

Organic Emissions from Petroleum-Contaminated Soil Fixed in Concrete

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ABSTRACT: This study investigated a solidification treatment process for soils that are contaminated with hydrocarbons at levels of 0.5 and 3.0% by weight of benzene. The contaminated soils were bound in a concrete matrix and the migration of organics from the concrete to air was evaluated. If the hydrocarbon emissions are sufficiently attenuated, the concrete containing such contaminated soil can be used for exterior construction applications.

The experimental specimens consisted of concrete mixtures in which 40% of the sand was replaced with the contaminated soil. The mixtures' ratio of cement, aggregate, sand, and water is 1:1.5:1.5:0.5 by weight. The study included specimens with and without class C fly ash replacing 10% of the cement. In addition, two unfixed control specimens were prepared for each contamination level. The concrete-soil mixtures were placed in sealed jars and air was passed through the head space of the jars and then through carbon adsorption tubes for measurement of contaminant flux from the surface of the specimens. Measurements were made during and after concrete curing. The results were fitted to a Fickian diffusion model to estimate effective diffusivity in the concrete-soil specimens.

The test results showed that the effective diffusivity of the contaminant within the concrete was reduced by three to five orders of magnitude over the molecular diffusivities in unfixed contaminated soil used as control. It was observed that the presence of fly ash in the concrete affects the hydrocarbon release and causes an additional decrease in effective diffusivity of about one order of magnitude. Contaminant emissions during the curing phase were found to exceed rates predicted by the Fickian model. This is apparently due to the water used in the concrete. Total emissions, however, never exceeded values emitted from the unfixed controls. This study indicates that fixation of low hydrocarbon levels within concrete is a technically viable and safe technology for recycling petroleum-contaminated soil.

KEY WORDS: concrete, contaminated soil, diffusivity, emission, fixation, fly ash, hydrocarbons.

I. INTRODUCTION

A. Statement of the Problem

Spills, leaks, and other releases of gasoline, diesel fuels, heating oils, and other petroleum products often result in the contamination of soil and groundwater. Soil

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contaminated by virgin petroleum products is a pervasive problem in the U.S. and foreign countries, both accidentally as well as intentionally. The problem has existed due to the transportation, storage, and use of these products. It was estimated that several hundred thousand underground storage tanks (UST), used for the storage of petroleum products, are leaking (Dowd, 1984). Currently, it is estimated that 30% of the existing 3.0 million UST used to store petroleum products leaks, with the likelihood of leakage increasing with tank age (Kostecki and Calabrese, 1990). Such leaks pose serious threats, especially to nearby groundwater sources.

Once a spill or leakage occurs, the hydrocarbon liquid will move downward to the groundwater table, partially saturating the soil in its path. Most petroleum hydrocarbons are considered immiscible with water; therefore, they are primarily transported in the vadose (unsaturated) zone in the soil. Gasoline-range hydrocarbons contain significant quantities of certain compounds that are partially soluble in water. Some of these compounds are carcinogenic and USEPA-listed hazardous waste compounds (such as the so-called BTEX compounds: benzene, toluene, ethylbenzene, and xylene). The presence of such compounds in the subsurface environment presents a significant health hazard to both human and plant life.

A particular problem is the disposal of soil that is contaminated below the level that would result in classification as a hazardous waste. Such materials cannot be used as clean fill, yet do not merit the expense of hazardous waste disposal options. Regardless of the cleanup volume, the responsible party should investigate environmentally and financially advantageous recycling options. The state of New Jersey has generated 500,000 t of petroleum-contaminated soil (PCS) for disposal. The disposal rate for such soil varies from \$75.00 to \$150.00/t, depending on the location and quantity. With the projected substantial increase of PCS quantities and the limited availability of solid-waste disposal facilities, research is needed to investigate viable reuse options of such soils. This study assists in finding an environmentally responsible solution by returning PCS to the economic mainstream in the form of products.

PCSs are not hazardous wastes under any of the current RCRA regulation unless it fails the toxicity characteristic leaching procedure, TCLP (Kostecki and Calabrese, 1990). The maximum concentration of benzene for the TCLP test is 0.5 mg/l. PCS with less than 3.0% total contamination is considered a solid waste by the New Jersey Department of Environmental Protection and Energy (NJDEPE), and is classified ID-27 rather than a hazardous waste. Such a waste, while not a hazardous waste subject to RCRA, cannot be used as clean fill, and must be disposed of in a secure landfill or treated, according to the state of New Jersey solid waste regulations. Recently, the state has allowed ID-27 waste to be classified as "recyclable." This makes it easier to implement treatment or reuse options.

B. Scope of Investigation

This paper is an environmental investigation of a study evaluating the feasibility of using PCS in concrete for exterior, nonresidential construction purposes. Other investigations evaluated the structural aspects of the problem (Ezeldin, *et al.*, 1991, 1992a, b). The overall results of the structural study indicate that these materials meet American Society for Testing and Materials (ASTM) and ACI requirements for strength and durability, and can be useful in nonresidential construction.

In order to ensure that the PCS can be safely reused in construction applications, the leaching properties of contaminated soils fixed into a concrete matrix have to be evaluated. These properties should cover not only dispersion of contaminant into an aqueous solution, but also its migration from the concrete surface to the atmosphere. Significant movement in the vapor-phase can be attributed to vapor phase diffusion, which is several orders of magnitude larger than aqueous diffusion. The rate of hydrocarbon release should be sufficiently low such that environmental concentrations would not accumulate to undesirable levels, which could have adverse effects on the surrounding environment.

The leachability of organics to water from concrete samples was previously evaluated by others (Bradford, 1992). This paper discusses the emissions of hydrocarbon organics to the atmosphere from PCS bound in a cement matrix.

C. Background

The most common soil contaminants in the U.S. are volatile organic compounds (VOCs). The low aqueous solubility of such organics makes their removal from soil difficult by conventional pump and treat technology. The solidification/stabilization (S/S) process has been examined recently for the containment of VOCs. To understand this process, it is necessary to define the terms solidification and stabilization independently of one another, as they are often used interchangeably but mean different things. *Stabilization* refers to treatments that reduce the hazard potential of a waste by converting the contaminants into their least-soluble, mobile, or toxic form. The physical nature and handling characteristics of the waste are not necessarily modified by stabilization. *Solidification*, which occurs without a chemical reaction between the waste and the solid matrix, is the act of tying up free water in a waste by encapsulating the waste in a monolithic solid of high structural integrity. The encapsulation may be on fine waste particles (“microencapsulation”), coarser waste agglomerated particles, or even large waste blocks (“macroencapsulation”). The treatment of wastes requires that it be solidified as well as stabilized. Wastes that have been treated in this manner are called “fixed” wastes.

D. Literature Review

Most previous studies discussed air emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs). Although the act of mixing the waste will release a significant percentage of the organics present to the air, the addition of binders that increase the waste temperature during mixing further increases the emissions (Weitzman *et al.*, 1990). The results of a series of tests conducted on organics-contaminated soils show a sizeable release of these organics during the mixing period. Other studies indicated that a significant portion of the organic constituents will continue to volatilize over time from the solidified waste matrix (EPA/540/M5-89/011, October 1989). In fact, the U.S.EPA is in the process of proposing regulations that will require control of organic emissions from the S/S process if the waste contains more than a small amount of volatile organics (RCRA Air Emissions Standards, March 1988). Despite these facts, there are still very little data available on the emission of organics from the surface of a solidified waste in a concrete matrix.

II. THEORY

A. Molecular Diffusion

At any temperature above absolute zero, the individual molecules of a substance move incessantly and at random, apparently independently of each other. Frequent collisions occur between particles, so that the path of a single particle is a zigzag one. However, an aggregation of diffusing particles has an observable drift, from places of higher to places of lower concentration. For this reason, diffusion is known as transport phenomena. Because the aim of this investigation was to quantify the vapor diffusion of the contaminant and evaluate its surface volatilization from the concrete matrix to the atmosphere, a detail description of the process is reported. The desorption phenomena from the concrete block occurs through three consecutive mass-transport steps, as shown in Figure 1:

1. Intraparticle diffusion from the interior to the outer surface of the concrete block
2. Mass transfer of the contaminant from the outer surface of the concrete to the gas phase, (interfacial mass transfer)
3. Bulk transport of the contaminant in the gas phase

B. Diffusion Model

The intraparticle diffusion from the interior to the outer surface of the concrete block (1) can be modeled as a purely Fickian diffusion process. In a porous

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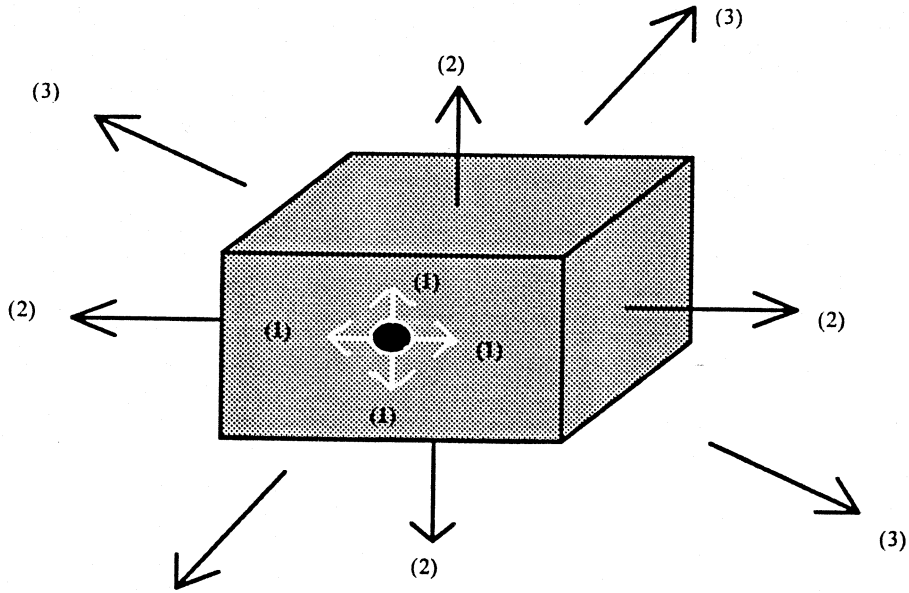


FIGURE 1. Diffusional transport phenomena from a concrete block.

material such as concrete, the diffusivity coefficient is reduced due to the reduced area for diffusion and tortuosity of the diffusion path. Assuming an homogeneous initial concentration distribution (C_o), and zero surface concentration, the Fickian model for semiinfinite plate can be presented as (Batchelor, 1990):

$$C(x,t) = C_o \cdot \operatorname{erf} \frac{x}{\sqrt{4D_e \cdot t}} \quad (1)$$

where $C(x,t)$ is the concentration of the contaminant as a function of space and time (M/L^3), C_o the initial concentration of the contaminant in the sample (M/L^3), erf an error function, x the distance from the interfacial surface (L), D_e the effective diffusion coefficient (L^2/T), and t the cumulative time (T).

The exact expression for a plate with a finite thickness (L) is (Jost, 1960):

$$f = \frac{m_e}{M_o} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\left[\frac{(2n+1)\pi}{L}\right]^2 D_e \cdot t\right\} \quad (2)$$

$$N = \frac{1}{A} \cdot \frac{\partial}{\partial t} m_e = \frac{8M_o}{A \cdot \pi^2} \cdot \frac{\partial}{\partial t} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\left[\frac{(2n+1)\pi}{L}\right]^2 D_e \cdot t\right\} \quad (3)$$

↓

$$N = \frac{8M_o \cdot D_e}{A \cdot L^2} \cdot \sum_{n=0}^{\infty} \exp\left\{-\left[\frac{(2n+1)\pi}{L}\right]^2 D_e \cdot t\right\} \quad (4)$$

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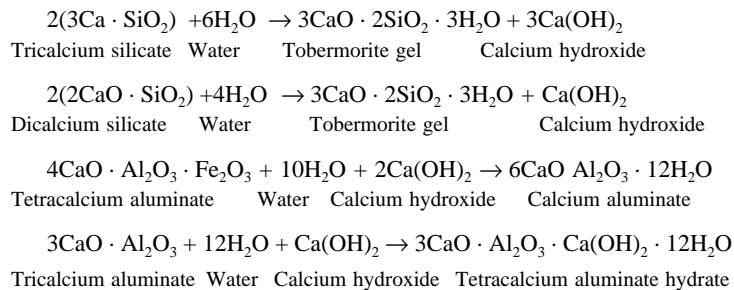
where M_0 is the original mass of contaminant added to the matrix, m_e the mass of contaminant emitted, f the fraction emitted, N the flux, D_e the effective diffusivity, A the concrete block surface area, L the concrete block side length, and t the interval of the time period after which m_e is measured.

C. Cementitious Criteria

Concrete consists of four major components: coarse and fine aggregate, water, Portland cement, and additives. When these are mixed, the Portland cement chemically reacts with the water and binds to the aggregate, and within as little as 1 to as long as 24 h, the mass sets up into a monolith. Portland cement is a mixture of a number of minerals, the most important being calcium silicates, calcium aluminates, and iron oxide. The cement used in this study is type I, which, according to the Portland Cement Association, contains the following compound ratios:

- Tricalcium silicate (53%) • Dicalcium silicate (24%)
- Tricalcium aluminate (8%) • Tetracalcium aluminate (8%)

When it is mixed with water, Portland cement triggers numerous chemical reactions:



From these reactions, it can be seen that the fate of most of the water in the cement mixture is to be included into the solid phase. First, the water reacts to form the hydrates. This clearly satisfies the criterion of chemical reaction. As the cement hardens, the crystal structure further incorporates water into it. This is generally still considered to be chemically bound water, although the binding is generally not as strong as in the first case. Finally, water remains on the surface and in the capillaries or pores of the cement. The significance of these reactions is that the concentration of organics dissolved in the water will increase as they proceed. This can change the state of the contaminants. For example, removal of water may cause the organic concentration in the remaining liquid water to exceed the solubility, resulting in the formation of a pure organic phase.

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III. EXPERIMENTAL PROGRAM

A. Methodology

The experiment involved quantifying emissions from a concrete matrix containing artificially contaminated soils (ACS) during and after solidification. The rate of organic release to the atmosphere was determined in terms of mass emission, cumulative fraction emission, total flux, and a diffusion coefficient.

A single contaminant, benzene, was chosen to represent hydrocarbon contamination in soil for this experiment. Unleaded gasoline is comprised of approximately 15% BTEX, which are considered the most environmentally significant components of gasoline (Kostecki and Calabrese, 1990). Benzene has a relatively high water solubility, volatility, and toxicity which makes it the chemical of greatest concern in a gasoline. Benzene represents from 1 to 3% of the constituents in gasoline. Two levels of benzene contamination, 0.5 and 3.0% weight of benzene to weight of soil, were used to simulate gasoline contamination in soil. Each of these two levels was mixed with and without fly ash. In addition, a test was conducted on soil samples in an unfixed form “without cement” as a positive control. Furthermore, a negative control was prepared to test the clean concrete. The benzene used in these experiments was obtained from Fisher and was certified grade and of 99% purity. The methylene chloride was also obtained from Fisher and was high-performance liquid chromatography-gas chromatography/mass spectroscopy (HPLC-GC/MS) grade, having a purity of 99.9%. Both were used as received without alteration.

B. Soil Preparation and Mixing Procedure

The following concrete mixtures ratios were used, by weight:

Cement : Aggregate : Sand : Water
[1] [1.5] [1.5] [0.5]

The petroleum-contaminated soil was used to replace 40% of the sand by weight in all samples except the control mixture. Class C fly ash, classified as an industrial byproduct by the NJDEPE, was incorporated in the study. Samples with fly ash had 10% of the cement replaced with the ash. All mixtures were performed at room temperature (20°C).

ACS was prepared by sieving coarse sand through a #60 sieve. The resulting fine sand was kept in an oven at 105°C for 4 h to drive off any original contaminants. After that, the fine soil was left uncovered overnight to allow rehydration. Preparation of ACS was performed by placing the virgin soil in a polyethylene bag and adding an adequate amount of benzene using a pipette. The concrete compo-

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nents were then added into the bag, excess air was evacuated, the bag was sealed by a heat sealer, and the concrete constituents were mixed according to ASTM method C-31 (ASTM, 1989). The mixing was performed manually to decrease the possibility of losing a fraction of organic due to agitation during mixing. The specimens were prepared from the five different mixes listed in Table 1.

C. Analytical Method

The gas chromatograph (GC) used to analyze the data in the experiments was a Varian 3700 GC. All injections were repeatable within 5% difference on the same day and within 15% difference during the 4 weeks these measurements were made. A standard was injected into the GC daily to record any deviation of the instrument response factor. The chromatographic conditions applied in this study are listed below:

- Injection port temperature, 150°C
- Isothermal column temperature, 170°C
- Column type, Supelco 60/80 Carboxen B, 1% SP-1000 “packed column”
- Detector, flame ionization detector

The detector output was analyzed using a Shimadzu CR601 integrator, which had the following parameters:

- width, 5 s
- slope, 38.8795 $\mu\text{V}/\text{min}$
- minimum area, 10 counts
- attenuation, 3 mV/full scale

By applying the chromatographic conditions mentioned above, the retention time of benzene was found to be in the range of 2.7 to 3.0 min.

TABLE 1
Mix Components and Quantities of ACS Specimens (grams)

Mix I.D.	Cement	Aggregate	Sand	PCS	Fly Ash	Water	Benzene
Control 1	—	—	—	390.22	—	—	0.37
Control 2	—	—	—	390.22	—	—	2.27
Control (-)	126.13	189.20	189.20	—	—	63.10	—
0.5%	126.13	189.20	113.52	75.31	—	63.10	0.37
0.5 FA	113.52	189.20	113.52	75.31	12.62	63.10	0.37
3.0%	126.13	189.20	113.52	73.41	—	63.10	2.27
3.0 FA	113.52	189.20	113.52	73.41	12.62	63.10	2.27

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To ensure analytical quality (QA/QC), all tests were conducted in duplicate experiments and duplicate analysis for a total of four replicates for each of the samples. All glassware used in both experiments was washed with laboratory detergent, thoroughly rinsed with hot tap water, triple rinsed with acetone, methanol, and distilled water, and oven dried overnight at 105°C. Data integrity was evaluated by analyzing blanks, control samples, and standards in duplicate daily. The benzene standards were prepared daily from stock solution because overnight storage resulted in detectable benzene loss.

D. Details of Test Specimens

After mixing, the soft concrete was poured directly into 473-ml Qorpak glass jars with Teflon-lined caps and tightly sealed. The jars were filled to half-volume, so that fugitive emissions to the remaining airspace could be evaluated. The mixture was allowed to harden in the sealed container in order to quantify air-emissions during the early age of the concrete mixture. The jar caps had input and output fittings that were connected to a peristaltic Cole-Parmer Masterflex pump. The air flow was recycled in a closed system to avoid any losses or contamination. The output of the container was connected to the pump through a SKC sorbent tube. This tube contains two separated parts of activated carbon. The first section is used for analysis, and the second part records any breakthrough occurrence in the tube. The air flow through the sorbent tubes was maintained at nominally 10 ml/min. Emissions from the concrete are swept into the sorbent tube and trapped there for later analysis (Figure 2).

The sorbent tubes were removed for analysis and replaced every 2 d for the first 2 weeks of the experiment and every 4 d after that. The contents of these tubes were

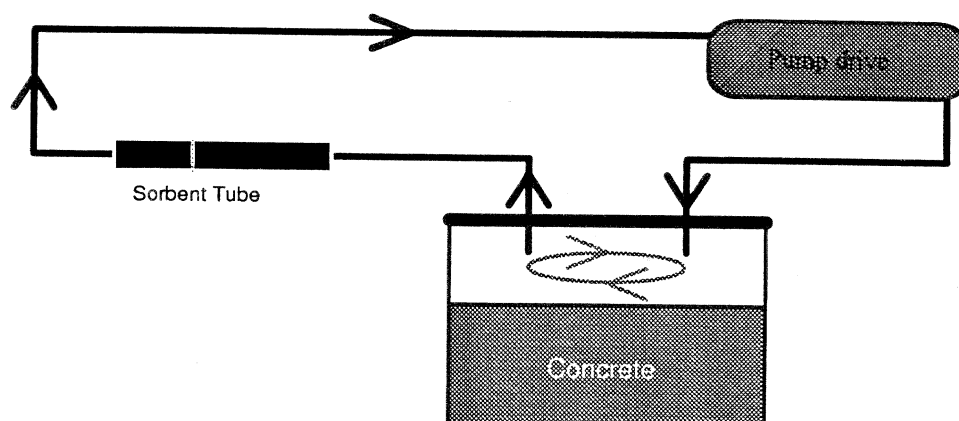


FIGURE 2. The emissions experiment set-up.

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placed in a vial sealed with silicone septum and containing 5 ml of methylene chloride (CH₂Cl₂). The vials were mixed and left at room temperature for 1 h to reach equilibrium. Then, 1 µl of the solution was withdrawn from the vial with a gas-tight syringe and injected into the GC for hydrocarbon analysis as described before. Tests showed the methylene chloride produced almost complete desorption of benzene from the activated carbon. From these results, the mass of contaminant emitted over a period of time could be measured.

IV. TEST RESULTS

The mass of contaminant emitted was used to compute the fraction emitted, *f*, and the flux, *N*. Then, by fitting the results to Equation 4, the effective diffusivity could be computed. These data parameters were used to evaluate the immobilization of benzene fixed in a solidified matrix and the rate of its atmospheric migration vs. time. Table 2 shows the measured mass emission (*m_e*) from the surface of the concrete block. The mass emission is the number of milligrams emanated from the concrete and trapped into the sorbent tube particles:

$$m_e = C \cdot V_s \quad (5)$$

TABLE 2
Mass-Emission from the Surface of the Concrete Block (milligrams)

Day	Control (-)	0.5% (A)	0.5% (B)	0.5% (FA) ^a	3.0% (A)	3.0% (B)	3.0% (FA)	Control 0.5% (+)	Control 3.0% (+)
1	0.035	2.088	2.139	0.655	20.867	20.697	4.286	93.016	202.864
2	0.031	0.249	0.332	0.251	2.480	1.793	0.556	0.835	81.659
4	0.060	0.370	0.252	0.082	8.610	2.978	0.858	0.119	7.981
6	0.057	0.284	0.680	0.179	10.139	4.376	1.119	0.027	2.283
8	0.041	0.518	1.060	0.489	11.302	4.661	2.112	N/D	1.082
10	0.023	0.964	1.973	0.628	12.643	7.754	1.857		0.506
12	0.022	1.369	2.208	0.756	13.671	10.290	2.060		0.428
14	0.016	1.034	1.837	0.614	12.833	9.248	1.568		0.229
16	N/D	0.736	1.214	0.568	11.189	7.284	1.612		0.125
18		0.610	1.033	0.502	10.773	6.831	2.084		0.124
20		0.559	0.814	0.460	9.532	6.815	1.297		0.065
22		0.491	0.658	0.566	9.090	6.288	1.550		0.050
26		0.564	0.779	0.649	10.582	7.363	1.122		0.023
30		0.563	0.603	0.434	10.171	7.051	1.025		N/D
34		0.359	0.392	0.218	8.013	6.229	0.125		
38		0.310	0.262	N/D	5.826	5.025	N/D		
45		0.419	0.335		7.459	7.587			

^a Fly ash.

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where C is the concentration of benzene emitted from the concrete matrix and V_s is the volume of the solvent in which equilibrium occurs.

For each level of contaminant concentration, two specimens (A and B) were prepared. These samples were tested with and without fly ash. Moreover, two types of control were incorporated into the experiment: a negative control that consisted of the clean concrete without any contaminated soil replacement, and a positive control that was prepared by placing loose contaminated soil in the jars without any fixation step.

The benzene peak area was used to obtain the concentration of the organic releases by dividing this area by the response factor of benzene. This response factor is the slope of a calibration curve that relates the chromatographic areas to the concentrations of benzene standards. The maximum deviation of this slope compared with the daily response factor of the machine was found to be not more than 17%.

The fraction of mass emission (f) can be defined as the ratio of the mass emission (m_e) to the original mass of contaminant added to the matrix (M_o). The cumulative values of this fraction for each sample are shown in Table 3.

$$f = \frac{m_e}{M_o} \quad (6)$$

TABLE 3
Cumulative Fraction Emission from the Concrete Block (mg/mg)

Day	0.5% (A)	0.5% (B)	0.5% (FA) ^a	3.0% (A)	3.0% (B)	3.0% (FA)
1	0.0056	0.0058	0.0018	0.0077	0.0077	0.0016
2	0.0063	0.0067	0.0024	0.0086	0.0083	0.0018
4	0.0073	0.0074	0.0027	0.0118	0.0094	0.0021
6	0.0081	0.0092	0.0032	0.0156	0.0111	0.0025
8	0.0095	0.0121	0.0045	0.0198	0.0128	0.0033
10	0.0121	0.0174	0.0062	0.0245	0.0157	0.0040
12	0.0158	0.0234	0.0082	0.0296	0.0195	0.0048
14	0.0186	0.0283	0.0099	0.0344	0.0229	0.0053
16	0.0206	0.0316	0.0014	0.0385	0.0256	0.0059
18	0.0222	0.0344	0.0128	0.0425	0.0281	0.0067
20	0.0237	0.0366	0.0140	0.0461	0.0306	0.0072
22	0.0251	0.0384	0.0155	0.0494	0.0330	0.0078
26	0.0266	0.0405	0.0173	0.0533	0.0357	0.0082
30	0.0281	0.0421	0.0185	0.0571	0.0383	0.0086
34	0.0291	0.0432	0.0191	0.0601	0.0406	0.0086
38	0.0299	0.0439		0.0622	0.0425	
45	0.0310	0.0448		0.0650	0.0453	

^a Fly ash.

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The flux (N) was computed for each sample as the mass emission to the headspace of the jar per day per square meter of the concrete surface area:

$$N = \frac{m_e}{A_s \cdot t} \quad (7)$$

where A_s is the surface area of the concrete block exposed to the air and t is the interval of time after which m_e is measured.

Table 4 shows the computed flux values. The values are much lower than the control values and compatible with the results obtained from a previous study (Bradford, 1992) that measured the hydrocarbon release to water. The data from Table 4 were used to compute the effective diffusivity and the log relative diffusivity.

Equation 4 was used to compute the effective diffusivity of benzene within the concrete block of length $L = 5$ cm and surface area $A = 49.0$ cm². The series solution was truncated to 500 terms and calculated with a computer program. The solution was found to converge reasonably after 500 iterations. The effective benzene diffusivity for each matrix is shown in Table 5.

V. ANALYSIS AND DISCUSSION

The obtained results were used to plot Figures 3 and 4 for the concrete samples. As seen in these figures, the largest flux values were emitted from the surface of

TABLE 4
Flux Values of Artificially Contaminated Soils (mg/d/m²)

Day	Control (-)	0.5% (A)	0.5% (B)	0.5% (FA) ^a	3.0% (A)	3.0% (B)	3.0% (FA)	Control 0.5% (+)	Control 3.0% (+)
1	7.08	426.03	436.36	133.68	4,257.12	4,222.50	874.41	18,976.27	41,386.5
2	3.17	50.88	67.73	51.18	505.94	365.74	113.39	170.29	16,659.3
4	3.05	37.73	25.71	8.37	878.27	303.80	87.50	12.18	814.15
6	1.94	29.01	69.34	18.26	1,034.22	446.40	114.10	2.74	232.83
8	1.04	52.84	108.15	41.15	1,152.87	475.47	215.48		110.34
10	0.47	98.35	201.27	64.05	1,289.62	790.96	189.39		51.58
12	0.37	139.61	225.19	77.13	1,425.13	1,049.67	210.08		43.64
14	0.24	105.49	187.41	62.60	1,309.04	943.38	159.97		23.37
16		75.05	123.89	57.91	1,141.36	743.05	164.40		12.72
18		62.19	105.41	51.23	1,098.86	696.85	212.63		12.62
20		57.00	83.00	46.97	972.28	695.17	132.27		6.66
22		50.04	67.12	40.04	927.26	641.37	158.07		5.09
26		33.11	39.71	28.78	539.72	375.55	57.22		1.17
30		28.71	30.75	22.12	518.73	359.63	52.28		
34		18.32	19.99	11.12	408.68	317.67	6.40		
38		15.81	13.38		297.15	256.29			
45		12.22	9.75		217.40	221.10			

^a Fly ash.
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TABLE 5
Effective Diffusivities of the Samples (cm²/s)

Day	0.5% (A)	0.5% (B)	0.5% (FA) ^a	3.0% (A)	3.0% (B)	3.0% (FA)	Control 0.5% (+)	Control 3.0% (+)
1	7.2×10^{-9}	7.5×10^{-9}	7.1×10^{-10}	1.9×10^{-8}	1.8×10^{-8}	8.1×10^{-10}	1.4×10^{-5}	1.8×10^{-6}
2	1.8×10^{-10}	2.2×10^{-10}	2.0×10^{-10}	5.4×10^{-10}	2.8×10^{-10}	2.9×10^{-11}		
4	2.2×10^{-10}	1.0×10^{-10}	1.2×10^{-11}	3.2×10^{-10}	3.9×10^{-10}	3.2×10^{-11}		
6	2.0×10^{-10}	1.1×10^{-9}	7.9×10^{-11}	6.8×10^{-9}	1.2×10^{-9}	8.2×10^{-11}		
8	8.9×10^{-10}	3.7×10^{-9}	5.4×10^{-10}	1.1×10^{-8}	1.9×10^{-9}	3.9×10^{-10}		
10	3.8×10^{-9}	1.6×10^{-8}	1.6×10^{-9}	1.7×10^{-8}	6.6×10^{-9}	3.8×10^{-10}		
12	9.3×10^{-9}	2.4×10^{-8}	2.8×10^{-9}	2.0×10^{-8}	1.4×10^{-8}	5.6×10^{-10}		
14	6.2×10^{-9}	1.9×10^{-8}	2.2×10^{-9}	2.7×10^{-8}	1.3×10^{-8}	3.8×10^{-10}		
16	3.5×10^{-9}	9.7×10^{-9}	2.1×10^{-9}	2.2×10^{-8}	9.3×10^{-9}	4.5×10^{-10}		
18	2.7×10^{-9}	7.9×10^{-9}	1.8×10^{-9}	2.3×10^{-8}	9.2×10^{-9}	8.6×10^{-10}		
20	2.5×10^{-9}	5.5×10^{-9}	1.7×10^{-9}	2.0×10^{-8}	1.0×10^{-8}	3.7×10^{-10}		
22	2.2×10^{-9}	3.9×10^{-9}	1.4×10^{-9}	2.0×10^{-8}	9.5×10^{-9}	5.8×10^{-10}		
26	8.5×10^{-10}	1.6×10^{-9}	8.5×10^{-10}	8.0×10^{-9}	3.8×10^{-9}	9.0×10^{-11}		
30	9.8×10^{-10}	1.1×10^{-9}	5.8×10^{-10}	8.5×10^{-9}	4.1×10^{-9}	8.6×10^{-11}		
34	4.5×10^{-10}	5.4×10^{-10}	1.6×10^{-10}	6.0×10^{-9}	3.6×10^{-9}	1.6×10^{-11}		
38	3.7×10^{-10}	2.7×10^{-10}		3.5×10^{-9}	2.6×10^{-9}			
45	2.6×10^{-10}	1.7×10^{-10}		2.2×10^{-9}	2.3×10^{-9}			

^a Fly ash.

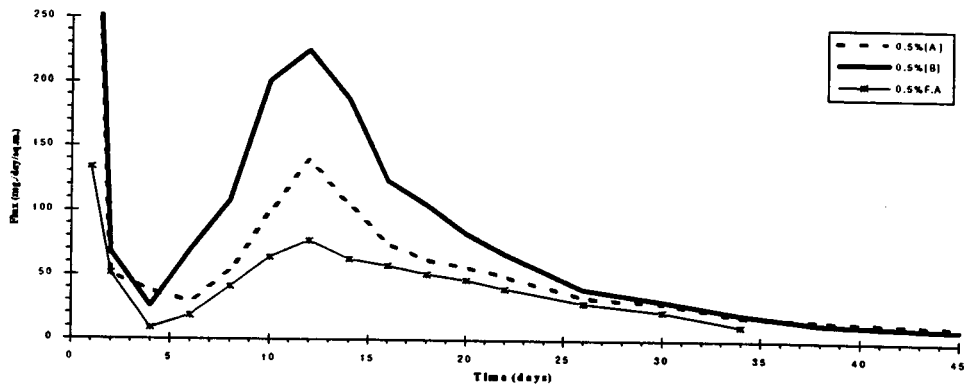


FIGURE 3. Emission rate from 0.5% samples.

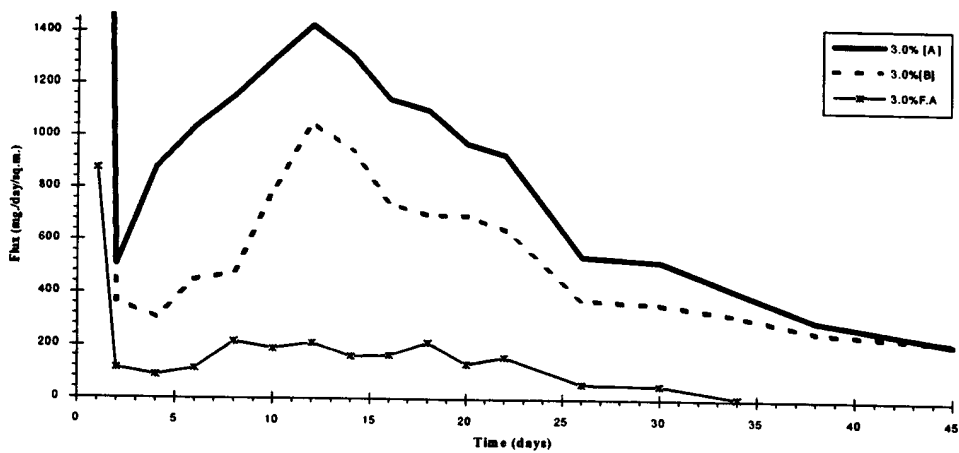


FIGURE 4. Emission rate from 3.0% samples.

specimen (3.0% A), which also had the greatest mass emission, the highest diffusion coefficient, and therefore the lower log relative diffusivity.

Duplicate experiments showed large variability. The differences may reflect inhomogeneity in the mixture pore structure. The presence of fly ash apparently decreased the emission of contaminants from the surface of the samples.

The flux values of all samples were extremely high during the first 24 h. Obviously, the mixtures evaporate while hardening due to the high temperature of the cement reaction. The concrete loses about 25% of its contamination while it is still soft. The high temperature of the mixtures during the earliest age of concrete hardening may enhance emission from the surface of the samples.

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The maximum amount of mass flux from the surface of the hard concrete for all the specimens occurred at 10 to 12 d after hardening, where the mixtures are fully cured. It is possible that as the mixtures set and water is taken up as hydrates, some benzene is forced from a dissolved to a separate phase.

The positive control samples emitted a higher flux during the first 24 h. The loose sand contaminated with benzene lost about 68% of its contamination after the first day. The high void ratio of the loose soil compared with the concrete matrix and the low fixation ability of the sand may be the reason for the obviously faster release of the organic.

The relative diffusivity, R_D , was used as an indication of the degree of attenuation. It can be defined as the ratio of the effective diffusivity of the contaminant in a reference system to its effective diffusivity in the concrete matrix.

$$R_D = \frac{D_{\text{reference}}}{D_e} \quad (8)$$

The effective diffusivity (D_e) is obtained from Table 5. $D_{\text{reference}}$ is the first-day effective diffusivity of the nonsolidified soil having the same concentration as the sample being computed. The difference between these two diffusivity values is due to the tortuous paths that benzene molecules are required to take through the concrete porous media.

$\log R_D$ represents the degree of immobilization of the contaminant in the matrix; the higher the $\log R_D$, the greater the degree of immobilization of the contaminant in the matrix. Table 6 shows the values of $\log R_D$ obtained for each sample.

Figures 5 and 6 show the cumulative fraction emission rates. The emissions had not abated at the end of that time period; however, their rates appeared to be decreasing and the fraction tended to be mostly stable after approximately 30 d.

VI. SUMMARY

As expected, the 3.0% benzene samples emit much more than the 0.5% benzene samples. However, the difference in flux values between the two samples did not have the same magnitude as the level of concentration. The initial benzene concentration was found to affect significantly the relative diffusivity.

The high log relative diffusivity obtained for the fly ash samples enhanced the use of this byproduct as an effective factor for immobilization of the contaminant in the matrix. In other words, the presence of fly ash decreased the contaminant diffusivity. Samples with fly ash were found to release 40% fewer hydrocarbons in the case of 0.5% concentration, and 80% fewer hydrocarbons in the case of 3.0% concentration.

The overall findings of this study indicate that the diffusion phenomena are influenced by factors other than the Fickian model. The concrete was able to significantly decrease the mobility of organic contaminants.

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TABLE 6
Log Relative Diffusivity for the Concrete Specimens

Day	0.5% (A)	0.5% (B)	0.5% (FA) ^a	3.0% (A)	3.0% (B)	3.0% (FA)
1	3.31	3.29	4.32	1.98	1.98	3.35
2	4.90	4.81	4.85	3.52	3.81	4.78
4	4.81	5.15	6.07	2.74	3.67	4.75
6	4.87	4.11	5.27	2.43	3.16	4.34
8	4.22	3.60	4.44	2.21	2.98	3.66
10	3.58	2.96	3.96	2.01	2.44	3.68
12	3.20	2.79	3.72	1.95	2.11	3.51
14	3.38	2.88	3.83	1.82	2.14	3.68
16	3.61	3.18	3.84	1.91	2.29	3.60
18	3.73	3.27	3.90	1.90	2.29	3.32
20	3.76	3.43	3.92	1.96	2.25	3.69
22	3.83	3.57	4.02	1.96	2.28	3.49
26	4.24	3.96	4.24	2.35	2.67	4.30
30	4.18	4.12	4.4	2.33	2.64	4.32
34	4.51	4.44	4.95	2.48	2.70	6.04
38	4.59	4.74		2.71	2.84	
45	4.74	4.94		2.97	2.89	

^a Fly ash.

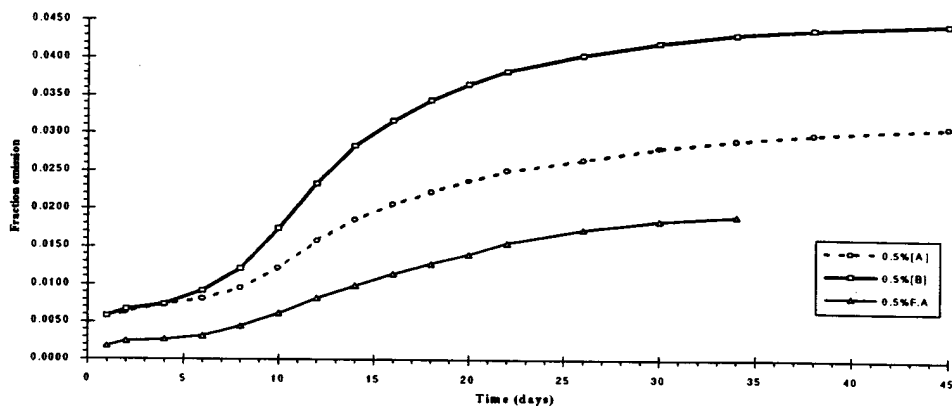


FIGURE 5. Cumulative fraction emission from 0.5% samples.

A. Conclusions

1. The fixation process, by tying up the water in the waste, eventually decreases the emission of semisoluble components such as VOCs.
2. Fly ash further decreased the emissions from the surface of the solidified matrix, compared with samples without fly ash.

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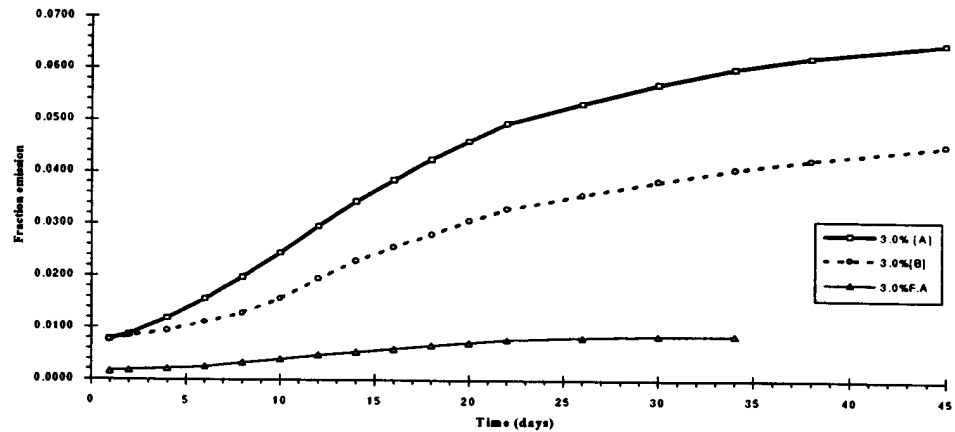


FIGURE 6. Cumulative fraction emission from 3.0% samples.

3. The maximum amount of flux was emitted from the concrete surface when the mixture reached a full curing.
4. Solidification will prevent the emissions from being increased by environmental factors, such as wind or activities that would disturb a quiescent contaminated soil.

B. Recommendations for Further Research

1. The use of cement fixation for petroleum hydrocarbon-contaminated soils should be restricted to soils with contaminants that are dispersed or adsorbed onto the soil matrix, and not present in a separate concentrated phase. The contaminant could become, in effect, a pure compound suspended in a medium in which it cannot dissolve.
2. This experiment was performed on concrete cylinders contained in glass jars in which basic parameters as the shape, the volume of the jar, and the depth of the sample could affect the results. A three-dimensional emission experiment should be considered.
3. Different percentages of fly ash replacements should be incorporated in order to control the effect of byproducts on water leachability and air emission of solidified concrete.
4. Emission testing should be extended until all the contaminant previously added is released to the atmosphere in terms of mass emission.
5. Losses during the mixing of concrete should be evaluated.

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6. Other surrogate contaminant should be tested to identify the effect of the solubility and the vapor pressure of the contaminant on the solidification process.

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