A LABORATORY AND FIELD EVALUATION OF THE MOBILITY OF COBALT-60/EDTA

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ABSTRACT

We have observed a time and soil type dependence in the ability of the organic complexant EDTA to keep cobalt-60 in solution. Test results indicate that short term adsorption tests lasting 5 days or less can be misleading. In short term tests using cobalt-60/EDTA and soil from the Hanford site, low sorption in batch tests and high mobility in column tests were observed. During long term batch test using cobalt-60/EDTA, the percentage of cobalt remaining in solution decreased from 90% after 7 days to less than 10% after 500 days. In laboratory and field column tests where low water flow rates allowed long contact time, virtually no cobalt movement was observed even though in the field test tritium was transported over 4 meters. Long term batch tests using cobalt-60/EDTA and soil from Savannah River burial grounds showed that cobalt remaining in solution dropped to 30% of the total cobalt added after 5 days and to less than 1% after 15 days. Batch tests using soil from Oak Ridge burial grounds were less dramatic showing cobalt in solution decreasing from 90% after 5 days to 70% ater 35 days. The cobalt-60/EDTA complex appears to be dissociating and leaving uncomplexed cobalt which is readily sorbed. The dissociation seems to be rather complete in Hanford and Savannah River soil but limited in the Oak Ridge soil. The implication to waste management is that the potential for transport of cobalt by EDTA may not be as serious at all burial sites as once thought.

INTRODUCTION

In recent years, it has been shown that radionuclides, normally sorbed onto and retained by soils, can be mobile after the formation of organic complexes. At Oak Ridge National Laboratory, cobalt was observed migrating from burial trenches in the form of a cobalt-EDTA complex (Means et al. 1978). In the Oak Ridge study, it was determined that the cobalt-EDTA complex was very stable in the presence of 10^{-7}M EDTA. Laboratory studies revealed that the complexed cobalt species had a Kd value close to 1 which was three to four orders of magnitude lower than uncomplexed cobalt species. These research results are significant when one realizes the prevalence of organic chemicals in the nuclear industry, in several forms, including cleaning and decommissioning fluids, scintillation cocktails, and animal carcasses.

In 1978, a series of experiments were inititated at Pacific Northwest Laboratory (PNL) as part of the National Low-Level Waste Management Program to investigate the behavior of the cobalt-EDTA complex in an arid environment. These tests included laboratory column tests, batch Kd tests and a large-scale field tracer test. In 1980, a second project was begun at PNL to study effects of several organic complexants including EDTA, on radionuclides including cobalt. Selected results from these projects are presented here to illustrate the complex behavior of the cobalt-EDTA compound and to show how different this behavior can be in different soil systems. These results indicate that the effects of organic complexation of radionuclides on environmental mobility are still incompletely understood.

EXPERIMENTAL PROCEDURES

Laboratory Tests

Small column laboratory tests were run by introducing a pulse of cobalt-60/EDTA (10^{-2}M EDTA) into the top of 0.3-m long columns. Columns were then steadily flushed with water at several flow rates such that from 2 to 6 days (5 to 6 pore volumes) were required for the pulse to completely pass through the column. The soil columns were packed with alkaline, sandy sediments (pH 8), taken from the Hanford reservation and were maintained partially saturated (48 to 58% water saturation) throughout the course of the experiment.

A large column test was also conducted in the laboratory with a soil column 1.6 m in length using the sandy soil from Hanford. Cobalt-60/EDTA (10^{-2}M EDTA) was added to the column at a depth of 0.6 m in a spiked soil layer 2-cm thick. Water additions were begun 60 days after the spiked soil was placed in the column and continued for 14 months. During the first year, 28 cm of tap water were applied, with 78 cm added during the final 2 months along with tritium to act as a tracer. Total water added was 106 cm representing approximately 4.0 pore volumes at an average volumetric water content of 12%.

In batch sorption tests, cobalt-60/EDTA (10^{-7}M EDTA) solutions were contacted with three different soils for varying periods of time. Initial tests on the sandy soil found at Hanford were for 7 days. Later, longer contact times (500, 35, and 15 days) were used with soils from Hanford, Oak Ridge and Savannah River Laboratories, respectively. In the long-term test, the percentage of cobalt remaining in solution was monitored through time.

Field Tests

Field-scale tracer tests were conducted in lysimeters filled to a depth of 8 m with the Hanford sandy soil. In April 1978, a layer of soil spiked with cobalt-60/EDTA (10^{-2}M EDTA) was placed at a depth of 60 cm and then the caisson was backfilled to the surface. Cobalt concentration was monitored from 1978 until April 1982 by a downwell NaI scintillation probe as well as destructive sampling through horizontal access ports located in the caisson wall. A final sampling by excavation was done in September 1982. Rainfall was less than 2 cm for the first 150 days of the test with total precipitation during this three-year time period being 59 cm (3.0 pore volumes based on a volumetric water content of 6%). Of that total

precipitation, approximately 5 cm (0.25 pore volumes) of drainage water reached the bottom of the column (8 m).

RESULTS

The results of the short-term batch and column adsorption tests using Hanford sandy soil are shown in Table I. Calculated distribution coefficients (Kd) are shown for cobalt-60, both complexed and uncomplexed, and tritium. These short-term tests show the same behavior as reported by Means et al. (1978). There was a three order of magnitude change in sorption between the complexed and uncomplexed cobalt species. The cobalt-60/EDTA complex behaved in a manner similar to tritium samples, giving nearly identical Kd values and similar column breakthrough curves in small column tests.

TABLE I. Results of Short Term Adsorption Tests Using Soil from Hanford Site

	Kd (ml/g)	
RADIONUCLIDE	7-DAY BATCH	30 cm COLUMN
COBALT-60	4.5×10^3	-
COBALT-60/ EDTA	1.0	0.1
TRITIUM	0.1	0.01

Figure 1 shows cobalt concentration with depth after 0.4 and 3.6 pore volumes of water passed through the large laboratory column. The concentration measured at 60 cm varied erratically over time and never reached original spike concentration. This was attributed to errors in sampling the small 2-cm thick band of spiked soil. In Fig. 1, the concentration at 60 cm is shown as >140 pCi/g for both sampling times. The concentration profiles are essentially identical and show that some initial cobalt movement took place early in the test, but no movement took place during the majority of water application. Cobalt concentrations in the column effluent showed an early spike representing less than 1% of the total cobalt added to the column. This inital spike came through in the first 0.4 pore volume. After that, there was no cobalt detected in the effluent.

The field-scale tracer test was monitored for three years and during that time no movement of cobalt could be detected by the downwell probe or by destructive sampling within 15 cm of the tracer placement. Excavation of the caisson revealed some cobalt movement to a depth of 70 cm; however, the peak concentration remained at the initial depth of 60 cm. Results of the excavation sampling are shown in Fig. 2. Also shown in Fig. 2 are the results of a tritium tracer test conducted in an adjacent caisson. The tritium test was started at the same time as the cobalt test with tritium also being placed at an initial depth of 60 cm. The tritium was sampled in April, 1981 (2 years after tracer placement) while the cobalt was sampled in September, 1982 (3.5 years after tracer placement). Figure 2 shows that the tritium has been transported an average distance of 4 m (peak concentration) while the cobalt peak remains at the original 60 cm.

Figure 3 shows the results of the long-term batch adsorption tests. The figure shows percentage of cobalt remaining in solution versus time for Hanford, Oak Ridge and Savannah River soil samples. The data indicate that in all three cases some, if not all, of the cobalt has left solution. The assumption is that the cobalt-60/EDTA complex is breaking down allowing

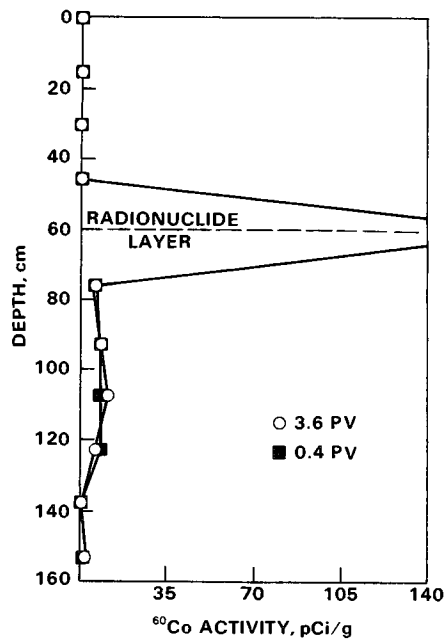

Fig. 1. Cobalt Concentrations Versus Depth for the 1.6-m Laboratory Leach Test After 0.4 and 3.6 Pore Volumes (PV) of Leaching with Tap Water

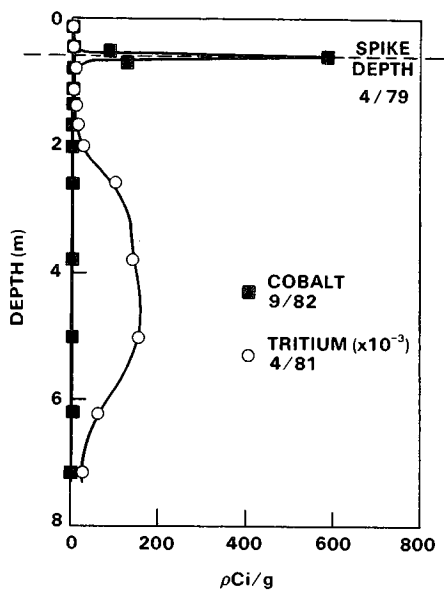

Fig. 2. Comparison of Cobalt-60/EDTA and Tritium Mobility Under Field Conditions at Hanford

the uncomplexed cobalt species to be sorbed onto the soil. While this appears to be happening to all three solutions, it happens at very different rates and to varying degrees for each soil. In the Savannah River soil, the dissociation of the complex appears to be very rapid and complete. After 15 days, less than 1% of the original cobalt remained in solution. For the Oak Ridge soil, equilibrium appears very quickly, however, at a much lower state of dissociation. The removal of cobalt from solution essentially stopped after 5 to 10 days; however, 70% of the cobalt was still in solution.

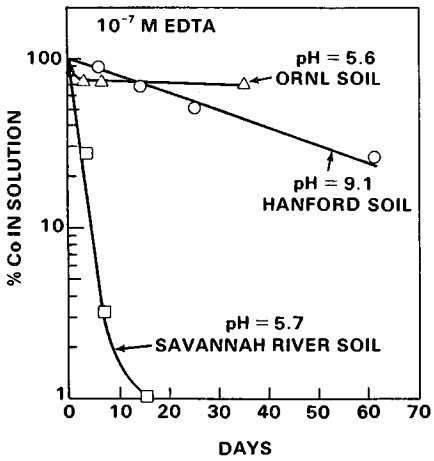

Fig. 3. Comparison of Cobalt-60/EDTA Stability Between Hanford, Oak Ridge, and Savannah River Soils

Results of tests using Hanford soil were intermediate to those of the other two soils. The rate of dissociation of the cobalt-60/EDTA complex was much slower than for either Savannah River or Oak Ridge soil, but to a much higher degree than the Oak Ridge soil. After 60 days, equilibrium conditions were not reached and only 30% of the cobalt remained in solution. Further testing of the Hanford soil revealed that after a 500-day contact time, equilibrium had still not been reached and the amount of cobalt remaining in solution had dropped to 7%.

DISCUSSION

The results of cobalt-60/EDTA adsorption tests using Hanford soil show major differences between short- and long-term tests. In 7-day batch tests, the cobalt-60/EDTA complex appears stable and column tracer tests reveal low sorption and high mobility similar to tritium. In the large laboratory column tests, initial water application was delayed 60 days with only 20% of the total water added within the first year. This water application pattern resulted in some initial leaching of cobalt followed by a very stable cobalt distribution, even when large amounts of water (3 pore volumes) were applied one year after tracer placement. Results of the field-scale test are even more dramatic showing that under field conditions, tritium was transported on the order of 4 m while the cobalt was essentially sorbed in place. The key factor in determining the field results seems to be that very little water flow was occurring during the first six months of the field test giving sufficient time for complexed cobalt to dissociate from the EDTA and to sorb onto the soil.

Results from these tests are consistent with results from the long-term batch test. During the 7 days needed to run the short-term batch test and the short column test, essentially no cobalt is lost from solution contacting Hanford soil (see Fig. 3). Even after 60 days, when water was added to the large laboratory column, there would have been some uncomplexed cobalt present that would move and give the results shown in Fig. 1. In the field tracer test, the cobalt-60/EDTA had all spring and summer to break down and be sorbed before fall and winter rains provided the water necessary to transport the cobalt. By that time, very little if any, cobalt would have remained in solution.

CONCLUSIONS

These results may appear to contradict the earlier results of Means et al. (1978). However, the data in Fig. 3 show that for soils found at Oak Ridge, the cobalt-60/EDTA complex is very stable as reported. Mobilization of cobalt by complexation with EDTA is indeed a viable mechanism at Oak Ridge. On the other hand, one would not expect to see similar results at the Savannah River burial grounds. In these soils it appears that very litte, if any, cobalt-60/EDTA would exist. In Hanford soils, the conclusions are not so straight-forward. The kinetics of the dissociation are not rapid, so time and water flow patterns are important. However, at the depth of burial normally used, the water flow rates are low enough that sufficient time is available for the complex to dissociate, so that significant transport of cobalt due to complexation with EDTA would be unlikely.

FUTURE WORK

At the present time, there is no apparent explanation for the differing behavior of the cobalt-60/EDTA complex among the soils tested. No obvious correlations exist between pH, texture, or calcium content and the behavior of the cobalt-60/EDTA complex. Experiments on dissociation kinetics of cobalt-60/EDTA with the three soils shown in Fig. 3 are being repeated in such a way as to track the EDTA as well as the cobalt. In this way, we hope to be able to understand why the cobalt-60/EDTA complex breaks down and what new species, if any, are formed.

BIBLIOGRAPHY

Means, J. L., D. A. Crerar, J. O. Duguid. 1978. Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents. Science 200:1477-1481.