seen.

In equilibrium studies with trace amounts of cobalt-60, a very low cobalt concentration of about 1 E-14 M in solution was detected. This level of detection could be reached because of the superior sensitivity of the NaI detector as compared to the Ge(Li) detector. The cobalt concentration was independent of the presence of the chelates.

When the equilibrium cobalt studies were run using an inactive cobalt carrier, the cobalt concentration in solution was about 1 E-6 M , but was independent of the presence of the chelates (see Fig. 3). With higher cobalt amounts in the samples, the solubility limit of cobalt hydroxide is reached, whereas with trace amounts of cobalt, the equilibrium concentration may be affected by sorption on the cement.

The results of equilibrium studies without cement, summarized in Fig. 3, show very clearly that cobalt forms soluble complexes with EDTA, NTA, and citrate in alkaline solutions (pH adjusted to 12.5 using sodium hydroxide). The influence of the cement on the stability of the cobalt complexes can be explained by the large calcium inventory of the cement. At high pH values in connection with high calcium concentrations, the stability of the cobalt complexes is decreased. The same results were observed for the stability of actinide complexes of EDTA, NTA, and citrate in the system cemented waste form/NaCl solution (10).

It is important to note that correct cobalt results were only obtained with filtered samples. Therefore, all values

TABLE II
Equilibrium Concentrations of Inorganic Species in
Cement/Leachant Systems (2g Cement Waste Form, 30 mL Solution)

Solution	pH	Concentration (M)		
		Calcium	Magnesium	Sodium
Distilled water	12.6	1.4 E-2	-	8 E-2
Saturated Sodium Chloride	12.2	-	-	9
23.5 % Magnesium Chloride	7.1	-	2.5	-
Q-brine	6.9	-	2.5	0.33

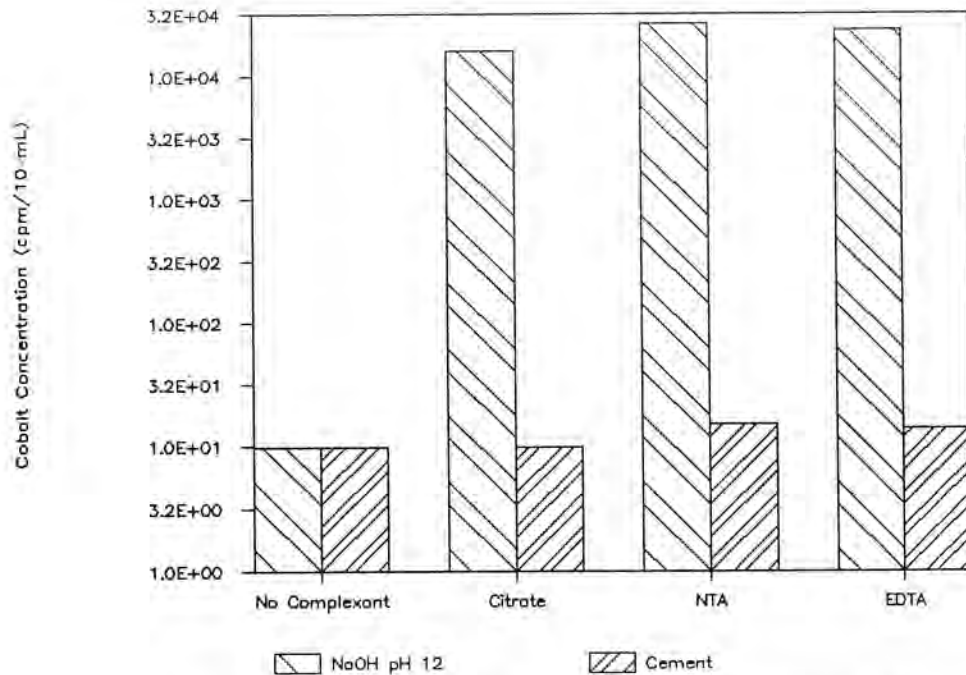


Fig. 3. Cobalt Concentrations in Alkaline Solutions with 1% Chelate.

given here were measured with samples after filtration with amicon systems (1.8 nm). This is an indication that colloids from the cement play an important part in the system, cemented waste form/distilled water (11).

CONCLUSIONS

EDTA, NTA, and citrate show a different behavior in the leach and equilibrium studies. In both studies, the fraction of EDTA released from the cement was independent of the amount present, but the EDTA fraction released was lower than the cesium fraction released. This suggests that the release of EDTA is not only determined by diffusion. In addition adsorption may control the amount of EDTA in water around waste forms containing EDTA.

The concentration of citrate in solution was independent of citrate immobilized in the cement. For citrate, the release therefore is dominated by the solubility of calcium citrate. Therefore, the release rate of citrate from a waste form will be more dependent on the rate of flow of water than the amount of citrate in the waste.

NTA in cement behaved in a fashion intermediate to citrate and EDTA. When cement is loaded with much higher amounts of NTA, the concentration of NTA in should be constant. For lighter loads the NTA release fraction should be constant.

The concentration of cesium, cobalt, calcium, and sodium and the pH were seen to be independent of the chelate used over the concentration ranges studied. For solutions without measurable amounts of magnesium, the pH was

established by the alkalinity of the cement. In solutions with significant magnesium concentration, the magnesium hydroxide solubility set pH's.

As expected, the leach behavior of the non complex forming cesium was not affected by the presence of the chelates. This is similar to results from other investigations.

In all the leach studies, independent of the presence of chelates, the amount of cobalt released from the cement was not noticeable above the background. When a trace amount of cobalt was added to the leach solution in equilibrium studies, the equilibrium concentration was very low. When a significantly larger amount of inactive cobalt was added, the equilibrium concentration was higher, but in all cases the cobalt concentration was not affected by the presence of the chelates.

In equilibrium studies without cement, the strong complex formation of cobalt with EDTA, NTA, and citrate at pH 12 was observed. This result shows the important role of cement as part of the near field, limiting the release of radionuclides from the waste form.

The goal of these studies is to start understanding the mechanisms affecting the EDTA, NTA, and citrate leaching and equilibrium concentrations. This insight will be useful in predicting the behavior of chelates and of the radionuclides in waste when water intrusion occurs. As already

mentioned, the investigations with the chelates must be continued to obtain more detailed information.

ACKNOWLEDGEMENT

The authors would like to thank Mrs. I. Kahl for performing a large part of the experimental work with cesium-137 and cobalt-60 and Mr. W. Kluger, both from KfK, for providing the methodology used in determining the concentrations of the chelates and for overseeing these measurements.

REFERENCES

1. G. RUDOLPH, P. VEJMEKKA, and R. KOESTER, "Equilibrium Concept for the Assessment of the Actinide Release from Waste Forms into Salt Brines," *Mat. Res. Soc. Proc.*, Vol. 127, Material Research Society (1989).
2. J. C. WESTALL, J. L. ZACHARY, and F. M. M. MOREL, "MINEQL- A Computer Program for the Calculation of Chemical Equilibrium Compositions of Aqueous Systems," MIT Technical Note No. 18, 91p (1976). Modified by EIR Switzerland in the Technical Report by M. Schweingruber, EIR AN-45-84-39.
3. K. J. JACKSON and T. J. WOLERY, "Extension of the EQ3/6 Computer Codes to Geochemical Modelling of Brines," *MRS*, 44, 507 (1984).
4. S. NIMNUAL, "Applications of Multi-Group Diffusion Theory to Mechanistic Modelling of Leaching Behavior of Solidified Low-Level Radioactive Waste Forms," Ph. D. Dissertation, University of Arizona, Department of Nuclear and Energy Engineering, Tucson, Arizona (1986).
5. S. NIMNUAL, P. COLOMBO, and M. E. WACKS, "Mechanistic Modelling of Long-Term Leaching Behavior of Cement-Based Radioactive Low-Level Forms," *Waste Management '87*, Tucson, Arizona, Vol. 3, 369, Arizona Board of Regents (1987).
6. R. SHUMAN, V. C. ROGERS, and R. A. SHAW, "The Barrier Code for Predicting Long-Term Concrete Performance," *Waste Management '89*, Tucson, Arizona, Vol. 2, 701, Arizona Board of Regents (1989).
7. J. PHILIP, and J. R. CLIFTON, "Durability of Concrete for Underground Containment of LLW," *Waste Management '89*, Tucson, Arizona, Vol. 2, 707, Arizona Board of Regents (1989).
8. G. RUDOLPH, and R. KOESTER, "Stoffliche Untersuchungen zur Verfestigung mittelaktiver Abfalloesungen mit Zement: Auslaugbarkeit von Cesium und Strontium," KfK 2842, (Aug. 1979).
9. H. A. FLASCHKA, *EDTA Titrations*, Second edition, Compton Printing Ltd., London, 116 (1967).
10. P. VEJMEKKA, G. RUDOLPH, and R. KOESTER, "Source Term Evaluation for Actinide Elements in the System Cemented Waste Form/Salt Brines-Influences of Organic Complexants," *Migration 89*, International Conference on Geochemistry and Migration of Actinides and FP, Monterey, California, November 6-10, 1989, (1989).
11. J. D. F. RAMSAY, R. G. AVERY, and P. J. RUSSEL, "Colloids Related to Low-Level and Intermediate Level Waste," *EUR 12077*, Characterization of Radioactive Waste Forms, Vol. 1, Progress Report for 1987, Ed. K. Brodersen, K. Nilsson, 129 (1989).