BIODEGRADATION TESTING OF BITUMEN*

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ABSTRACT

An estimate of the rate of biodegradation of bituminous material is necessary to predict the long-term stability of low- and intermediate-level waste solidified using bitumen. Data from a series of scoping experiments have been analyzed to determine the rate of degradation of blown bitumen samples under a variety of conditions. Among the variables investigated were the effect of soil type, moisture, sample surface area and microbial strain. The rate of degradation was measured by monitoring metabolic CO_2 release. Using this data it was found that, for degradation in soil, a mean rate of 5.5×10^{-4} cm/yr represented all data to within a factor of about two. This mean rate is nearly that for distilled bitumen samples measured by other workers.

INTRODUCTION

Bituminous materials are being used or have been proposed for use for the solidification of low- and intermediate- level wastes (see, for example, [1,2,3]). Because it is a hydrocarbon-based material, bitumen may be more susceptible to biological degradation when compared to other materials commonly used as solidification agents, e.g., cement.[8] A number of reports discuss the biodegradation of bitumen and tar. These include general summaries of the biodegradability of the material [4,5] as well as specific studies which quantify the susceptibility of bitumen toward microbial degradation by measuring the growth of cultures [2,3,6,7,8]. In addition, rate data have been obtained [7,9]. The qualitative aspects of these studies indicate the following:

1. Microbial attack of bitumen is most likely to occur under aerobic conditions.
2. Degradation can occur under varying conditions of available water.
3. A large number of bacterial and fungal strains are capable of degrading bitumen.
4. The various fractions in bitumen appear to degrade at different rates.
5. Degradation of bitumen is expected to result in the generation of gases (H_2, CH_4, CO_2 and H_2S) and organic liquids.
6. There is little or no effect on the release of radionuclides due to microbial attack of bituminous waste.

Under 10 CFR Part 61, Class B and C waste must remain stable for a minimum period of 300 years. The concept of stability (defined as structural stability) requires resistance to the stresses that the disposal site places upon the waste, including microbial attack. Testing methods and acceptance criteria which have been recommended to demonstrate stability are described in the Technical Position on Waste Form (TP) [10]. The TP recommends that two culture growth tests, ASTM G21 and ASTM G22, be run to demonstrate resistance to microbial attack. For those waste forms which

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exhibit susceptibility in the ASTM tests, further testing to determine the rate of degradation is recommended. This test determines the rate of degradation by measuring the rate of CO_2 evolution from small sample forms using a method developed by Bartha and Pramer [11].

In order to better define the conditions of the Bartha-Pramer test recommended in the TP and to determine the effects of soil type, moisture, temperature and sample size on test results, the NRC sponsored a series of tests. The data resulting from these tests has been published by Bowerman et al. [9]. However, the treatment of the data presented in Reference 9 was such that only qualitative statements could be made concerning the effects of the parameters mentioned above. This data has been analyzed to determine the rate of degradation of blown bitumen as well as an estimate of the uncertainty in this rate for each set of experimental conditions. Using the results of this analysis, it is possible to make general statements about some of the factors affecting the rate of degradation of bitumen as well as to indicate directions for additional work in this area.

EXPERIMENTAL

The details of the experimental procedure are given in Bowerman et al. [9] and are summarized here. A list of experimental conditions is given in Table I.

Table I. Experimental conditions for degradation experiments. Samples consisted of 4 nominal 1-cm x 1-cm-sized cylinders except where noted.

Expt. No.	Medium	Microbe	Surface Area (cm^2)	Pre-test Moisture (Weight Percent)	Length of Test (days)
1	Barnwell soil	gen. soil	30 ± 3	2.6 ± -	177
2	Upton soil	gen. soil	30 ± 3	5.1 ± 2.6	197
3	Upton soil	Pseudomonas	30 ± 3	5.1 ± 2.6	35
4	Richland soil	gen. soil	30 ± 3	5.2 ± 0.3	197
5	Barnwell soil	gen. soil	30 ± 3	5.6 ± 0.2	196
6	Barnwell soil	gen. soil	30 ± 3	18.3 ± 0.4	181
7	Barnwell soil	gen. soil	20 ± 2[a]	5.6 ± 0.2	192
8	Barnwell soil	gen. soil	134 ± 13[b]	5.6 ± 0.2	206
9	agar	Pseudomonas	30 ± 3	- ± -	54
10	agar	fungi	30 ± 3	- ± -	59

[a]Nominal 2-cm x 2-cm cylinder.
[b]1-mm-thick sheet.

A blown bitumen (PIONEER 221 density = 1.01 g/cc) was used in these tests. It was fabricated into three shapes:

1. Right circular cylinders of nominal diameter and height of 2 cm (2 x 2),
2. Right circular cylinders of nominal diameter and height of 1 cm (1 x 1),
3. Sheets approximately 1 mm thick.

The samples for each experiment were obtained by taking approximately 7 grams of one of the three sample types. Thus, for each experiment, the volume of material was constant while the surface area varied depending on the type of sample used. For 2 x 2 samples, the surface area was approximately 20 cm^2 and one form was used. For 1 x 1 samples, four forms were used and the surface area was approximately 30 cm^2. Finally, the 1-mm sheet samples had a surface area of about 130 cm^2. It is estimated that the variation in the surface area for each of the sample types was approximately 10%.

Two growth media were used in these experiments, soil and nutrient agar. Three types of soil were used. Two were backfill soils obtained from the low level waste disposal sites at Barnwell, SC and Richland, WA. These soils have been characterized previously [12]. The third was a surface soil sample obtained at BNL. It has not been extensively characterized. All soils were used in their field moist condition (see Table 1). In addition, for two experiments on Barnwell soil, conditions of full saturation and one half field moist were used. The nutrient salts agar medium supplied all essential nutrients except a source of carbon.

For most of the soil experiments, the indigenous soil microbes were used. In the single exception (Experiment 3), the soil was sterilized by gamma radiation and inoculated with Pseudomonas aeruginosa. For the two sets of experiments run in agar, inoculation was with either the mixed fungal culture perscribed in ATSM G21 or with Pseudomonas aeruginosa which is prescribed in ASTM G22.

The experimental procedure was as follows. Bitumen samples were loaded into the Bartha-Pramer flasks along with the medium (agar or soil). Sets of four replicates were used in each experiment. Controls consisted of growth medium plus microbe but with no bitumen. Three replicates were used for controls. Atmospheric CO_2 was excluded by means of an Ascarite filled tube. The experimental apparatus is illustrated in Figure 1. The amount of CO_2 released from controls and samples was determined by titration of the 0.1 N KOH solution in the side arm of the flask. The KOH solution was withdrawn from the flask at periodic intervals which varied over the course of each experiment and replaced with fresh solution. Each sample was titrated with standard HCl solution (either 0.5 or 0.1 N) and the incremental amount of CO_2 generated in the sample and control flasks calculated.

RESULTS AND DISCUSSION

The cumulative carbon dioxide released was determined for samples and controls by summing the incremental data. The resultant cumulative data was fit using a linear least squares regression analysis. A plot of the cumulative CO_2 released from bitumen in Richland, WA soils is shown in Figure 2 as an example (Experiment 4). The net CO_2 release rate was determined by subtracting the least squares line of the samples from that of the controls. The slope of the line (degradation rate) was then converted to units of thickness of bitumen consumed/year. These results are shown in Table 2. The variation in the rates given in this table reflect the uncertainties in the surface area measurement as well as the sample-to-sample variation in the CO_2 released by both the samples and controls.

The rate data presented in Table II provide a means to estimate the magnitude of the effects of changing conditions on the stability of bitumen. The effect of microbe type can be seen from the comparison of the rates observed in experiments 2 and 3 as well as 9 and 10. In experiment 2, microbes indigenous to the soil were present, while in experiment 3, the soil was sterilized and innoculated with a particular bacterial strain,

Pseudomonas aeruginosa. Comparison of the mean rates indicates that the indigenous soil microbes degraded the bitumen some 70% faster than the bacterial culture. Experiments 9 and 10 show the effect of a change in microbe in a nutrient salts agar. Two microbe cultures were used, a single bacterial strain (experiment 9) and a mixture of five fungal strains as specified in ASTM procedure G21. The rate observed due to attack by the fungi was significantly higher (approximately 2.5 times based upon mean values).

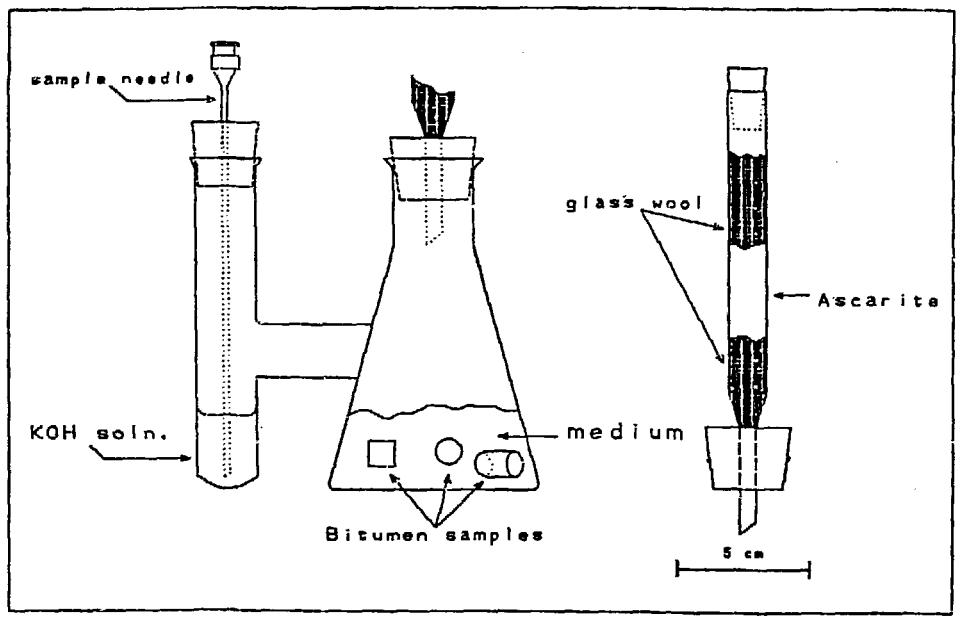

Figure 1. Experimental apparatus used in Bartha-Pramer experiments.

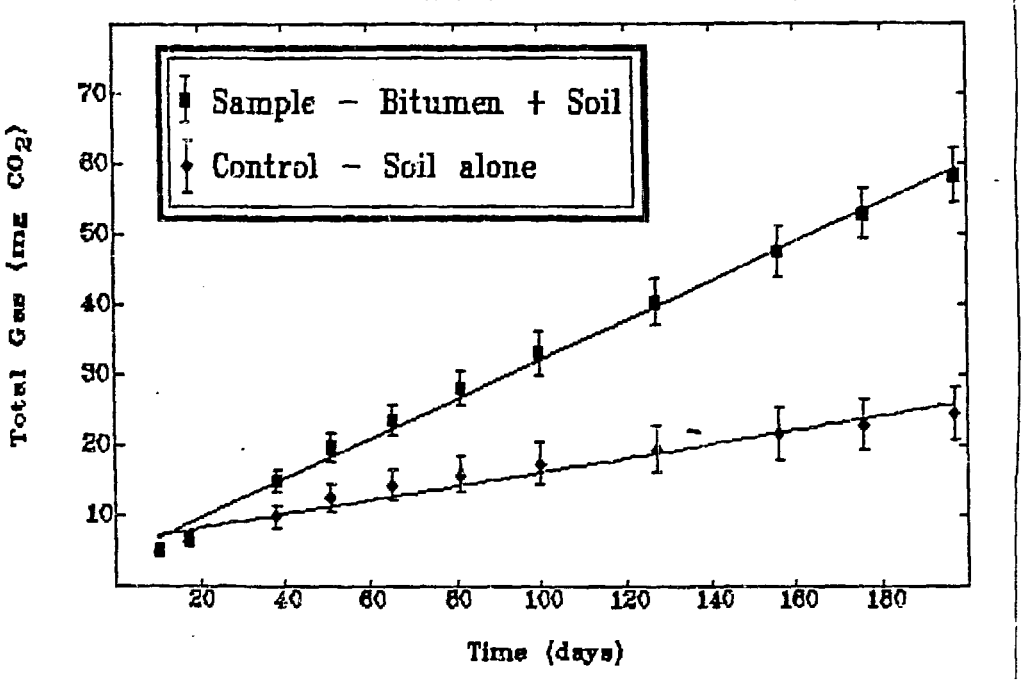

Figure 2. Cumulative CO_2 released from bitumen in Richland soils vs time.

Table II. Degradation rates of blown bitumen based on cumulative CO_2 released in modified Bartha-Pramer test. Experimental conditions are defined in Table I.

Expt. No.	Rate (cm/yr)
1	5.78E-04 ± 1.2E-04
2	3.65E-04 ± 5.6E-05
3	2.11E-04 ± 1.4E-04
4	5.96E-04 ± 2.5E-04
5	1.05E-03 ± 1.3E-04
6	4.58E-04 ± 8.1E-05
7	6.37E-04 ± 1.6E-04
8	5.43E-04 ± 6.5E-05
9	2.44E-03 ± 4.1E-04
10	5.56E-03 ± 6.2E-04

Similarly, the effect of the growth medium is seen by comparison of those studies done in nutrient salts agar (experiments 9 and 10) with those conducted in soil. The agar represents an idealized growth medium in which all nutrients except a carbon source are provided by the medium. Comparison of the observed mean degradation rates given in Table II shows that the lowest rate in agar is 2.3 times higher than the highest rate seen in soil. These differences are magnified when experiments 3 and 9 are compared. The sole difference in these experiments was the growth medium. In both experiments the microbial population was the same, namely, a single strain of bacteria. The mean rates in these experiments varied by almost an order of magnitude. The rate in soil was lower.

Considering the wide range in experimental conditions, the observed variation in the rate of degradation is surprisingly small. For example, with the exception of the Barnwell 1 x 1 samples at 5.6% initial soil moisture (see below), Figure 3 shows almost no variation of the observed rate with initial soil moisture. For all experiments conducted in soil (experiments 1 through 8), the mean degradation rate is plotted versus initial soil moisture in Figure 3. The average of these degradation rates was $(5.5 \pm 2.3) \times 10^{-4}$ cm/yr. This rate would result in about a 1% volume change in a 55-gallon drum of bitumen over 300 years. Further, the average rate observed for blown bitumen compares favorably with the rate measured on blocks of distilled bitumen containing simulated $NaNO_3$ waste measured by Abdellah and Pederson of 6×10^{-4} cm/yr [7].

Figure 3 also illustrates the variation which can be expected in the observed degradation rate as a function of sample size. The rates plotted in this Figure are normalized to a unit surface area. Thus, one would expect that all the degradation rates observed for bitumen in Barnwell soil at 5.6% initial soil moisture would be the same if the degradative process is controlled by the surface area of the bitumen. It can be seen from the figure that the data for the sheets of bitumen and the 2 x 2 samples are the same within experimental error. The rate observed for the 1 x 1 samples under field moist conditions are significantly higher. The reason for this different rate is unknown.

CONCLUSION

The results of these experiments indicate that environmental factors

studied here have a surprisingly small effect on the rate of biodegradation of bitumen as measured by CO_2 generation. One limitation of this technique is that the effects of biodegradation on samples are only measured indirectly. Further, anaerobic degradation accompanied by the evolution of CH_4 is not measured at all. While this test provides a useful means for estimating degradation rates for regulatory purposes, additional work to correlate the generation of carbon dioxide with long-term waste form performance would be useful. More importantly, the biodegradation rate of bitumen containing actual or simulated radwaste should be measured to determine if the effect of these additives is to enhance or inhibit the degradation rate. In the absence of such waste form specific and disposal site specific data, however, the results of these tests indicate that it may be possible to bound the performance of more protoypic samples through short-term, generic tests.

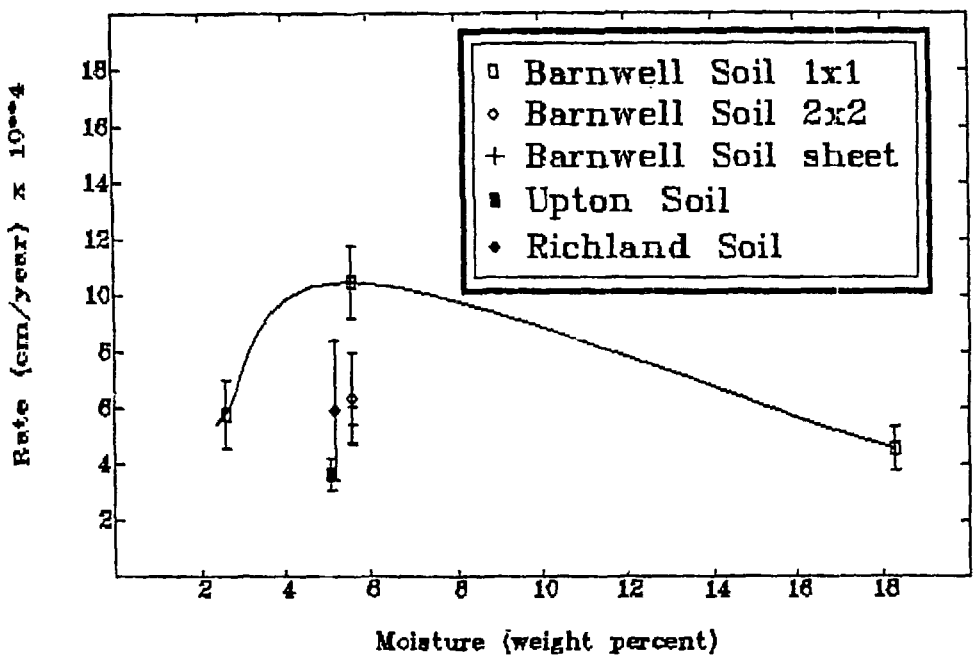

Figure 3. Mean degradation rate of bitumen in various types of soil versus initial soil moisture. Data connected by spline fit represents bitumen samples in Barnwell soil in which the soil moisture content has been intentionally varied.

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