

THE SEPARATION OF RADIONUCLIDE MIGRATION BY SOLUTION AND PARTICLE TRANSPORT IN LLRW REPOSITORY BUFFER MATERIAL

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ABSTRACT

Laboratory-scale lysimeter experiments were performed with simulated waste forms placed in candidate buffer materials which have been chosen for a low-level radioactive waste repository. Radionuclide releases into the effluent water and radionuclide capture by the buffer material were determined. The results could not be explained by traditional solution transport mechanisms, and transport by particles released from the waste form and/or transport by buffer particles were suspected as the dominant mechanism for radionuclide release from the lysimeters. To elucidate the relative contribution of particle and solution transport, the waste forms were replaced by a wafer of neutron-activated buffer soaked with selected soluble isotopes. Particle transport was determined by the movement of gamma-emitting neutron-activation products through the lysimeter. Solution transport was quantified by comparing the migration of soluble radionuclides relative to the transport of neutron activation products. The new approach presented here for monitoring radionuclide migration in soil facilitates the determination of most of the fundamental coefficients required to model the transport process.

INTRODUCTION

There are several potential mechanisms for the aqueous transport of radionuclides in porous media. The most important mechanisms include solution transport of ionized and complexed species, and particle transport of colloids and pseudocolloids. While considerable progress has been made in the analysis of solution transport, the simulation of particle transport is especially difficult because of the large number of parameters that have a major effect on the transport, such as surface charge, particle size distribution, and the degree of consolidation of, and channeling in, the media.

An approach is outlined where the contribution of particle transport and solution transport of strongly adsorbing cations can be resolved and quantified, irrespective of the structural inhomogeneities present in the porous media. Basically the experiments involve the simultaneous introduction of dissolved radioactive species and their adsorbent into the porous media with saturated or unsaturated flow passing through the media. A portion of the adsorbent is neutron activated, equilibrated with soluble radionuclides and then introduced into the porous media. The migration of soluble Co-58, Sr-85, and Cs-137, and neutron activated soil were monitored simultaneously. Particle transport is determined by the migration of neutron activation products, while solution transport is computed from the difference between the migration of dissolved radionuclides and neutron activation products.

LABORATORY-SCALE LYSIMETER EXPERIMENTS

The development of the experimental approach was prompted by difficulties in the interpretation of laboratory-scale lysimeter results (1). The lysimeters formed part of a program to qualify an engineered barrier, i.e., a buffer layer placed at the bottom of a low-level radioactive waste repository, designed to effectively retard the migration of radionuclides and also facilitate the drainage of water. The porous structure of the barrier

will allow transport of particles during infiltration or flooding.

The lysimeter experiments were performed to couple the leaching of waste forms with the migration of radionuclides through buffer materials. The experimental program and some of the results have been reported before (1,2,3). The waste forms, placed in the centre of the lysimeters, were sodium phosphate traced with Co-60, Sr-85, and Cs-137, and immobilized in bitumen. The buffer material surrounding the waste was a 90/10 weight ratio of local coarse (0.2 mm) fluvial sand and Dochart clay, a local glacial deposit containing rock flour, illite and chlorite. About a 5 to 6 cm thick buffer layer separated the waste form from the drain. A schematic diagram of the lysimeter is shown in Fig. 1. Typical operating conditions are presented in Table I. The lysimeters were subjected to infiltration for up to 115 days. Radionuclide content of the effluent water and of the soil cores upon completion of the infiltration were determined. The early break-through of all three isotopes was inconsistent with a solution transport mechanism considering the relatively high distribution coefficients obtained in batch type experiments for all three isotopes. The observed phenomenon is more consistent with particle transport.

To elucidate the transport mechanism, a few grams of sand/clay buffer were neutron activated, thoroughly mixed with a larger portion of buffer, and then soaked with a solution of Co-58, Sr-85, and Cs-137. A 1 cm thick layer of this soil was incorporated into the lysimeter where the bottom of the waste form was located in previous lysimeter experiments (Fig. 1). Radionuclide desorption experiments indicated that all of the gamma-emitting neutron-activation products remained with the bulk material. Thus, any displacement of activation products would be exclusively by particle transport. The radionuclide content of the effluent water was monitored during each lysimeter experiment. At the end of each experiment, the buffer was cored at the centre and the radionuclide content of thin buffer slices was determined. To evaluate the spreading of neutron activated clay during lysimeter packing and coring, an identical control

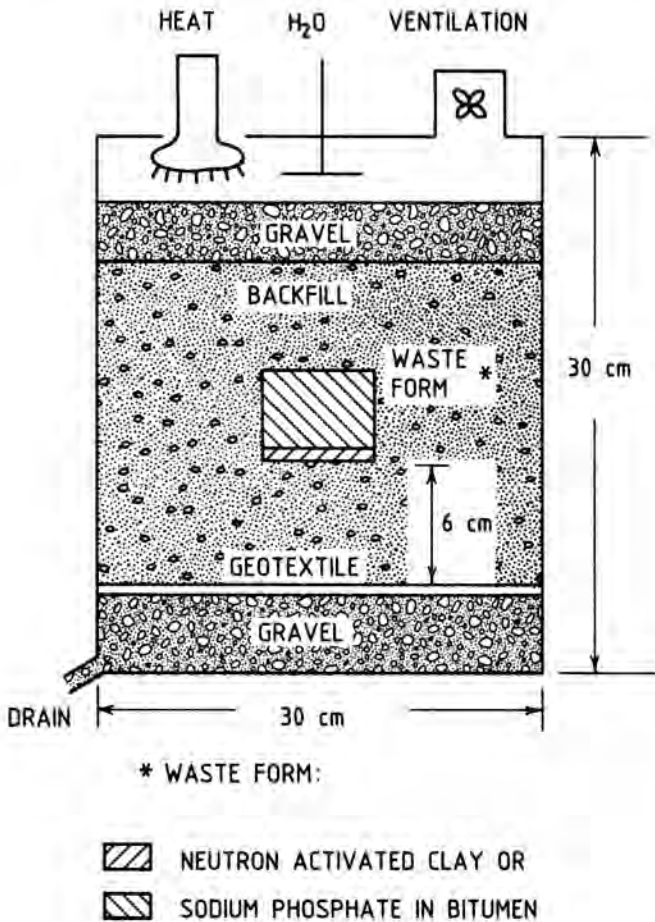


Fig. 1. Schematic of the Lysimeter.

lysimeter was prepared without the dissolved radionuclide addition. The control lysimeter was not subjected to water infiltration, but was cored soon after packing.

RESULTS

Gamma spectrometry results of the effluent water from the lysimeter containing activated buffer and dissolved radionuclides are illustrated in Fig. 2. Clay particle transport can be estimated from Co-60, a dominant gamma-emitting activation product. Dissolved radionuclides added to the activated buffer and released from the lysimeter are included in Fig. 2. The elution pattern of Sr-85 is very similar to the elution pattern of the other activated and dissolved radionuclides albeit at about 10% of their relative concentrations. The concentrations of the radionuclides from a vertical soil core taken at the end of the experiment are presented in Fig. 3. The elution pattern for Co-60, a tracer for the clay particles and the pattern for Co-58 and Cs-137 in both the effluent water and in the soil cores are similar and suggest

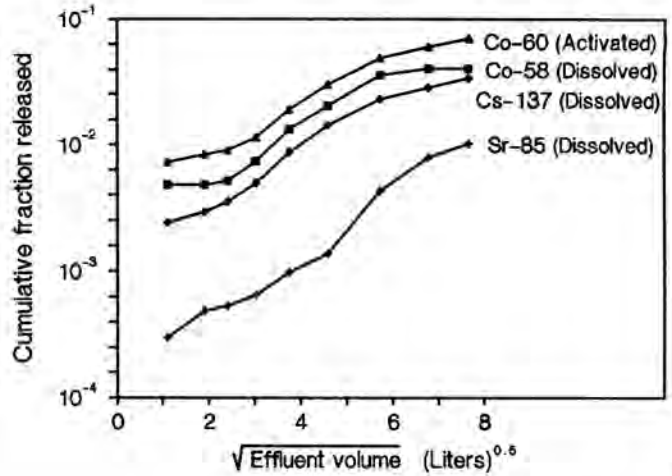


Fig. 2. Radionuclide Release From Lysimeter Containing Activated Buffer and Dissolved Radionuclides.

that the latter two radionuclides were strongly bound to clay particles and were eluted with them with only **Solution Transport**

In Fig. 3, solution transport causes the Cs-137 peak to shift about 1.5 mm downstream from the Co-60 peak. From this shift and total linear displacement of water during infiltration, a retardation factor of 375 was calculated. The Co-58 data points were too few to facilitate a detailed analysis of peak shape, though it appears to be identical to the particle transport rate because the available data points nearly coincide with the activation product, Co-60. The Sr-85 peak migrated downstream 14 mm and also broadened, consistent with a liquid phase transport mechanism. For Sr-85, the retardation factor is 40 based on peak displacement.

Particle Transport

The transport of neutron-activated clay-particles by infiltration was estimated from the difference between the concentration of those particles in the lysimeters used for infiltration and the control lysimeter. This procedure compensated for the mixing of radionuclides during packing and coring. The semi logarithmic plot of the concentration difference as a function of distance is presented in Fig. 4.

The data can be fitted to two straight lines. Similar results were obtained by Eichholz et al. (4) when neutron-activated clay-particles were added to water and the mixture percolated through a column of pulverised limestone or basalt. The phenomenon was ascribed to filtration close to the source and particle adsorption further downstream. Saltelli (5) developed a mathematical model for colloid filtration that accounts for both of the above particle capture mechanisms. Capture coefficients (w) were calculated for the filtration and particle adsorption

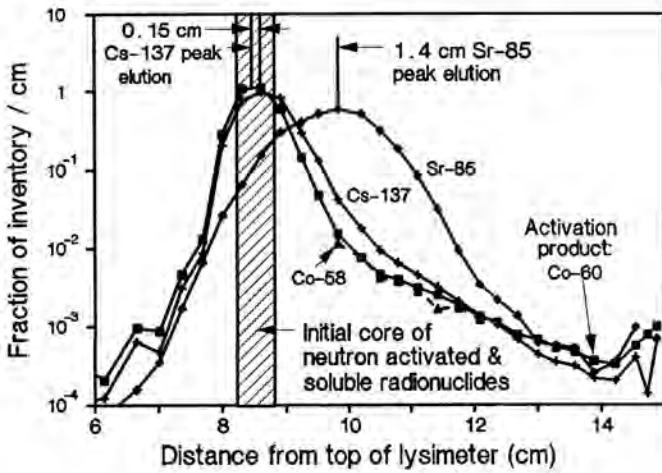


Fig. 3. Radionuclide Concentration in Lysimeter Core Containing Activated Buffer and Dissolved Radionuclides.

the lysimeter, an adsorption equilibrium exists, where the rate of radionuclide adsorption is equal to the rate of desorption. As the particle moves downstream from the above region of equilibrium, it enters a region where the radionuclide concentration in solution is orders of magnitude lower than in its previous environment. The rate of radionuclide adsorption becomes negligible and the particle loses its radionuclide content at a rate equal to the desorption rate. In the region of the lysimeter, where particle transport of radionuclides dominates, the decline in radionuclide concentration, C , with distance, x , from the source can be expressed by the following relationship:

$$\ln C^*/C = \ln C_o^*/C_o (G/V)*x \quad (\text{Eq. 2})$$

Where:

C^* = Adsorbed radionuclide concentration

C_o^* = Initial adsorbed radionuclide concentration

V = Darcy velocity, 2.67 mm/h

G = First order desorption rate constant

A semi-logarithmic plot of the ratio of [Cs-137]/[Co-60] as a function of distance in the lysimeter is presented in Fig. 5. The slope of the line is equal to $-G/V$ from Eq. 2 above. The desorption rate constant is $2.8 \times 10^{-5} \text{ s}^{-1}$, corresponding to a desorption half-life of 6.3 hours. The desorption rate is expected to be low for radionuclides with high distribution coefficients, and high for radionuclides with low distribution coefficients. So, the relative concentrations in the initial breakthrough of radionuclides by particle transport will be in the reverse sequence when compared to breakthrough by solution transport. This is evident in Fig. 2, where the radionuclide with the lowest distribution coefficient, Sr-85, has the lowest release rate.

Calculation of the Adsorption Rate Constant

From the desorption rate constant calculated above and the distribution coefficients (K_d) calculated from

processes for monodispersed particles using the following relationship:

$$C = C_o e^{-wx} \quad (\text{Eq. 1})$$

where C is the concentration of neutron activation product (that is proportional to particle concentration) at a distance, x , into the bed, and C_o is the initial concentration. The values of w , for filtration and particle adsorption, were 0.33 mm^{-1} and 0.083 mm^{-1} respectively. Natural colloids, such as clay particles responsible for radionuclide transport in this system, usually have log normal particle size distributions, i.e., particles are polydispersed (4). It is thus surprising and as yet unexplained in these experiments that the particle transport conforms to dynamics that are characteristic of the filtration of mono-dispersed particles.

Desorption of Cs-137 from Mobile Particles

We can reasonably assume that within the radionuclide peak, in this case the activated clay region of

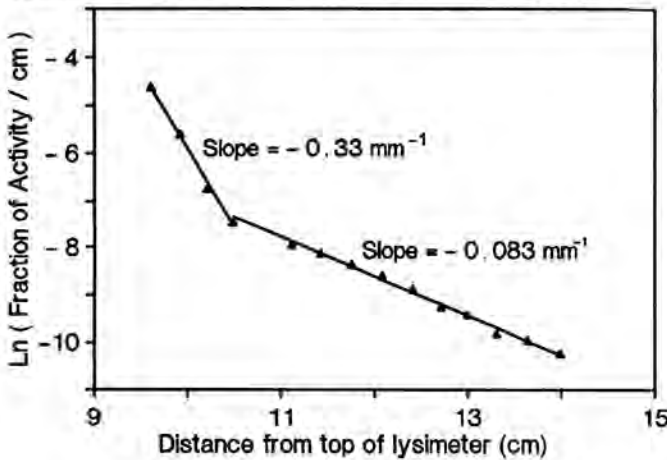


Fig. 4. Neutron Activation Product in Lysimeter Core Corrected for Mixing.

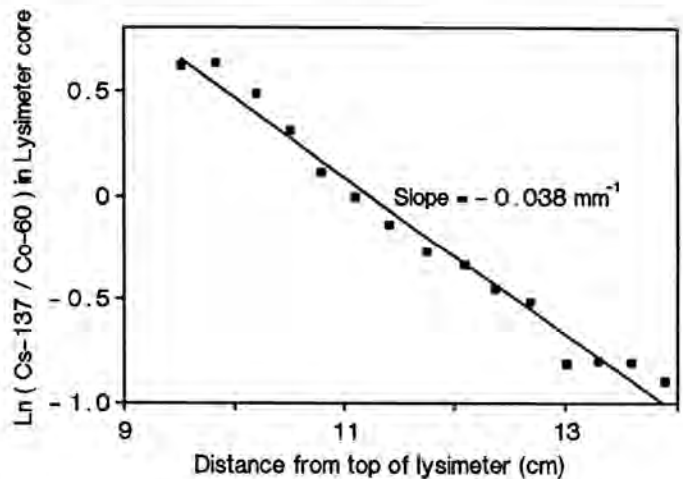


Fig. 5. Desorption of Cs-137 from Colloid particles.

peak shifts, the adsorption rate constant, A , can be calculated since at equilibrium the adsorption and desorption rates are equal:

$$A = G \cdot K_d \quad (\text{Eq. 3})$$

The calculated forward rate constant for Cs-137 is $8.3 \times 10^{-3} \text{ s}^{-1}$ corresponding to an adsorption half life of 1.4 minutes. The value of the adsorption rate constant is only approximate because the distribution coefficient was obtained for the buffer material, while the forward rate constant was determined from the colloid clay particles responsible for particle transport. The colloid clay particles may have a distribution coefficient different from that of the bulk buffer material, although the rather close correspondence of Co-60 (activation product) and Co-58 (soluble salt addition) concentration profiles in Fig. 3 suggest that the above difference in the distribution coefficients was not significant in this experiment.

MECHANISMS OF RADIONUCLIDE TRANSPORT WITH BITUMINIZED SODIUM PHOSPHATE WASTE FORMS

The results and interpretation of data from lysimeters containing neutron activated clay were used to evaluate previous results from lysimeters containing two candidate buffer materials; sand/clay and sand/clinoptilolite mixtures, and the waste form, sodium phosphate in bitumen. A mathematical model was developed which incorporated the following:

- leach results for Cs-137 and Co-60 from the bituminized sodium phosphate waste form were used as source terms (Fig. 6 and 7); and
- radionuclide transport through the buffer was based on the soluble radionuclide release data from the lysimeter containing neutron activated clay.

The model was developed to include the following stages in radionuclide release and transport: (i) radionuclides leave the bituminized waste form as dissolved species; (ii) they are chemisorbed on the surface of the buffer components adjacent to the waste form; and (iii) radionuclides move through the buffer layer by particle transport. Results of the model calculations, the waste form leaching results, and the actual radionuclide release from the lysimeters are presented in Fig. 6 and 7 for Cs-137 and Co-60 respectively.

Cesium Transport Mechanism

In Fig. 6, a comparison of the waste form cesium leach rate and release rate from the lysimeter indicate a significant retardation of cesium in the buffer layer with the amount released about three orders of magnitude lower than the amount leached. Calculated and actual release from the lysimeter differ by about a factor of 2 to 8, a relatively small difference compared to the capture of cesium by the buffer layer. Thus, the leaching and

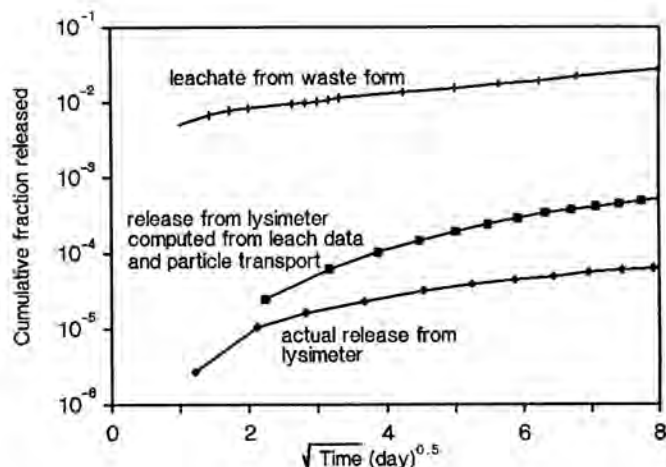


Fig. 6. Release of Cs-137 from the Waste Form and From the Lysimeter.

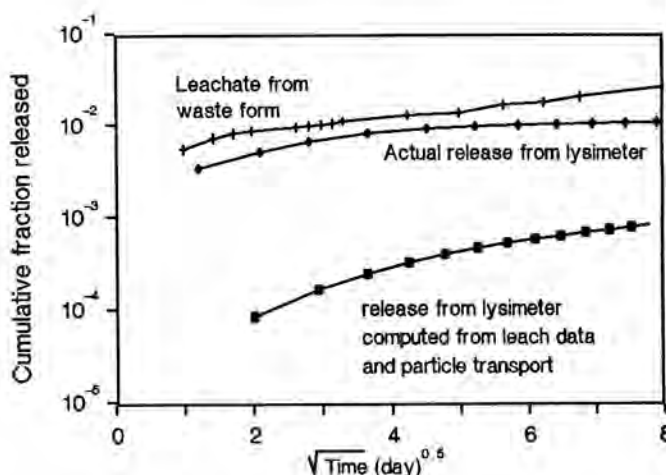


Fig. 7. Release of Co-60 From the Waste Form and From the Lysimeter.

transport mechanism assumed in the modeling of Cs-137 movement is reasonable.

Cobalt Transport Mechanism

Comparison of Fig. 6 and 7 indicates a different behaviour of cobalt from that of cesium. A majority of the cobalt leached from the waste form was released from the lysimeter. In a separate experiment, soluble cobalt salts soaked into sand were retarded much more effectively than the cobalt leached from the waste. Plausible explanations for the low retention of cobalt in the lysimeter include: (i) the release of colloidal, rather than dissolved cobalt species from the waste form; and (ii) a significant lowering of the distribution coefficient due to the presence of phosphate ions. Batch distribution coefficient experiments indicate that the Co-60 distribution

coefficient is lowered by phosphate ions by over an order of magnitude to about 60 (1). However the early breakthrough of Co-60 observed would be characteristic of solution transport with a distribution coefficient value of 5 or less. Also, a low distribution coefficient should develop a uniform activity profile in the soil core. The substantial decline in activity with distance in the lysimeter experiments is contrary to an expectation of solution transport as the dominant mechanism.

Another approach to differentiate between solution and particle transport was to calculate the distribution coefficient in the lysimeter, computed from the radionuclide content of the liquid effluent released at the end of the experiment from the lysimeter, and the radionuclide content of the bottom soil. The geometric mean distribution coefficient for Co-60 was 28 for ten lysimeters containing bituminized or compacted waste forms. Again the distribution coefficient should be associated with uniform radionuclide distribution in the soil core and breakthrough of radioactivity from the lysimeters at about 30-50 days. However, in our experience, major radionuclide releases took place in the first effluent sample taken at one to five days after the commencement of water infiltration. The evidence from the above experiments suggests that colloid transport is responsible for the early release of Co-60.

To understand the migration properties of Co-60 in the lysimeter, we first examined the chemical form of cobalt in the waste form. The simulated bituminized waste was prepared by the dissolution of trisodium phosphate and the introduction of radionuclide solution followed by drying of the solution and incorporation of the solid into the bitumen. The sodium phosphate solution is basic. As an example, a 0.1 N trisodium phosphate solution has a pH of 12. The Co⁺² salt introduced into the waste form readily forms cationic aggregates, highly charged inorganic polymer products at this high pH (6)(7). The Co(OH)₂ colloid is positively charged (8) and since clay has a negative charge, the cobalt colloid would be expected to be adsorbed by the soil upon release. Based on the observed high mobility of the cobalt in the lysimeters, it is more likely that the cobalt was incorporated into the crystal structure of other, negatively charged colloids in the waste form.

Strontium Transport Mechanism

It is reasonable to assume that in the vicinity of the waste buffer interface, adsorption equilibrium exists. As the buffer particle moves downstream from the above region of equilibrium, it enters a region where the radionuclide concentration in solution is orders of magnitude lower than in its previous environment. The rate of radionuclide adsorption becomes negligible and the particle loses its radionuclide content at a rate equal to the desorption rate. Since the desorption rate of radionuclides is expected to be low for radionuclides with high distribution coefficients, and high for radionuclides with low distribution coefficients, the radionuclide concentrations in the initial breakthrough by particle transport are

expected to be in the reverse sequence when compared to breakthrough by solution transport.

While the relative fraction of radionuclides released from the activated clay lysimeter was in the order: Co-58 Cs-137 Sr-85, the order in nearly all of the bituminized sodium phosphate lysimeters was: Co-60 Sr-85 Cs-137. In Table II, the average distribution coefficients for batch and lysimeter experiments are summarized. It is apparent that the addition of phosphate reduces the Cs-137 distribution coefficient and substantially increases the Sr-85 distribution coefficient. If we assume that both isotopes are transported by mobile clay colloids, then based on the principles outlined above, the change in relative concentrations can be attributed to the changes in distribution coefficients. However, it is difficult to explain how the sparingly soluble strontium phosphate is immobilized on colloid clay particles. Thus, further experiments are required to understand Sr-85 transport in the presence of phosphate ions in the sand/clay mix.

Experiments in Buffer Columns

Preliminary experiments were recently performed applying the principles outlined above to sand/clay buffer columns. These experiments were very similar to the lysimeter experiments, but the conditions were better controlled and the buffer was saturated with water. Clay colloids with particle size μ m were separated from neutron activated clay; they were equilibrated with Co-58, Sr-85, and Cs-137 isotope solution. The mixture was pumped into the column. The longer path length in the column experiments, compared to the lysimeter experiments, facilitated longer residence times for the colloid particles. From these experiments, we have concluded that both strong and weak adsorption sites were present in the sand/clay buffer material. Desorption rates from the strong adsorption sites were so low that they could not be determined. The portion of strong adsorption sites were 18% of the total sites for Sr-85 and 72% for Cs-137. It is obvious that the strong adsorption sites are the most important ones for the long term retardation of the radionuclides.

SUMMARY AND CONCLUSIONS

Radionuclides may be released from waste forms as dissolved ionized species, as complexes or as colloids. The results from the experiments presented here indicate that the chemical speciation of the radionuclides in the waste form may determine their transport properties in the buffer materials. It is thus desirable to test the leaching of waste forms in combination with the buffer retardation to discover the controlling mechanism for radionuclide transport. For lysimeter experiments with sodium phosphate in bitumen waste forms, Cs-137 was released as ionized species and was preferentially adsorbed on and transported by colloid clay particles. Colloid particles in the waste form contained $60\text{Co}(\text{OH})_2$. These particles were released from the waste form and were subsequently transported through the buffer layer. The release and transport mechanisms were arrived at with the aid of complementary lysimeter experiments,

where the waste form was replaced by neutron-activated buffer materials soaked in isotope solutions. The latter experiments mimic the release of ionized species from a waste form and facilitate the separation of radionuclide migration by solution and particle transport mechanisms.

The time scale of the experiments has an important effect on the dominant transport mechanism. In the transport of Cs-137, for example, particle transport in the buffer layer dominates early and lasts until break-through by solution transport takes place, because only a small fraction of the released inventory is adsorbed on colloid particles.

While purely solution-based transport mechanisms apply to most of the low-level nuclear waste disposal modeling, the assessment of the contribution by colloid transport should be made using realistic chemical conditions. The approach presented here is suitable for such an assessment.

REFERENCES

1. L.P. Buckley, N.B. Tosello, and B.L. Woods, "Leaching Low Level Radioactive Waste in Simulated Disposal Conditions", presented at the 4th International Hazardous Waste Symposium, Atlanta, Georgia (May, 1987).
2. J. Torok and L.P. Buckley, "Physical and Chemical Environment and Radionuclide Migration in a Low-Level Radioactive Waste Repository", Atomic Energy of Canada Limited Report, AECL-9685 (1987).
3. L.P. Buckley, K.E. Philipose, and J. Torok, "Engineered Barriers and Their Influence on Source Behaviour", presented at the IAEA Symposium on the Management of Low- and Intermediate-Level Radioactive Wastes, Stockholm, Sweden (May, 1988). Also, available as Atomic Energy of Canada Limited Report, AECL-9618 (1988).
4. G.G. Eichholz, B.G. Wahlig, G.F. Powell, and T.F. Craft, "Subsurface Migration of Radioactive Waste Materials by Particulate Transport", Nucl. Technol., Vol. 58, pp 511-20 (1982).
5. A. Saltelli, A. Avogadro, and G. Bidoglio, "Filtration in Glauconitic Sand Columns," Nucl. Technol., Vol. 67, pp 245-254 (1984).
6. F.G.R. Gimblett. Inorganic Polymer Chemistry. Butterworths. London. p 77. (1963).
7. K. Nilsson, B.S. Jensen, L. Carlsen, "The Migration Chemistry of Cobalt", EUR-9781. p. 47 (1985).
8. G.A. Parks, "The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems". Chem. Rev., Vol. 65, pp 177-198, (1965).