

# ENVIRONMENTAL BEHAVIOR OF $^{14}\text{C}$ -TAGGED POLYACRYLATE POLYMER: FLOW TANK STUDIES OF RETENTION IN SAND

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**ABSTRACT.** A highly absorbent consumer-product, polyacrylate polymer material tagged with  $^{14}\text{C}$  was dosed to a simulated diaper and buried in a horizontal flow tank containing sand. Two slightly different formulations of the polymer exhibited a mobile fraction, 1.9 percent and 3.48 percent of which was discharged in the tank effluent during the passage of 6 pore volumes. Most of the remainder was retarded along the flow path near the source by the sand. It is expected that more conventional landfill soils would provide even greater retention of the polymer materials studied. The use of a  $^{14}\text{C}$ -tagged polymer proved to be a successful method for studying the behavior of these complex materials; pilot-scale studies are planned in lysimeters to determine if microbial decomposition affects the migration of these polymers under landfill conditions.

## INTRODUCTION

In a previous paper the authors have described a study of the potential environmental implications of the disposal of over 3 billion pounds (1.36 Tg) annually of consumer products which contain about 0.3 billion pounds (0.136 Tg) of highly absorbent polyacrylate polymers (1). A series of soil column experiments were conducted in which various leaching fluids were used to determine the rates of release of forms of the polymer in sand. Such experiments allowed a wide range of chemical and hydrogeological conditions to be examined and were convenient for chemical mass balance circulations; however, a major drawback to the sand column experiments was their inability to represent three-dimensional transport characteristics. Experimentation in a field setting would overcome this difficulty and would obviously provide a much closer representation of landfill conditions, particularly with regard to scale, but it also introduces many variables that cannot be controlled and must

often remain unknown without extensive and expensive site investigation including drilling. Furthermore, field studies require exhaustive monitoring and are not well suited for determining a chemical mass balance.

As a compromise solution, the studies described here used a controlled simulation of landfill flow conditions by use of a fully instrumented aquifer simulation tank which allowed the polymer to behave as a point contaminant source in a flow field for which the hydraulic gradient can be held within the range experienced in field situations. All physical and chemical conditions can be carefully controlled, and a chemical mass balance can be achieved by collecting and analyzing the tank effluent and determining any residual retention in the soil matrix used.

The primary objectives of the experiments described here were to determine, under simulated landfill conditions, the rate and degree of release to the aquifer environment of a polymer from a manufactured consumer product and the retention characteristics of landfill soils that may retard such releases. These studies build upon and extend the

earlier work using flow columns by a closer simulation of landfill conditions.

## METHOD

Migration and retention of polyacrylate polymer material was determined for sandy soils for two slightly different formulations of the polymer structure. Both tests involved water movement past a simulated diaper sample containing typical polymer product that was tagged with  $^{14}\text{C}$ . The test configuration is reported in detail by Howard and Jones (2).

The study was designed to comprise two major phases: (a) aquifer simulation in sand using a flow tank to provide a one-dimensional regional flow system into which the polymer could be introduced as a contaminant source and subsequently monitored through a system of installed sampling devices, and (b) analysis of cores from the sand tanks to determine the retention of the polymer by the sand. These two phases were conducted for two slightly different formulations of the absorbent polymer, the second differing from the first principally by having a higher gel fraction when exposed to moisture. The test product was a lightly cross-linked, high molecular weight polyacrylate polymer which had been labelled with  $^{14}\text{C}$  on the 2,3 carbon of the polymer backbone. This use of a radiotracer afforded straightforward measurement of migration of the polymer due to fluid flow, and was especially useful for determining retention of the polymer by the sand.

The design of the flow tank (2) is shown in Fig. 1. The tank was 1.22 m long, 0.23 m wide and 0.45 m deep with 6 access ports at each end that were arranged vertically at a spacing of 5 cm. During the experiments the ports located 20 cm above the base

of the tank were used for water inflow and outflow. Piezometers were attached at the 10 cm ports to monitor hydraulic heads and allow estimates of hydraulic gradient. To obtain a uniform one-dimensional flow field, inflow and outflow reservoirs were constructed at the ends of each tank. This was achieved by insertion of 13 mm open-grid plastic partitions 5 cm from the tank ends. Each partition was wrapped in a layer of fine (100 mesh) polypropylene filter screen and supported by wire mesh.

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 (3, 4, 5), because it was the same material as in an adjacent disused landfill, and the material provided a limiting case landfill condition in which the polymer materials might be disposed. If minimal migration were confirmed for sand such as this, then other less permeable landfill soils could be expected to offer even greater retention of the polymer or breakdown fragments.

### Flow and Migration Studies

The array of sampling sites for the flow and migration studies is also shown schematically in Fig. 1. Water samples were obtained at 5 principal centerline locations along the flow-line that passes through the contaminant site; two deep locations (at sites 2 and 4) and lateral locations allowed detection of dispersion transverse to the direction of flow. The sampling sites were chosen so as to avoid undue disturbance of the one-dimensional steady state flow regime. Sampling was performed by drawing water from a network of seven 15-cm and

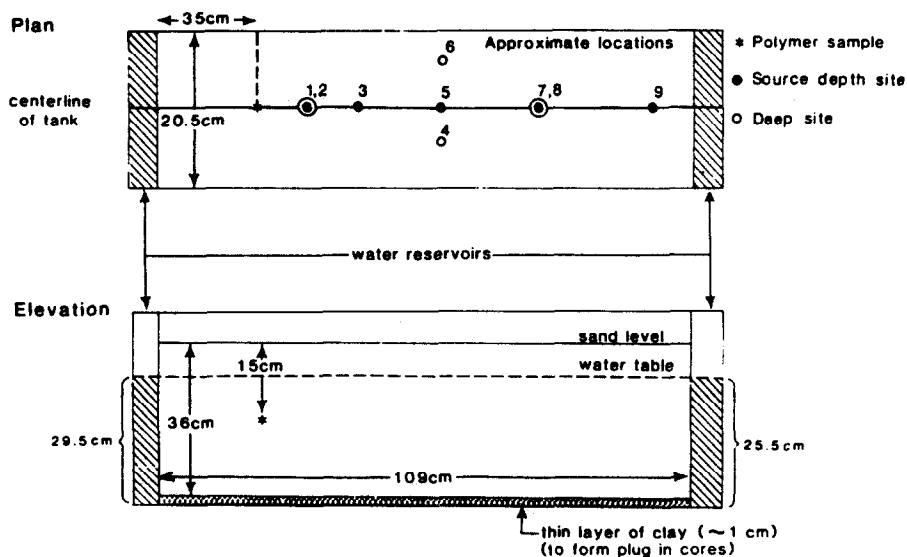


FIGURE 1. Experimental Design of Horizontal Flow Tank Showing Liquid Sampling Sites Relative to Polymer Source.

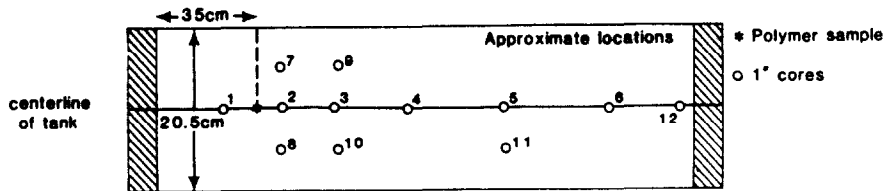


FIGURE 2. Location of Vertical Sand Core Samples from the Horizontal Flow Tank Relative to Polymer Sample.

two 30-cm syringe needles. These needles were attached to a plastic support brace, and the tip of each needle was securely enclosed in a filter medium comprising a hollow plug of fritted glass, 2 cm long and 1 cm in diameter. Two additional needles were placed adjacent to the screen in the outflow reservoir to monitor the tank discharge.

Although the primary data on polymer migration were derived from measurements of the  $^{14}\text{C}$  tracer, chloride tracer studies were performed to examine the behavior of the newly filled sand tank, to identify any anomalies, and to provide direct information on the tank dynamics. The chloride tracer, which was injected into a steady state flow field, is transported without retardation (1); thus, it provided direct information on the velocity of groundwater flow. The tank flow rate was 11.5 mL/min and the head difference over the 1.1 m tank length was maintained at 4.2 cm.

The polymer migration measurements were obtained from measurements at the sampling sites of the  $^{14}\text{C}$ -tagged polymer by collecting 0.3 mL samples for liquid scintillation counting. The tagged polymer was placed in a cellulose pad with a plastic backing, and set horizontal, plastic side down, into a hole excavated to a depth of 15 cm, 10 cm upflow of the first sampling site. The pad in the first experiment contained 46.3 mg of  $^{14}\text{C}$ -tagged polymer with a total activity of 236.9  $\mu\text{Ci}$  (8.77 MBq). In the second tank, which contained the polymer with the larger gel fraction, the pad contained 162.3 mg of polymer with a total activity of 584  $\mu\text{Ci}$  (21.6 MBq). The increased activity in the second tank allowed better counting statistics with small samples.

The movement of the polymer was monitored by collecting 0.3 mL samples at each of 9 sampling sites. Only sites 1, 2 and 3 were sampled until it was established that the polymer was moving; however, as early as 4 hours into both experiments it was necessary to include sample sites 4, 5 and 6. Before the end of the first 24 hours all of the sampling sites were being monitored on an hourly basis. After about 50 hours, sampling was restricted to sites along the source groundwater flow-line as no significant amounts of polymer were being detected at either the lateral or deep sites. At many of the flow-line sites the levels of activated polymer remained high for a considerable period after their

initial detection. Consequently, although it became possible to reduce the frequency of sampling, the length of the experiment was considerably longer than initially planned. The experiments were finally concluded when measured concentrations of  $^{14}\text{C}$  in the samples became insignificant and remained that way for several days. Sampling was carried out for a total of 623 hours (26 days) for the first tank and 418 hours (17 days) for the second tank.

#### Analysis of Tank Core Samples

At the end of the flow experiments vertical cores were extracted from the sand tank in order to study retention of the polymer by the sand. The cores were taken at sites shown in Fig. 2 by forcing 25 mm aluminum tubes to the base of the tank and withdrawing them carefully. These core samples were frozen to prevent sand shift; they were then selectively cut at various depths to ascertain the concentration of the polymer to indicate the retention pattern. A sand sample of about 5 grams was taken at each cut by removing a thin uniform layer across the core at the point of the cut. At least two layers were taken from each core to establish the distribution of the material; and additional ones added if indicated.

Whereas the dispersed plumes of the  $^{14}\text{C}$ -tagged polymer in the flow field could be measured by direct liquid scintillation counting of the extracted liquid samples, analyses of the sand for retention of the  $^{14}\text{C}$  polymer required combustion of the sand to drive off the  $^{14}\text{C}$  polymer as  $^{14}\text{CO}_2$ , which was trapped in chemicals specific for  $\text{CO}_2$ . The combustion method has been described in earlier work (6). Studies were done using  $^{14}\text{C}$ -tagged polymer and clean sand to establish a recovery fraction of 50 to 70 percent when combusted for two hours 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  $^{14}\text{C}$  standards traceable to the National Bureau of Standards.

The cellulose pad used as the polymer source was also analyzed for residual activity by slurring it in about 800 mL of distilled, deionized water and taking several aliquots of the slurry for analysis. The sand layer just above and below the diaper sample was also collected for analysis.

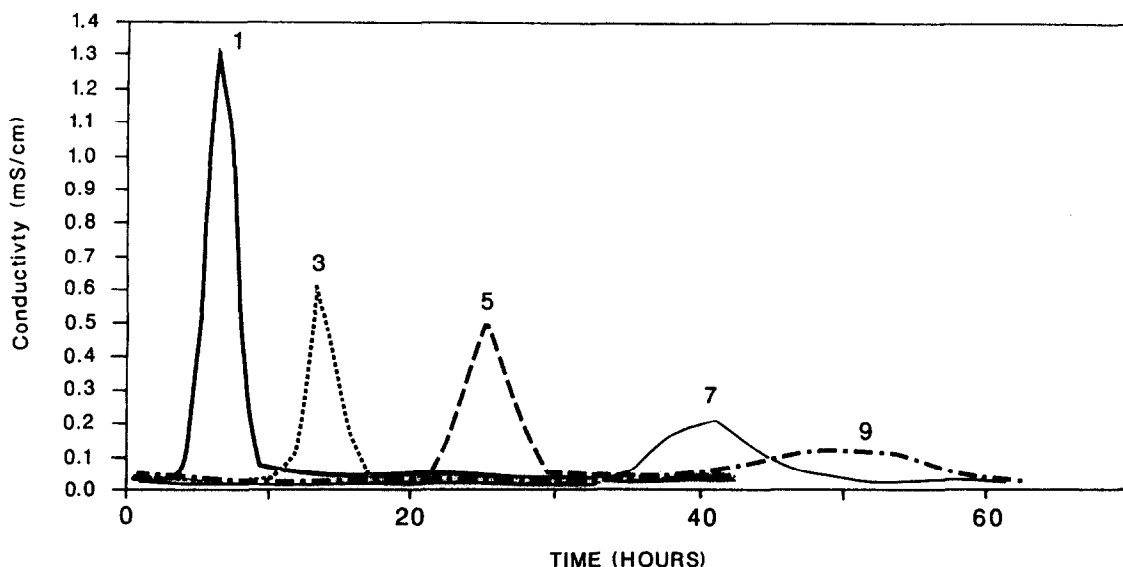


FIGURE 3. Chloride Tracer Concentration Determined from Conductivity Measurements of Extracted Samples showing time of Arrival and Persistence at Sites 1, 3, 5, 7, and 9 along the Flow Tank Centerline.

## RESULTS

### Chloride Tracer Tests

The chloride tracer tests showed uniformity of the advective flow field near the centerline sampling sites; no significant chloride tracer was observed at the lateral or deep sites. Shown in Fig. 3 are the chloride concentration measurements from the second test tank (the first tank data were similar) at the centerline sampling sites as a function of time after release of the tracer. These data indicate the uniform flow of the tracer and the reduction and broadening of intensity at the downstream sites, and they correlate well with theoretical predictions (2). Since the chloride tracer is not retarded, these data were useful for establishing the advective flow conditions of the tank for comparison with the  $^{14}\text{C}$  polymer tracer data.

### $^{14}\text{C}$ Polymer Migration

The polymer migration studies were generally similar to the chloride tracer tests in terms of source configuration and sampling sites with slight differ-

ences in tank flow conditions and amount of tagged polymer in the spiked pads. These data are shown in Table 1. Also shown in Table 1 are the total percentages of polymer released in the tank effluent of both tank experiments. In general, the polymer contained a mobile fraction that was quite small suggesting that either the polymer was not released from the spiked pad or it was retained in the sand matrix.

The results of the  $^{14}\text{C}$  tracer analyses are presented in Figs. 4 and 5 for test tanks one and two, respectively. The most prominent feature is a sharp peak that occurs at site 1, 7.5 cm from the nearest edge of the source site 5 hours after introduction of the polymer. For test tank 2 (Fig. 5) the peak can be followed through sites 3, 5, 7 and 9, becoming less in intensity and broader as it moves. The velocity of movement averaged 1.8 cm per hour which was about 80% of the advective water velocity. Significantly the polymer was not detected at either the deep or lateral sites in either tank experiment. Only 1.9% of the polymer was released from the first test tank after passage of 6 pore volumes; for the second

TABLE I  
 $^{14}\text{C}$  Polymer Tracer Test Data

	Sample Activity	Tank Flow ml/min	Velocity cm/hr	Pore Volume Flow Time (hr)	Effluent Release (%)
Test Tank 1 (low gel polymer)	263.9 $\mu\text{Ci}$	7.0	1.5 <sup>a</sup>	56	1.90%
Test Tank 2 (high gel polymer)	584 $\mu\text{Ci}$	9.53	1.8 <sup>a</sup>	47	3.48%

<sup>a</sup>Average of chloride transport times to 5 downgradient sites (see Fig. 3).

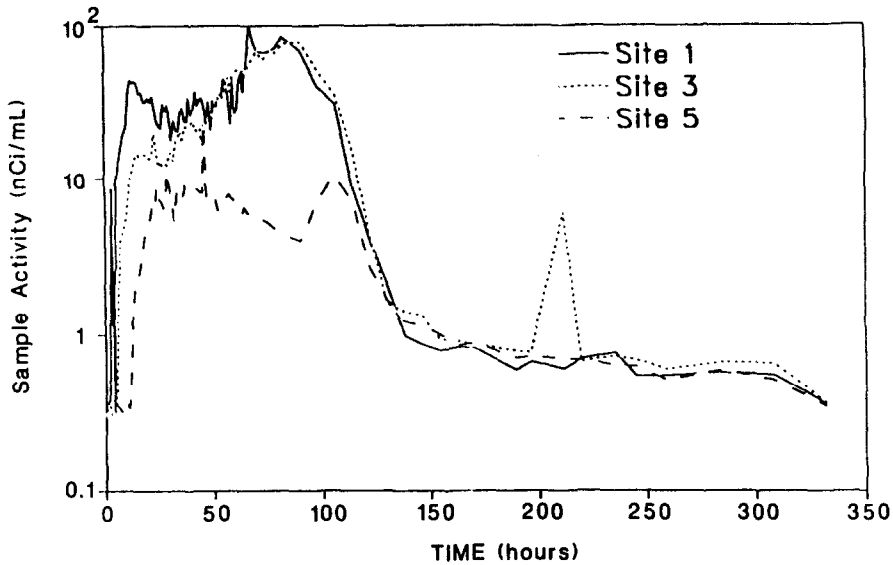


FIGURE 4. Horizontal Centerline <sup>14</sup>C Concentrations for Tank 1 Liquid Sampling Sites 1, 3, and 5 Versus Time after Flow began showing Arrival Time and Persistence of Mobile Polymer Fraction.

test tank 3.48% of the polymer was released. These releases took place within the second and third pore volumes, and, though somewhat lower, are generally representative of the fractions leached from similar pads employed in the flow column studies conducted earlier (1).

*Polymer Retention Studies*

Figures 6 and 7 show the distribution patterns of the retained polymer relative to the buried polymer sample. The precise locations of the points used to plot the data are uncertain by at least one cm since the sand was compressed when the cores were taken. Good characterization of the dispersion and retention of polymer on the soils was obtained. The data indicate that the polymer distributed as a

well-defined plume in the soil, with strong retention by the sand near the polymer sample.

The slurried diaper pad was used to determine the retention of the <sup>14</sup>C tagged polymer material within the spiked pad itself. The mean concentration of 5 aliquots of the slurry of the pad used in test tank 2 was about 201 nCi/mL (7.44 kBq/mL) which represented a total residual activity in the polymer sample of about 161 μCi (5.96 MBq), or about 28% of the initial radioactivity of 584 μCi (21.6 MBq). The sand layer immediately above the polymer sample was found to contain about 39.5 nCi/g (1.46 kBq/g); that immediately below measured about 1.5 nCi/g (55 Bq/g) indicating some near field migration of the imbedded polymer, most likely due to molecular diffusion.

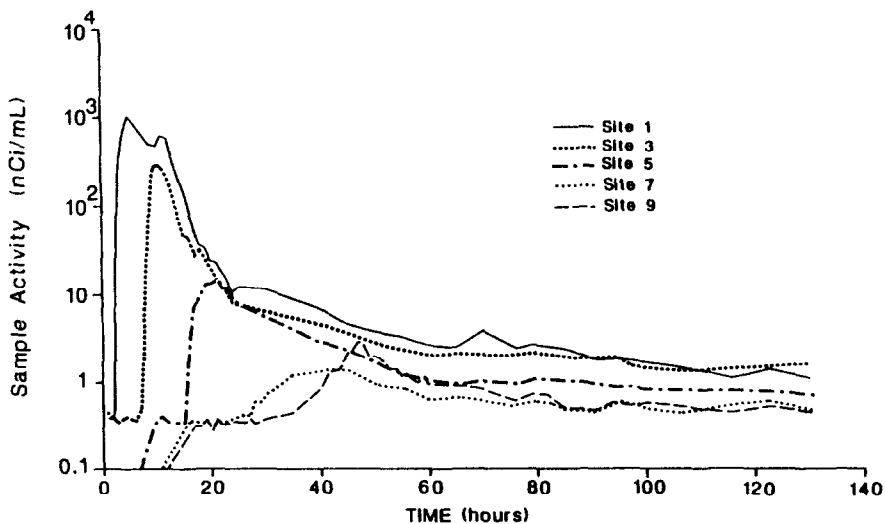


FIGURE 5. Horizontal Centerline <sup>14</sup>C Concentrations for Tank 2 Liquid Sampling Sites 1, 3, 5, 7, and 9 Versus Time after Flow began showing Arrival Time and Persistence of Mobile Polymer Fraction.

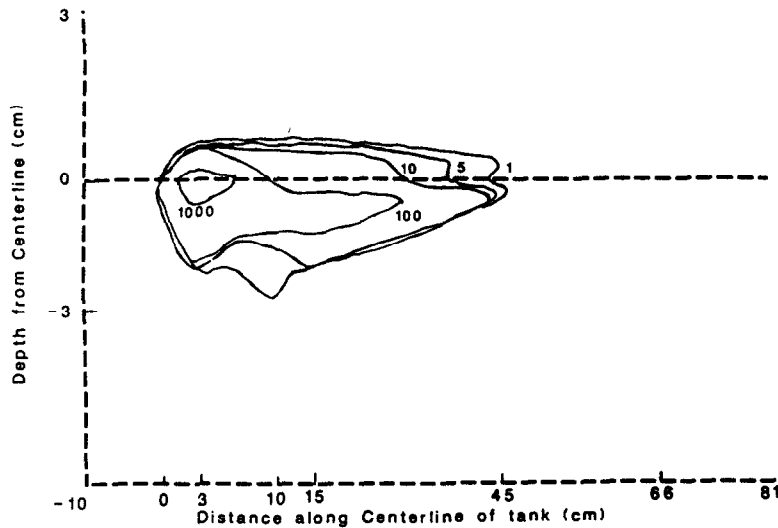


FIGURE 6. Isolines of  $^{14}\text{C}$  Concentration (nCi/g) Versus Sand Depth Along the Vertical Centerline of Flow Tank 1.

### DISCUSSION OF RESULTS

The polymer clearly moves in the tank flow field and away from the diaper pad burial site; it was registered at all sample sites located along the principal flow line which passed through the center of the diaper pad and also appeared in the tank effluent. Figure 5 shows a major response for the second flow tank at Site 1, 10 cm from the center of the diaper pad and 7.5 cm from its leading edge, just 5 hours into the test (a similar response was also found for tank one as shown in Fig. 4). This response can be traced through the remaining principal flow line sites, the resultant peaks appearing at times that are consistent with the average linear flow velocity. This velocity is close to the velocity at which a chloride tracer would be expected to move through the tank and demonstrates that the mobile fraction of the polymer is capable of being

transported with minimal retardation. These peaks for the polymer compare very well with those produced by the conservative chloride tracer (Fig. 3) which show a gradual broadening and reduction in intensity along the flow line.

The migration peaks produced by the polymer show a rapid decline between Site 1 and Sites 5 and 9, suggesting that the mobile fraction of the polymer is being adsorbed by the sand, a process which is somewhat inconsistent with the advective flow velocity data which indicate that the mobile fraction moves with minimal retardation. This apparent anomaly is an indication 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

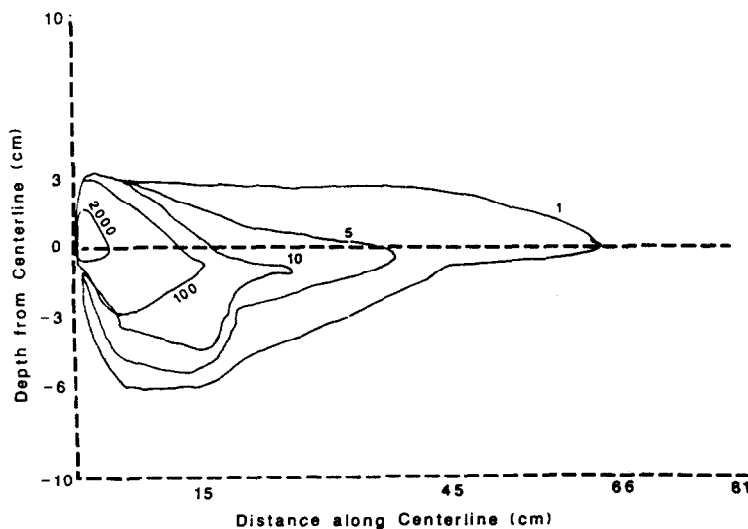


FIGURE 7. Isolines of  $^{14}\text{C}$  Concentration (nCi/g) Versus Sand Depth Along the Vertical Centerline of Flow Tank 2.

with a lower proportion of larger molecules increases the probability that the lower molecular weight mobile fraction will be adsorbed. The data shown in Fig. 6 demonstrated that the retardation factors are relatively high. As shown in Table 1 only a small fraction (1.9–3.48%) of the polymer is recovered in the tank effluent having traveled the 85 cm distance from the source site, most of which emerged soon after passage of one tank pore volume. Any possibility that the diminishing peaks are produced by lateral dispersion or sinking is denied by the absence of polymer in liquid samples from either the lateral sites or the deep sites.

The sand retention shown in Figs. 6 and 7 confirmed the strong adsorptive capacity of the sand since most of the polymer radioactivity was detained near the source. Although this phenomenon may be dominant for the less mobile, higher molecular weight components of the polymer, the pattern generally confirms that deduced for the mobile fraction based on the liquid concentrations measured at the flow sites.

One difference between tank experiments is the detailed responses observed at Sites 1, 3, and 5. The first tank experiment showed two to three closely spaced peaks (Fig. 4) which were tentatively attributed to different molecular weight fractions. The second experiment, which used the higher gel volume polymer formulation, did not show these peaks, an indication that the molecular weight fractions responsible are less important components of the higher gel volume polymer. The major finding in both experiments is that an early peak does appear in both and moves through the tank at a velocity close to the velocity of advective flow. In both cases it is the early peak (or the closely spaced early peaks in tank one) that accounts for the polymer recovered in the tank effluent.

Although the higher gel volume polymer has a slightly higher mobile fraction, there is a notable absence of any other fractions showing even the slightest tendency for transport. This is confirmed by the presence of a single major peak in the tank effluent after discharge of three pore volumes (Fig. 5 shows the passage of this major peak at all sites, but especially at site 1). As of now, the proportion of lower molecular weight components is not well established, even though the data reported here suggest that the higher gel volume polymer contains somewhat more of these components.

The dominant retardation processes are currently not fully understood. It is not clear, for example why the mobile polymer fraction moves close to the advective flow velocity (indicating minimal retardation), but reduces dramatically in concentration with increasing distance, suggesting that retardation is indeed playing a role. Neither is it clear whether

retardation of the mobile fraction is by physical entrapment or adsorption reactions or both. The tight retention patterns (Figs. 5 and 6) suggest that the adsorption reactions are not reversible. This finding suggests that retardation of the polyacrylate polymers tested will be substantial, and that consumer products containing these materials will produce little, if any, migration of polymeric materials out of land disposal locations containing less permeable soils and clays.

## CONCLUSIONS

Landfill simulation of the migration and retention of  $^{14}\text{C}$ -tagged super absorbent polyacrylate polymers used in consumer paper products such as diapers proved to be a successful study method. The results of such studies for two flow tank experiments led to the following conclusions:

1. Typical formulations of polymers used in highly absorbent consumer products contain a low molecular weight fraction which is highly mobile and which moves close to the advective flow field of the simulation tank. This fraction, although mobile, exhibits retardation in the sand matrix, being highly adsorbed near the source after the passage of about one pore volume of the flow tank, such that only 1.9 to 3.48% is released in the tank effluent.
2. The majority of the polymer is of high molecular weight which is adsorbed in sand very near the source, with some trailing off of the retention pattern down the flow field, presumably as the adsorption sites near the source become saturated.
3. The retardation processes of the polymer do not appear to be reversible; no significant polymer was recovered after the first 3 pore volumes and the passage of up to 10 pore volumes failed to move the polymer any significant distance.
4. The strong retardation of polyacrylate polymers by sand suggests that release of such polymers from landfills will be minimal, especially for more conventional, slow permeability landfill soils.
5. Use of a  $^{14}\text{C}$ -tagged polymer allows straightforward study of the migration and retention of polyacrylate polymers under controlled simulated conditions.

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