

ENVIRONMENTAL BEHAVIOR OF ^{14}C -TAGGED POLYACRYLATE POLYMER: COLUMN STUDIES OF FLOW AND RETARDATION IN SAND

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ABSTRACT. Flow columns filled with sand were used to study migration and retardation of a highly absorbent consumer-product, polyacrylate polymer material tagged with ^{14}C . Five flow column studies of a solution of the polymer demonstrated that a mobile fraction ranging between 32 and 58 percent migrated out of the columns after the passage of up to 50 pore volumes of leachate or distilled water, and most of this occurred well within the first 2 pore volumes. The remainder was highly retarded by the sand near the column inlet. When the polymer was introduced into two other columns as a simulated diaper pad, a much lower migration of 4.6 to 5.6 percent was observed, indicating a blocking phenomenon in the manufactured product form. The effect of typical landfill leachate on the migration and retention of the polymer reduced the migration and enhanced the retardation characteristics of the sand significantly.

INTRODUCTION

There are potential environmental implications when large quantities of any substance are discarded in domestic landfills. Large quantities of consumer products containing super absorbent polymers are currently being used in the form of disposable diapers, adult incontinent products, and feminine hygiene products. These products now use highly absorbent polyacrylate polymers to reduce bulk without loss of effectiveness, making them very popular with consumers. Over 300 million pounds (0.136 Tg) of polyacrylate polymers (1) are used annually in such products; thus, the environmental effects, if any, of their disposal in landfills is of interest. Any such effects are determined by the chemical, bio-chemical, and groundwater transport characteristics of the polymer in its natural state and their effect on its entrainment in leachates and migration by groundwater flow.

Numerous studies under laboratory and fixed conditions have been conducted of the migration

of wastes and their constituents in landfill environments. The studies of Cherry *et al.* (2,3) and Nicholson *et al.* (4) are typical as are a series of studies examined by the National Academy of Sciences (5). The recent discoveries of various chemicals in the groundwaters surrounding industrial waste sites emphasize the importance of this pathway for exposure of the public. A recent study by Cohen *et al.* (6) of four old landfills in Niagara Falls, New York, including Love Canal, has determined the importance of understanding the degree to which any new product may migrate from landfills. No such information has been established for the formulations of polyacrylate polymers used in consumer products.

The subsurface transport through soil of polymer material and its chemical derivatives depend on the rate and degree of release of the polymer from the product and the physical and chemical form of the components released. This behaviour and any associated retardation can be investigated using soil column experiments in which a wide range of chemical and hydrogeological conditions can be examined and a chemical mass balance determined. Sand

column experiments do not, however, represent three-dimensional transport characteristics, a difficulty that could be overcome by pilot studies and field tests with some loss of control of key variables.

The experiments described here used a series of flow column experiments to determine, under carefully controlled conditions, the amount of migration and retardation of a ^{14}C -tagged polymer used in a manufactured diaper product for various flow conditions using distilled and saline waters and treated leachate. The specific objectives were:

- (1) to use sand-filled flow columns to determine the degree to which physical entrapment and adsorption/desorption processes control retardation of polyacrylate polymer;
- (2) to examine the effect of typical landfill leachates on the release and migration of polyacrylate polymer; and
- (3) to determine the retention patterns of polyacrylate polymer on sand in the columns as a function of column depth and fluid type.

These types of measurements, especially those involving retention in soils, can be reasonably done for the polyacrylate polymer studied since it was tagged with ^{14}C . Use of such a tracer also allowed study of the distribution in the soil matrix, which is very important to understanding the migration patterns and retention mechanisms between the polymer and the soil medium. In this respect, this type of radiotracer technique was chosen for study of the polymer interaction with soil rather than more conventional soil tests such as the standard test used for pesticide behavior in soil.

METHOD

Migration and retention of polyacrylate polymer material was determined for sandy soils for two different physical forms of the polymer. The first set of tests involved fluid movement through five 20 cm columns that had received a pulse of filtered ^{14}C -tagged polymer in solution. The second set of tests was done with two 35 cm columns with fluid flow past a cellulose pad spiked with the same polymer material to simulate a typical product. The test product material was a lightly cross-linked, high molecular weight polyacrylate polymer which was prepared from acrylic acid which had been labelled with ^{14}C on the 2, 3 carbon of the polymer backbone (Procter and Gamble Co., Cincinnati, OH, USA). The ^{14}C labelled acrylic acid was prepared from $\text{Ba}^{14}\text{CO}_3$ by reacting $^{14}\text{CO}_2$ with molten lithium to form lithium carbide (^{14}C). Lithium carbide plus water gives acetylene 1, 2 (^{14}C), which was reacted with methanol and nickel carbonyl in the presence of HCl solution to give methyl acrylate 2, 3 (^{14}C).

The methyl acrylate was purified, diluted with cold methyl acrylate and hydrolyzed with a 20% KOH solution. The reaction mixture was acidified with 10% sulfuric acid and the acrylic acid 2, 3 (^{14}C) was extracted with ether containing the methyl ether of hydroquinone, which after purification and distillation, produced a suitably pure acrylic acid for use in the polymerization reaction.

The study comprised two major phases for each of the seven columns studied: (a) aquifer simulation in sand using the flow column to provide data on migration through a one-dimensional flow system into which the polymer could be introduced as a contaminant source and subsequently monitored in the effluent, and (b) analysis of the sand layers in the columns to determine the retention patterns of the polymer by the sand. The basic design of the test column system is shown in Fig. 1, the various configurations of which are reported in detail by Howard and Jones (7).

The columns were filled with clean, dried sand and set vertically so that the upward flow of distilled, de-aired water would dissolve and/or displace trapped air from the column, thereby helping to maintain uniform, one-dimensional laminar flow. Constant head conditions were maintained at the inflow end by a peristaltic pump. Distilled de-aired water was passed through the column for several hours to saturate the sand and to establish a steady flow rate. A pulse of chloride solution was then injected into the base of the column and the column effluent was continuously monitored using a chloride combination electrode to establish the pore volume for each column. After pore volumes and flow characteristics were established, the ^{14}C tagged polymer was introduced to determine migration and retardation of each test configuration; retention was determined by analyzing the ^{14}C concentration in the sand.

The sand grade material used in the series of experiments was collected from the University of Waterloo groundwater research site at Borden, Ontario. The material was selected because the site and material have been exhaustively studied (2, 3, 4), an adjacent disused landfill had confirmed that the materials are of a type that has been used in landfills, and the material provided a limiting case landfill condition in which the polymer materials might be disposed. If minimal migration were observed for sand such as this, then other more likely landfill soils could be expected to offer even greater retention of the polymer or breakdown fragments.

Flow and Migration Studies

The sampling system for the flow and migration studies is shown schematically in Fig. 1. Although the primary data on polymer migration were derived

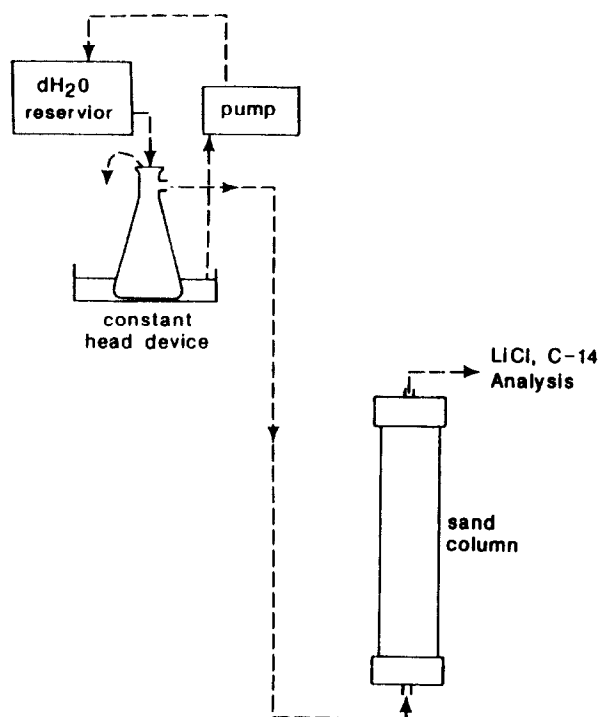


FIGURE 1. Experimental arrangement of flow columns showing the fluid flow system for sampling either a chloride tracer or ^{14}C -tagged polymer.

from measurements of the ^{14}C tracer, chloride tracer studies were performed to examine the pore volumes of the newly filled columns and to determine the flow characteristics. The chloride tracer, which was injected into a steady state flow field, is highly soluble and not retarded; thus, it provided direct information on the flow dynamics of the columns. Using a flow rate of 4 mL/min, it was established that the five 20-cm columns were essentially identical, each displaying a porosity of 42.6% and a pore volume of 151 mL. Each of the two 35-cm

columns had a pore volume of 198 mL.

Polymer migration data were obtained from measurements of the ^{14}C -tagged polymer in the effluent. The experiments involved injection into each column of a 15 mL pulse of filtered solution of ^{14}C -tagged polymer containing 864 nCi/mL under a range of different flow conditions, as shown in Table 1. The polymer pulse size, polymer pulse activity, and flow rate were kept the same for the five tests to allow comparisons to be readily made. For columns 1, 2 and 3, distilled de-aired water was used as the polymer transport medium. Although the experiment was more concerned with the eventual distribution of adsorbed polymer retained within the column than the release of polymer in the column discharge, detailed monitoring of the effluent was nevertheless undertaken. Effluent was collected at timed intervals of 5 to 45 minutes until several pore volumes had passed through each column. Following collection, 50 μL of each bulk sample were transferred to vials containing liquid scintillation fluid for ^{14}C analysis.

Testing of column 1 was stopped after passage of 2.9 pore volumes when it was clear that the first major polymer peak had passed through the column. Flow through columns 2 and 3 was ceased after passage of 47.3 and 97.5 pore volumes, respectively. Columns 4 and 5 were treated and monitored identically to column 2, with the exception that waters with high total dissolved solids were used as the polymer transport medium. Testing of column 4 involved passage of 43.7 pore volumes of sodium chloride solution containing a total dissolved solids concentration of 33 g/L. Column 5 was run with 46.4 pre volumes of filtered and sterilized leachate, which had inorganic chemical characteristics typical of landfill leachates (7). The leachate (Keele Valley Landfill, Maple, Ontario)

TABLE 1
Results of Flow Column Studies of Migration of ^{14}C -tagged Polyacrylate Polymers.

Column #	Transport Medium	Length	Pore Volumes Passed	% Polymer Transported
1	Distilled H_2O	20 cm	2.9	41.6 ^a
2	Distilled H_2O	20 cm	47.3	57.7 ^a
3	Distilled H_2O	20 cm	97.5	52.2 ^a
4	NaCl Solution	20 cm	43.7	45.5 ^a
5	Sterilized Leachate	20 cm	46.4	32.0 ^a
6	Distilled H_2O	35 cm	9+	4.6 ^b
7	Sterilized Leachate	35 cm	9+	5.6 ^b

^aFiltered polymer solution injected as a single pulse containing 12.96 μCi (0.48 MBq) of ^{14}C .

^bPowdered polymer fabricated into a 38 mm square cellulose pad containing 300 μCi (11.1 MBq) of ^{14}C .

contained 6 g/L of dissolved solids and had a conductivity of 8.2 mS/cm at 22 °C; it was sterilized to prevent any biological effect on the chemical and physical observations being made.

The two 35 cm column experiments were conducted with the polymer in dry powder form contained within small cellulose pads to closely simulate use of the polymer in its manufactured form. Flow conditions were tested using distilled water and sterilized leachate for transport fluids. Each pad was about 38 mm square and each contained about 300 μCi (11.1 MBq) of ^{14}C -tagged polymer. Each pad was placed into a small excavated hole parallel to the direction of flow which was maintained at 4 mL/min. As in the 20-cm column experiments, considerable care was taken to ensure that the columns behaved in a closely similar fashion.

Retention Studies

After the flow experiments were completed, the columns were selectively cut and sand samples were removed to study retention of the polymer by the sand as indicated by the concentration of the ^{14}C in the sand. Each sample was taken by removing a thin uniform layer from the center of the column at every other centimeter of column depth; each sample contained about 5 grams (determined by dry weight) for analysis. In order to determine whether an edge effect existed that might allow polymer migration along the column wall, samples were also removed around the perimeter of the cuts at 5-cm depths.

Whereas the effluent plumes of the ^{14}C -tagged polymer could be measured by direct liquid scintillation counting, analyses of the sand for retention of the ^{14}C polymer required combustion of the sand to drive off the ^{14}C polymer as $^{14}\text{CO}_2$. The combustion method (8) had been tested in earlier work using supplied ^{14}C -tagged polymer and clean sand to establish recovery fraction, reproducibility, and the lower limits of detection of ^{14}C . These factors were established by adding a known amount of activity to sand samples and running the test procedure. The recovery yield ranged between 50 and 70 percent using a two-hour combustion time at 700 °C. Since the soils had various moisture content, all samples were weighed after combustion and activity reported for dry soil weight. The data on calibration are based on ^{14}C standards traceable to the National Bureau of Standards.

RESULTS AND DISCUSSION

^{14}C Polymer Migration

The polymer migration studies for the five 20-cm columns were generally similar as shown in Fig. 2 with slight variations due to column conditions and

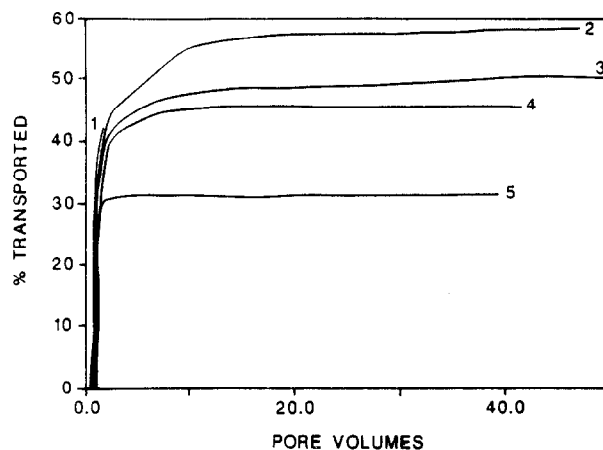


FIGURE 2. Percent of polymer transported versus fluid flow in 20 cm columns due to a 12.96 μCi (0.48 MBq) pulse of ^{14}C -tagged polymer showing rapid migration of the polymer and the effect of leaching fluid on the amount released.

the amount and type of fluid. Effluent polymer concentrations are plotted as cumulative percentages of transported polymer against total pore volume effluent. Also shown in Table 1 are the total percentages of polymer released in the effluent of each column experiment. In general, the polymer contained a mobile fraction that was released quickly from the columns. All three columns run with deaired distilled water displayed very similar characteristics; the polymer moved rapidly, showing up in the effluent after about one pore volume (as shown in the rapid rise of the curves in Fig. 2), and a relatively large amount was recovered in the column effluent. In contrast to the first three columns, the NaCl column showed a more sustained release of the polymer, and the polymer recovered amounts to just 46% of the initial pulse. The lower recovery for column 4 as compared to columns 1, 2 and 3 appears to be caused by a slight impairment to the mobility of the polymer, which reduced the intensity of the release for the first pore volume.

Leachate (column 5) transmitted only 32% of the initial pulse (Fig. 2), a percentage recovery considerably below that of the first four columns, suggesting a reduction in the mobility of the polymer fraction. It was determined that over 90% of the total recovered polymer emerged within the first 1.4 pore volumes. It is suspected that organics in the leachate are adsorbed onto the sand, which in turn, provide the blocking agent responsible for the increased retardation. Divalent cations in the leachate may also attach to the polymer and thereby alter its physical and chemical transport characteristics.

The migration results of the two 35 cm column experiments are contained in Fig. 3, which contains plots of cumulative percent polymer transported versus pore volume for each test. The two plots in

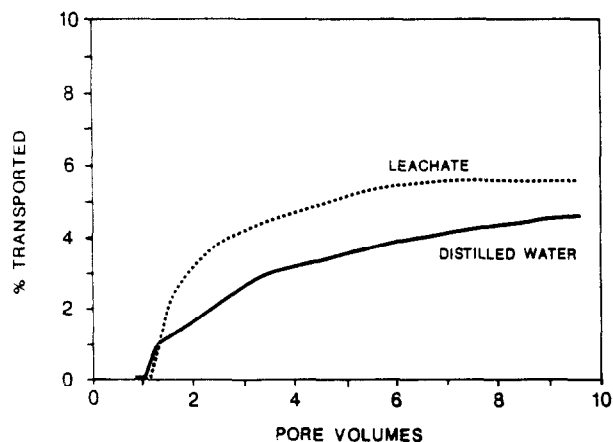


FIGURE 3. Percent of polymer transported versus fluid flow in 35 cm columns for pads containing 300 μCi (11.1 MBq) of ^{14}C -tagged polymer showing the pad retardation effect on polymer release during passage of 9+ pore volumes of distilled H_2O and sterilized leachate, respectively.

Fig. 3 indicate that both the type of polymer and the nature of the transport medium have a considerable influence on the mobility of the polymer. Most apparent is the presence of a highly mobile fraction which passes with relative ease through the 35 cm columns and accounts for about 5% recovered in the effluent, most of which appears soon after passage of the first pore volume. The influence of leachate on the polymer transport shows many similarities to the behavior observed in the 20 cm column experiments. Even though most of the mobile polymer appeared after passage of about one pore volume, the recovery percentage was still increasing after the passage of 9 pore volumes. This slower, continued rate of release may be the result of a gel-blocking effect which sets up in the pad matrix causing a delayed release of the mobile polymer fraction.

Several important differences in polymer behavior were noted when leachate was used as the transport medium and these characteristics may have at least general applicability even though only one type of landfill leachate was studied. In the 20 cm column using filtered polymer solution, the mobile polymer emerges up until the end of the 2nd pore volume (Fig. 2), after which time further release of polymer completely ceases. As a result, only 32% of the polymer is eventually recovered in the leachate flow, even after 46 pore volumes, compared to 58% for transport by distilled de-aired water. Similar behavior is observed in the 35 cm column where, although the total recovery of 5.6% for leachate flow exceeds the value of 4.6% obtained with the distilled water, it is clear (see Fig. 3) that this situation would have become reversed had the experiment continued well beyond the 10th pore volume. The retention measurements indicate that it is possible that

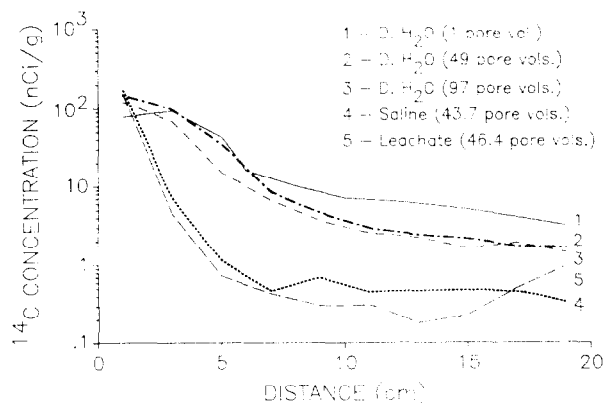


FIGURE 4. Concentration (nCi/g) of ^{14}C -tagged polymer retained on sand as a function of sand depth in five identical 20 cm columns showing effects on retention of the type and volume of leaching fluids introduced after an initial pulse containing 12.96 μCi (0.48 MBq) of ^{14}C -tagged polymer.

divalent cations in the leachate become attached to the mobile polymer and affect its physical and chemical transport characteristics. A more effective blocking agent, however, is believed to be organic material in the leachate which is gradually adsorbed on to the column sands and, in turn, acts as a receptor for the migrating polymer. The polymer clearly moves in the columns and away from the diaper pad burial site.

Polymer Retention Studies

Figures 4 and 5 show the distribution patterns of the retained polymer relative to the point introduced into the column for the 20 cm columns and 35 cm columns, respectively. The dispersion with depth of sand was well characterized and indicated that the polymer exhibited strong retention by the sand near the point of introduction of the polymer sample (either as a pulse or in a cellulose pad) regardless of

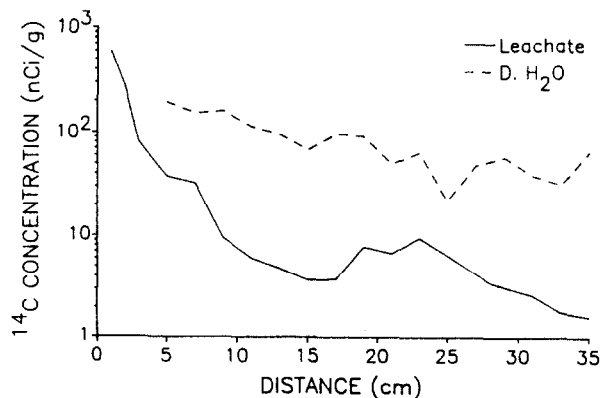


FIGURE 5. Concentration (nCi/g) of ^{14}C polymer retained on sand as a function of sand depth after passage of 9+ pore volumes of distilled H_2O and sterilized leachate through identical 35 cm columns, each of which contained 300 μCi (11.1 MBq) of ^{14}C -tagged polymer in a cellulose pad.

the fluid used. The concentration data for the perimeter samples (not shown) indicated no preferential flow along the column wall.

Although all of the column experiments showed strong retention of the polymer within the sand matrix, there are noteworthy differences in the patterns of retention due to the type of fluid used. In the 20 cm columns the retention patterns for distilled water are similar with some slight effect due to the passage of additional water through the columns (Fig. 4). A similar pattern also exists for distilled water flow in the 35 cm column (Fig. 5) even though the polymer had to first migrate from the cellulose pad and the total percent transported was smaller. There were definite effects on retention when the leaching fluid was saline or sterilized leachate. As shown in Fig. 4 for the 20 cm columns, there was sharper retention closer to the source for both fluids suggesting that the chemical and physical properties of the fluid components provided stronger adsorption and that this had little tendency to be reversed. These effects are essentially the same for both saline and leachate solutions; a similar pattern occurred for leachate in the 35 cm column study.

The presence of the broad peak of retention for leachate at about 20 cm in Fig. 5, which existed after about 9 pore volumes (about 1.8 L), may be due to a travelling pulse of the mobile fraction of polymer from the pad that had not yet emerged from the column. A similar increase also appears between 15 and 20 cm in the shorter (20 cm) column after passage of 4.6 pore volumes (or 6.9 L) of leachate, which is suggestive of an end effect of the column rather than a pulse since the total amount of leachate was considerably greater. In both cases, however, retardation of polymer material is enhanced if typical landfill leachate is the leaching fluid, as would be the case in actual landfill environments.

The migration of the polymer as shown by the variation of effluent concentration (Figs. 2 and 3) had suggested that the mobile fraction of the polymer was adsorbed by the sand. The patterns of retention in Figs. 3 and 4 indicate that the sand's capacity to adsorb the mobile fraction of the polymer is rapidly exceeded in the vicinity of the source, with the limited number of exchange sites showing preference for the longer chained, higher molecular weight fractions of the polymer. Further along the flow line an increased availability of exchange sites coupled with a lower proportion of larger molecules increased the probability that the lower molecular weight mobile fraction would be absorbed. Since these retention patterns existed after passage of several pore volumes (with the exception of column 1 in Fig. 4), it appears that the retardation reactions are non-reversible or the re-

tardation factors were relatively high. The physical and chemical processes by which retention occurs is currently not well understood.

CONCLUSIONS

Column studies proved to be useful for the study of the migration, retardation, and retention of ^{14}C -tagged super absorbent polyacrylate polymers used in consumer paper products. The results of such studies for two sets of column experiments led to the following conclusions:

1. A typical formulation of polyacrylate polymers used in consumer products contained a low molecular weight fraction which was highly mobile; when the polymer was introduced in solution up to 58% of this material migrated in distilled water passed through the columns. Although a highly mobile fraction existed, there was considerable retardation of the remainder in the sand matrix near the source after the passage of about one pore volume of the flow fluid.
2. When the polymer was contained in a cellulose pad and introduced into the flow field, the majority of the polymer was highly retarded in the product or in sand near the source, with some trailing off of the retention pattern down the flow column presumably as the absorption sites near the source became saturated.
3. When a typical landfill leachate was used as the transport medium, there was less migration of the mobile fraction of the polymer due to enhanced retardation by introduction of divalent cations which altered the physical and chemical transport characteristics of the sand.
4. Although the retardation processes of the product form in sand are strong, it is not known if these processes are reversible. A gradual increase in total migration was still occurring after the passage of nine pore volumes; however, this flow failed to move the polymer any significant distance.

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