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Pacific Northwest National Laboratory

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Study of Benzene Release from Savannah River In-Tank Precipitation Process Slurry Simulant

K. G. Rappé
P. A. Gauglitz

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Richland, Washington 99352

Summary

At the Savannah River Site, the in-tank precipitation (ITP) process uses sodium tetraphenylborate (NaTPB) to precipitate radioactive cesium from alkaline wastes. During this process, potassium is also precipitated to form 4-wt% KTPB/CsTPB slurry. Residual NaTPB decomposes to form benzene, which is retained by the waste slurry. The retained benzene is also readily released from the waste during subsequent waste processing. While the release of benzene certainly poses flammability and toxicological safety concerns, the magnitude of the hazard depends on the rate of release. Currently, the mechanisms controlling the benzene release rates are not well understood, and predictive models for estimating benzene release rates are not available.

The overall purpose of this study is to obtain quantitative measurements of benzene release rates from a series of ITP slurry simulants. This information will become a basis for developing a quantitative mechanistic model of benzene release rates. The transient benzene release rate was measured from the surface of various ITP slurry (solution) samples mixed with benzene. The benzene release rate was determined by continuously purging the headspace of a sealed sample vessel with an inert gas (nitrogen) and analyzing that purged headspace vapor for benzene every minute.

Nine 75-mL samples were measured for release rate. Two KTPB slurries, one with ~20,000-ppmv and one with ~10,000-ppmv benzene, were prepared by gently mixing the benzene with the slurry, and the release rates determined at room temperature. One KTPB slurry sample, with ~20,000-ppmv benzene, was prepared by gently mixing with the slurry, and the release rate determined at 45°C. Three KTPB slurries, one with ~20,000-ppmv, one with ~10,000-ppmv, and one with ~5,000-ppmv benzene, were prepared by homogenizing (energetically mixing) the benzene with the slurry, and the release rates determined at room temperature. Two additional KTPB slurry samples, each with ~20,000-ppmv benzene, were prepared by homogenizing the benzene with the slurry, and the release rates determined at 35°C and 45°C. Next, a KTPB slurry prepared by, first, homogenizing with ~10,000-ppmv benzene, and then gently mixing with ~10,000-ppmv additional benzene, was measured for benzene release at room temperature. And finally, the release rate from a slurry sample from a large demonstration experiment (DEMO slurry) containing-benzene generated *in situ* was determined at room temperature.

The release of benzene from KTPB slurry with readily releasable benzene droplets (freshly added benzene to the slurry) exhibited benzene release in two primary regimes. An initial regime existed in which benzene was released from the slurry for about one hour at 400- to 500-μg benzene/cm^2-min, as if it was present as a freestanding layer on top of the slurry. A second regime existed in which benzene was released at a lower rate (anywhere from 20- to 80-μg benzene/cm^2-min) until the slurry became depleted of benzene. It is believed that the magnitude and duration of benzene release in the second regime is heavily dependent on the agitation characteristics of the experiment. In comparison to earlier results (Rappé and Gauglitz, 1997) the current releases are higher, but this is expected because the gas purge flow through the apparatus was higher.

The release rates from homogenized slurry (no readily releasable droplets) had only a brief initial peak release rate (if any), followed by a steadily decreasing release rate. The peak release was well less than 100-μg benzene/cm^2-min, but the longer-term rates were comparable to those of the fresh slurry samples. Release rates during agitation from a test slurry blended from the two separate slurries containing readily releasable benzene droplets (fresh slurry) and homogenized slurry (no readily releasable droplets) has a release rate behavior intermediate to the results of the different slurries tested individually.

Experiments monitoring the release rates of benzene from quiescent slurry for the different slurry samples yielded quite interesting results. Slurry prepared by homogenization yielded higher releases of benzene from a quiescent sample (15- to 20-μg benzene/cm^2-min) than that of slurry prepared by gently premixing (8- to 10-μg benzene/cm^2-min). Additionally, the quiescent benzene release rate from a sample blended with both freshly added and homogenized benzene was greater than either of the two results discussed above.

Temperature elevation appeared to slightly enhance the migration of benzene droplets towards the slurry surface, resulting in an increased release from quiescent slurry for slurry samples prepared with freshly added benzene. The benzene release from quiescent slurry was also slightly increased for homogenized samples at elevated temperatures. Secondly, temperature elevation appears to provide homogenized slurry samples with somewhat more readily releasable benzene, resulting in an increased initial peak benzene release upon agitation.

The DEMO column slurry sample generating benzene *in situ* behaved like it contained dilute amounts of benzene in both droplet (freshly added) and dispersed (homogenized) form. The magnitude of benzene release during agitation was most similar to that of the homogenized slurry samples. However, the time variation of the release rate during the experiment most closely resembled that from freshly added benzene samples.

Acknowledgments

The authors wish to thank L. O. Dworjanyn for his important contributions to this work. In addition to his technical guidance, Dr. Dworjanyn provided all the slurry for the samples used in this study and provided the apparatus used for homogenization of slurry samples.

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Contents

Tables

Figures

Introduction

At the Savannah River Site, the in-tank precipitation (ITP) process uses sodium tetraphenylborate (NaTPB) to precipitate radioactive cesium from alkaline wastes. During this process, potassium is also precipitated to form 4-wt% KTPB/CsTPB slurry. Residual NaTPB decomposes to form benzene, which is retained by the waste slurry. The retained benzene is also readily released from the waste during subsequent waste processing. While the release of benzene certainly poses flammability and toxicological safety concerns, the magnitude of the hazard depends on the rate of release. The mechanisms controlling the benzene release rates are not well understood, and predictive models for estimating benzene release rates are not available.

In March of 1996, high benzene gas releases were observed during an ITP process. These releases were much higher than that expected from a benzene-saturated 5 molar sodium high-level waste (HLW) salt solution (Dworjanyn 1997). Due to the flammability and toxicological safety concerns, ITP operations were halted to investigate the phenomena of benzene generation, retention, and release from the slurry.

This led to PNNL microscopic studies of the mechanisms of excess benzene retention in the ITP slurries using a benzene sensitive dye staining technique. It was demonstrated that benzene is retained in the ITP slurry by various mechanisms, depending on the benzene concentration in the slurry and the extent of slurry premixing. With light handshaking, a stable suspension composed of benzene droplets coated by hydrophobic KTPB formed (Dworjanyn 1997). Upon further premixing, the benzene droplets seemed to disperse, forming a homogenized structure where the benzene coated the KTPB particles (Dworjanyn 1997). The release of benzene is expected to differ depending on the retention mechanism of benzene in the slurry. Benzene droplets are expected to have a higher release rate than slurry particles coated with benzene, but it is not yet known how much higher this release rate is.

It is necessary to know the benzene release rates of the different KTPB slurries exhibiting different benzene retention mechanisms. These studies are being conducted at Pacific Northwest National Laboratory at the Hanford Site in Washington State. This information will be compared with release rates and retention mechanisms of slurry samples taken from a large demonstration (DEMO) column experiment performed in an attempt to recreate the phenomenon of benzene generation and release *in-situ*. We will then better understand the phenomena which occurred during recent ITP processes, and we will be a step further towards predicting benzene release rates and understanding benzene retention mechanisms in ITP processes to come.

Objectives and Scope

The overall purpose of this research was to quantify the release rate of benzene from various ITP slurries exhibiting different benzene retention mechanisms as a result of different benzene concentrations and different degrees of mixing of the samples. The specific objective of the tests is to determine initial benzene release rates and to find trends in the release rate data that will help explain the mechanisms of benzene retention and release in the DEMO-column slurry sample that generates benzene *in situ*.

The following experiments were conducted to achieve the above objectives. First, stock KTPB slurry gently mixed with ~20,000-ppmv benzene was measured for benzene release at room temperature. To understand experimental reproducibility and to clear up some discrepancies in the data, three samples of this same material were analyzed for benzene release at room temperature. A fourth stock KTPB slurry sample gently mixed with ~10,000-ppmv benzene was measured for benzene release at room temperature.

Next, three KTPB slurries homogenized with ~20,000-ppmv, ~10,000-ppmv, and ~5,000-ppmv benzene were measured for benzene release at room temperature. Again, two samples containing KTPB slurry homogenized with ~20,000-ppmv benzene were analyzed at room temperature. Homogenization took place with a hand-held homogenizer and was performed separately on each sample just before analyzing release rates.

Then, a KTPB slurry sample gently mixed with ~20,000-ppmv benzene, and a KTPB slurry sample homogenized with ~20,000-ppmv benzene were measured for benzene release at elevated temperatures of 35°C and 45°C. The vessel used to analyze benzene releases was placed inside of a BEMCO oven for temperature control.

Next, a KTPB slurry prepared by, first, homogenizing with ~10,000-ppmv benzene, and then gently mixing with ~10,000-ppmv additional benzene, was measured for benzene release at room temperature.

And finally, the benzene release rate of a DEMO column sample that generates benzene *in situ* was examined.

Experimental Setup and Procedure

Flow System

Figure 1 shows a block diagram of the flow system used for these benzene release measurements. The supplied carrier gas for the system is nitrogen. The nitrogen bottle has a regulator set to provide approximately 25-psia to a Brooks 5850E 0 to 100 standard cubic centimeter per minute (sccm) mass flow controller. The flow throughout these tests was set at 30 sccm.

Flow from the Brooks flow controller passes through a 0 to 100 psia Digiquartz pressure transducer, and into a Bemco oven, before reaching a ball valve just before the sample vessel feed line. The sample vessel consists of a 100-mL flat bottom flask equipped with a dual channel impinger manufactured by Kontes Glass Company. The flask and impinger are equipped with a 24/40 standard ground glass joint, and the impinger dispersion tube is cut at a level that is approximately ½ to 1-cm above the surface of 75-mL of sample (including stir bar) inside the flask. The internal diameter of the flask at this level is approximately 5.08-cm (2 in.), resulting is an exposed sample surface area of approximately 20-cm^2. Total dead volume in the sampling vessel is approximately 38.5-mL. This includes the total headspace in the flat bottom flask and impinger over the liquid (35.7-mL) plus 1.83-meters (6-ft.) of 3.175-mm (1/8-in.) diameter stainless steel tubing with a 0.89-mm-thick (0.035-in) wall (0.467 mL/ft).

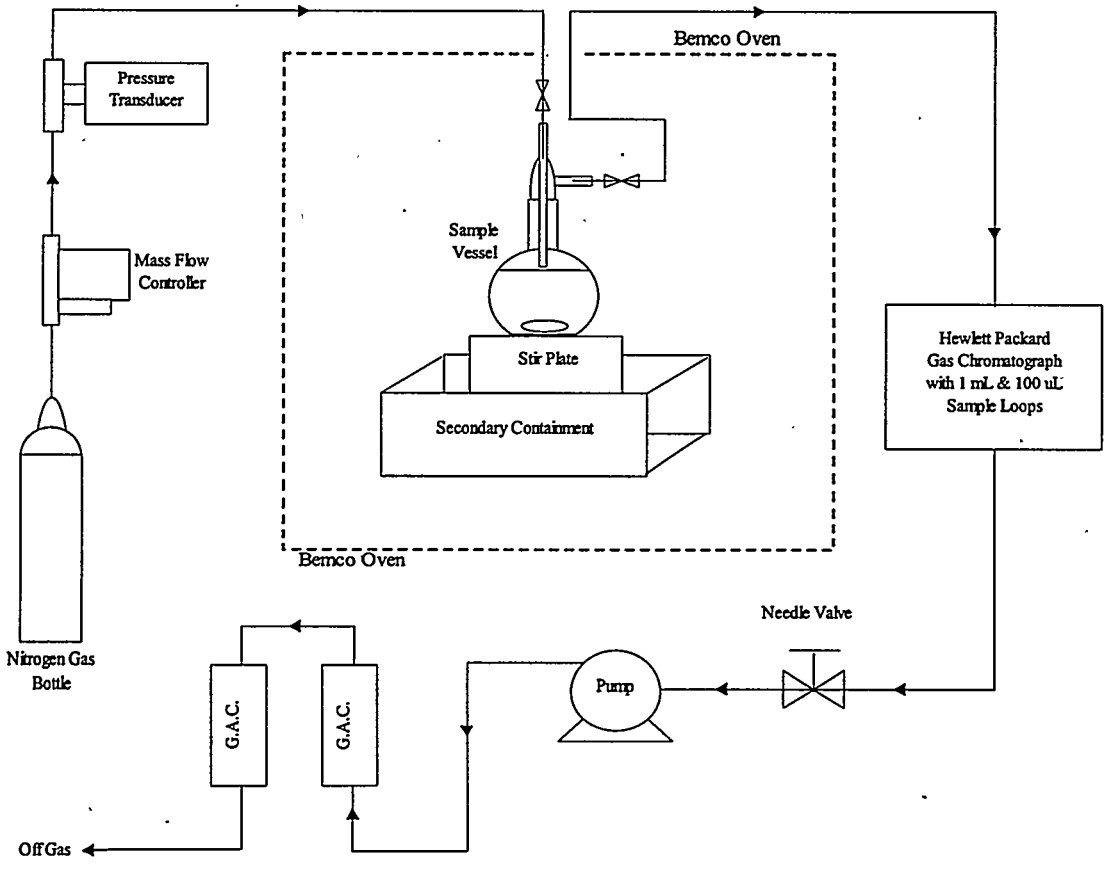

Figure 1. Flow System Diagram

The purged headspace from the sample vessel flows out through an exiting on/off throttle valve, out of the Bemco oven, to the 100-mL sample loop attached to the Supelco™ 10-port sample valve on top of the Hewlett Packard 5890 Series II Gas Chromatograph. The gas sample flows out of the sample loop, through another on/off throttle valve, through a needle valve, and to the GAST™ pump (vacuum pump).

The pressure in the reaction vessel can be monitored with the pressure transducer and was adjusted with the needle valve that is inline just before the pump. When testing was in progress and nitrogen was flowing through the sample vessel headspace, the pressure was kept at approximately 14.0-psia, making adjustments to the needle valve as necessary throughout each experiment.

The sample vessel was kept on a magnetic stir plate for agitation purposes. When agitation was necessary, the teflon-coated magnetic stir bar was rotated at a rate to keep the surface of the slurry/solution regenerating at a regular rate (i.e., steady with no noticeable vortex). The stir plate was kept inside a large plastic bin layered with towels to contain any vessel rupture. As mentioned above, the sample vessel, stir plate, and secondary containment (large plastic bin) were contained inside of a Bemco oven. The oven was used for temperature control, and it supplied shielding in the event of vessel rupture as well.

The benzene-containing gas is disposed of after the pump by flowing through two canisters of granular activated charcoal (G.A.C.) and then flowing into the building off-gas system.

Sample Preparation

All the samples were prepared in a fume hood. The Westinghouse-Savannah River Company (WSRC) provided a stock slurry simulant. A detailed chemical make-up of that simulant can be found in Table 1. WSRC provided the apparatus used for homogenizing samples of benzene in KTPB slurry. This was a PRO200 Handheld or Post Mounted Homogenizer manufactured by PRO Scientific Inc. WSRC also provided the *in situ* sample, obtained from the DEMO columns at Savannah River.

For each sample preparation, the amount of slurry was measured volumetrically (approximately) using a graduated syringe. The corresponding amount of benzene was then quantified gravimetrically.

For the gently premixed samples, the slurry was added to the sample vessel and the amount quantified gravimetrically. The benzene was then added by injecting below the slurry surface, the sample vessel was capped, and the sample was then agitated on a stir plate. Once sufficiently agitated, an initial sample of approximately 4-mL was removed, and the sample vessel was then placed inline in the flow apparatus.

For the homogenized samples, the slurry was added to the homogenization container, the amount quantified gravimetrically, and the benzene, again, was added by injecting below the slurry surface. The homogenizer was mounted on the container and turned on until the sample was sufficiently homogenized. The homogenizer was then removed and then an initial sample of approximately 4-mL was removed. The bulk of the slurry was added to the sample vessel, the amount quantified gravimetrically, and the sample vessel was placed inline in the flow apparatus.

Table 1. Composition and Properties of 4.2 M Na KTPB Stock Slurry

Batch Size, L		43.44	Estimated SpG
Batch Size, kg		51.25	1.18

Compound	Formula	FW	Pilot Demo grams
POTASSIUM SALT SOLUTION			
Sodium Hydroxide	NaOH	40.0	153.76
Potassium Nitrate	KNO_3	101.1	579.17
Potassium Nitrite	KNO_2	85.1	0
Cesium Nitrate	$CsNO_3$	162.91	1.28
Sodium Nitrate	$NaNO_3$	85.01	399.78
Sodium Nitrite	$NaNO_2$	69.01	2248
Sodium Chloride	NaCl	58.45	35.57
Sodium Fluoride	NaF	42.00	14.56
Sodium Sulfate	Na_2SO_4	142.05	30.85
Trisodium Phosphate 12-hydrate	$Na_3PO_4 X 12H_2O$	380.16	99.10
Water	H_2O	18.016	6125.40
Sum			9687.48
NaTPB SOLUTION			
Sodium Tetraphenylborate	$NaB(C_6H_5)_4$	342.23	2684.96
Sodium Hydroxide	NaOH	40.0	75.75
Water	H_2O	18.016	11334.09
Total Solution			14094.79
SODIUM SALT SOLUTION			
Sodium Hydroxide	NaOH	40.0	5453.42
Sodium Carbonate	Na_2CO_3	124.0	969.64
Aluminum Nitrate Nonahydrate	$Al(NO_3)_3 X 9H_2O$	375.14	2281.31
Water (subracted mass of trim soln's)	H_2O	18.016	14867.74
Sum			23572.12
MONOSODIUM TITANATE SLURRY			
$NaTi_2O_5H$, 10.54 wt % in slurry		199.8	329.68
ACIDIC METAL TRIM SOLUTION			
Copper Nitrate 2.5-Hydrate	$Cu(NO_3)_2 x 2.5H_2O$	232.62	1.81
Stannous Chloride 2-Hydrate	$SnCl_2 x 2H_2O$	225.65	0.19
Zinc Nitrate 6-Hydrate	$Zn(NO_3)_2 x 6H_2O$	297.49	1.52
Ferric Nitrate 9-Hydrate	$Fe(NO_3)_3 x 9H_2O$	404.02	0.44
ACID SOLUTION			
Water	H_2O	18.016	20
Nitric Acid	HNO_3	63.02	0.13
Sum Acid Solution			24.09
BASIC METAL TRIM SOLUTION			
Sodium Chromate	Na_2CrO_4	162.0	9.88
Potassium Molybdate	K_2MoO_4	238.13	1.29
NaOH	NaOH	40.0	0.4
Water	H_2O	18.016	100
Sum Basic Solution			111.57

Table 1. Composition and Properties of 4.2 M Na KTPB Stock Slurry (cont.)

Compound	Formula	FW	Pilot Demo grams
ORGANIC TRIM CHEMICALS			
Benzene	C_6H_6	78.11	31.27
Phenol	C_6H_5OH	94.11	5.43
Phenylboric Acid	$C_6H_5B(OH)_2$	121.9	5.43
Biphenyl	$(C_6H_5)_2$	154.2	6.52
Diphenylborinic Acid*	$(C_6H_5)_2BOH$	182	6.72
Triphenylboron**	$(C_6H_5)_3B$	242.1	70.29
Isopropyl Alcohol	$(CH_3)_2CHOH$	60.09	2.17
Methanol	CH_3OH	32.04	0.22
Sum Organics			128.05

* added as ethanolamine ester form

** added as sodium hydroxide adduct, 9 wt% in water

		wt % metal	Pilot Demo grams
SLUDE SLURRY			
12.42 wt % insolubles			
Ruthenium Trichloride		41.7%	0.48
Rhodium Nitrate Solution		4.9%	1.06
Palladium Nitrate Solution		15.3%	0.63
Silver Nitrate		63.5%	0.03
Total Trimmed Sludge			841.53
NOBLE METAL SOLUTION			
Ruthenium Trichloride (powder)		41.7%	0.08
Palladium Nitrate Solution		15.3%	0.11
Rhodium Nitrate Solution		4.9%	0.18
Water	H_2O		150
Sum Noble Metal Solutions			150.37

Rinse Water	2314.3	grams
Net Makeup	51.25	grams
Error from target	0.00	
Moles NaTPB	7.85	
Moles Na	205.31	
Moles K	5.74	
Projected KTPB	2056.48	grams
[Na], Slurry with nominal 1.18 SpG	4.73	M
Wt% Na, supernate	9.621	wt%
Supernate SpG from Correlation	1.2407	
Calculated Supernate Volume	39.54	Liters
[Na], Supernate	5.192	M
Calculated Solids Volume	1.86	Liters
Calculated Slurry Volume	41.40	Liters
Calculated Na in Slurry	4.96	M

Once inline in the flow apparatus, the sample vessel was initially sealed off from flow by having the throttle valves at the inlet and outlet of the vessel in the "off" position. The sample was then continuously gently agitated with a stir bar for approximately one hour. At that time, data accumulation was started, sample agitation stopped, and flow of nitrogen was directed through the sample vessel headspace by turning the ball valves to the "on" position. Agitation was restarted after approximately one hour (unless otherwise noted) of headspace purging without agitation. Data was accumulated over the next 24 hours, or longer if necessary.

Pictures were taken of two prepared slurry samples, one at 5,000-ppm benzene (dyed) homogenized with the slurry and one at 15,000-ppm benzene (dyed) freshly added to the slurry and mixed magnetically with a stir bar for approximately 2 hours (both WSRC prepared). These pictures can be found in Figure 2 and Figure 3, respectively. The pictures of the homogenized sample show the benzene evenly dispersed over the slurry, coating the TBP slurry surface. For the freshly added and magnetically stirred sample, the pictures show the benzene remaining in distinct droplets in the slurry.

Analytical System and Data Manipulation

The concentration of benzene in the headspace vapor was determined with a Hewlett Packard 5890 Series II Gas Chromatograph (GC) equipped with a short one-foot length piece of deactivated fused silica capillary column and helium carrier gas flows through it to a flame ionization detector (FID). A sample is obtained by flowing the headspace vapor through a 100-μL sample loop on a 10-port Supelco™ 2-position valve mounted on the top auxiliary heated zone of the GC and then loading the contents of that sample loop onto the GC column. A FID will record a response for species with bonds that ionize in a hydrogen/oxygen flame. This corresponds to a minimum response to some sulfur compounds and an intense response to almost all organic compounds. Alternatively, an FID will demonstrate no response to the permanent gases (N_2, O_2, H_2O, CO, CO_2, etc.).

A multi-point calibration performed before the onset of tests assured linearity of the FID's response throughout a range of over 2 orders of magnitude. A single point calibration (multiple analyses of a single standard of known concentration) was performed four to five times throughout the experiments. Calibration standards were prepared by injecting a known amount of benzene liquid (determined volumetrically) into a 1000 mL gas sample syringe, allowing the benzene to volatilize and then expanding at atmospheric pressure to a known volume. This was placed in a gas sample bag, diluted if necessary, and analyzed by pulling through the flow system (bypassing the sample vessel). Concentration units in the vapor phase are reported as ppm on a volume basis, the volume of benzene being estimated with the ideal gas law.

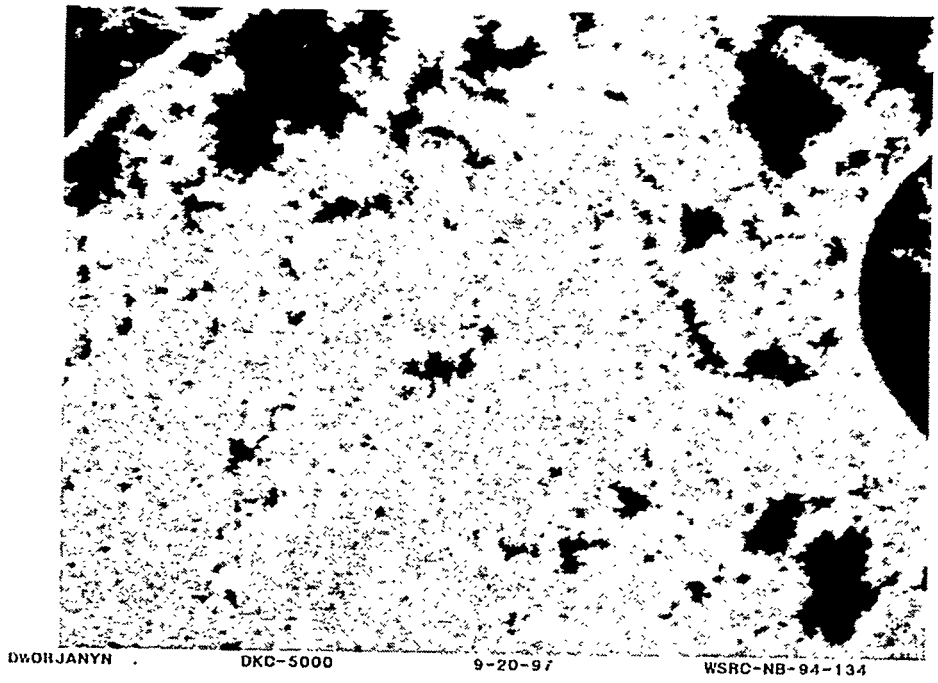

Figure 2. KTPB Slurry Homogenized with ~5,000-ppm Benzene (dyed red)

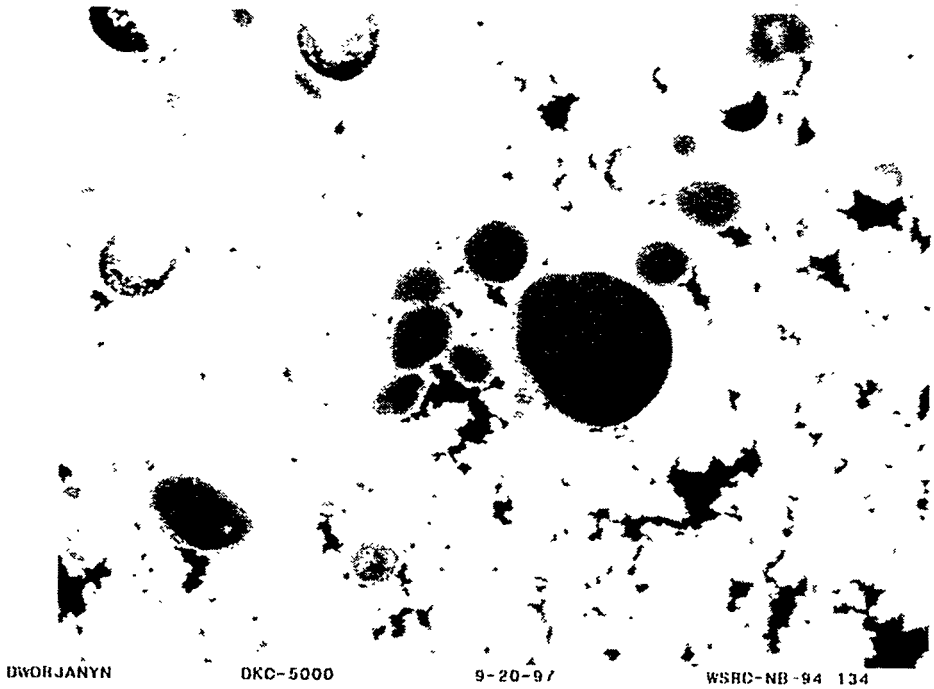

Figure 3. KTPB Slurry Freshly Added to ~15,000-ppm Benzene (dyed red)

Data generated are copied and pasted into a text file and stored appropriately. The data generated include GC file name, retention time of benzene, and FID response of benzene. These data can be imported into an Excel™ spreadsheet, parsed (name, time, date, etc., separated into columns), and manipulated. The FID response is converted into vapor-phase concentration by a calibration factor obtained from the most recent benzene calibration. The average benzene release rate {μg of benzene/cm^2-min} from the surface between time 0 and time 1, expressed as a flux, can then be calculated as follows:

$$\mathrm{Re}lease\_Rate_{benzene_{0,1}} = \frac{average[C_0, C_1] \times F_{avg} \times P_{avg} \times MW_{benzene}}{A_S \times R_G \times T} \quad (1)$$

where

C_0 and C_1 = the concentrations of benzene (ppm) at time 0 and time 1, respectively

F_{avg} = the average flow of N_2 through the sample vessel (mL/min) at times 0 and 1 (15.1 mL/min, unless otherwise noted)

P_{avg} = the average pressure in the sample vessel (atm) at times 0 and 1

$MW_{benzene}$ = the molecular weight of benzene (78.12 g/gmole)

A_S = the exposed surface area of the slurry (20 cm^2, unless otherwise noted)

R_G = the ideal gas constant {82.06 (cm^3)(atm)/(gmole)(K)}

T = the absolute temperature in Kelvin.

The total mass of benzene released between time 0 and time 1 can then be obtained by multiplying the average benzene release rate between time 0 and time 1 by the exposed surface area, A_S, and by the elapsed time in minutes between time 0 and time 1 (1 minute, unless otherwise noted).

Experimental Results and Observations

A total of 14 benzene release experiments are discussed in the following sections. These tests can be grouped into four general categories: samples of benzene gently mixed with KTPB slurry and analyzed at room temperature, samples of benzene homogenized with KTPB slurry and analyzed at room temperature, samples of benzene in KTPB slurry analyzed at elevated temperatures, and *in situ* benzene generating DEMO column slurry. The release data, as mentioned above, are release rates presented as a flux of benzene crossing the air/liquid (air/slurry) interface, μg benzene/cm^2-min. Release rates from the different concentrations of gently mixed samples are examined and compared, as are the release rates from the homogenized samples. Release rates from the gently mixed samples are compared and contrasted with the homogenized samples. The effects of temperature are examined as we discuss samples tested at 35°C and 45°C, one with benzene gently mixed with slurry, and one with benzene homogenized with slurry. And finally, release rates from the DEMO column slurry are examined and compared to the prepared slurries.

Figure 4 shows benzene release rate data from a standing layer of pure benzene on top of KTPB slurry. This was performed for two reasons: (1) to obtain a reference as to the release rate of pure benzene for comparison to other measured release rates, and (2) to integrate the total amount of benzene released and make a check on the data accuracy. It should be noted that the system was not agitated to insure very little mixing of the free layer of benzene and the slurry. Release rates are approximately 450-μg benzene/cm^2-min, with the highest release near 600-μg benzene/cm^2-min. This result represents the upper bound for all of the release rates in experiments discussed hereafter.

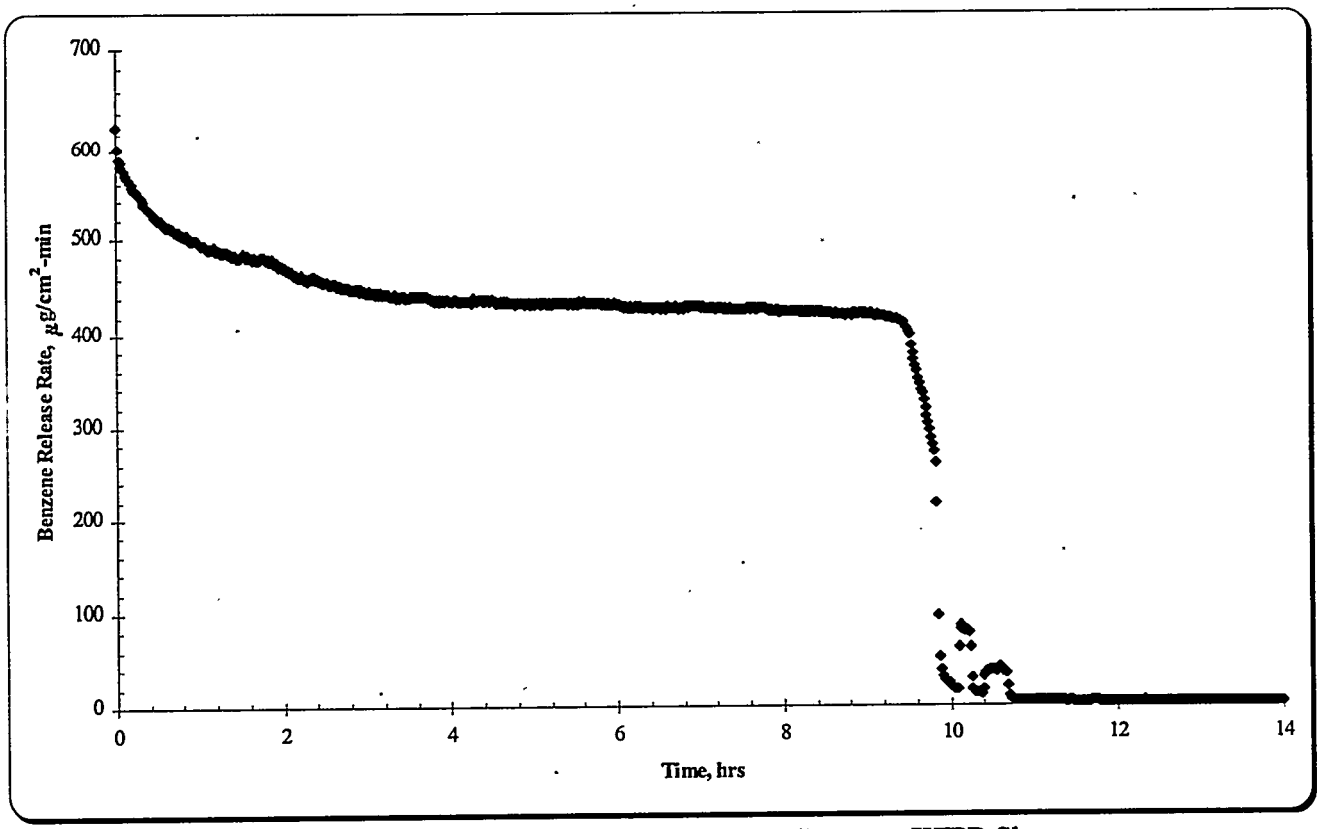

Figure 4. Benzene Release from Pure Benzene Layer on KTPB Slurry

Slurries with Gently Mixed Benzene

The first four sets of data (Figures 5a, 5b, 6a, 6b, 7a, 7b, 8a and 8b) show benzene release rate data from slurry samples prepared by adding benzene to stock KTPB slurry, gently premixing (no homogenization), and analyzing at room temperature. The first three experiments are essentially replicate analyses at ~20,000-ppmv benzene and the last is for a sample at half the benzene concentration.

Figures 5a and 5b show the benzene release data from one 94.10-g sample of KTPB slurry prepared by freshly adding benzene at approximately 15,730-ppm (by weight) and gently premixing. Figure 5a shows the initial release rate data obtained without agitation. Figure 5b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 5a.

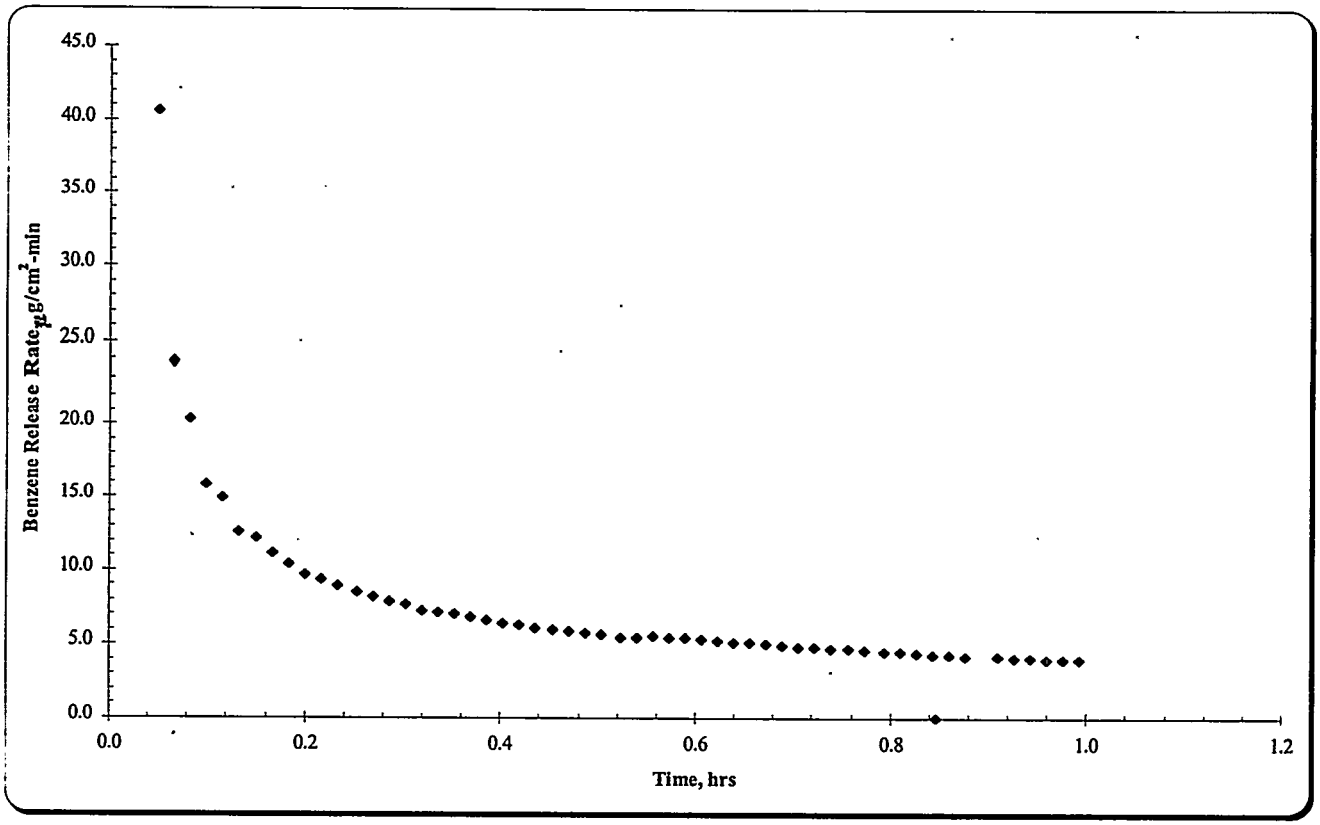

Figure 5a. Benzene Release from Quiescent Slurry Containing 15,730-ppm Freshly Added Benzene

From Figure 5a, we see the release rate of benzene from the quiescent slurry surface declines rapidly once the initial headspace is purged. It then begins to level off at approximately 10-µg benzene/cm^2-min after 0.2 hours, and become fairly level at approximately 4.0-µg benzene/cm^2-min after 1 hour of release. Once agitation was initiated, Figure 5b shows that the release rate of benzene, although fairly sporadic, remains at about 400-µg benzene/cm^2-min for approximately 1½-hours. After just 3 hours, the release rate begins a rapid decrease to approximately 100-µg benzene/cm^2-min, where it begins to level out somewhat and decline slowly from about 60-µg benzene/cm^2-min to 24-µg benzene/cm^2-min from the 5th to the 14th hour of agitation, respectively. Following the 14th hour, the rate of decline of the benzene release rate increases as it approaches zero, reaching 3.5-µg benzene/cm^2-min after 16 hours of agitation.

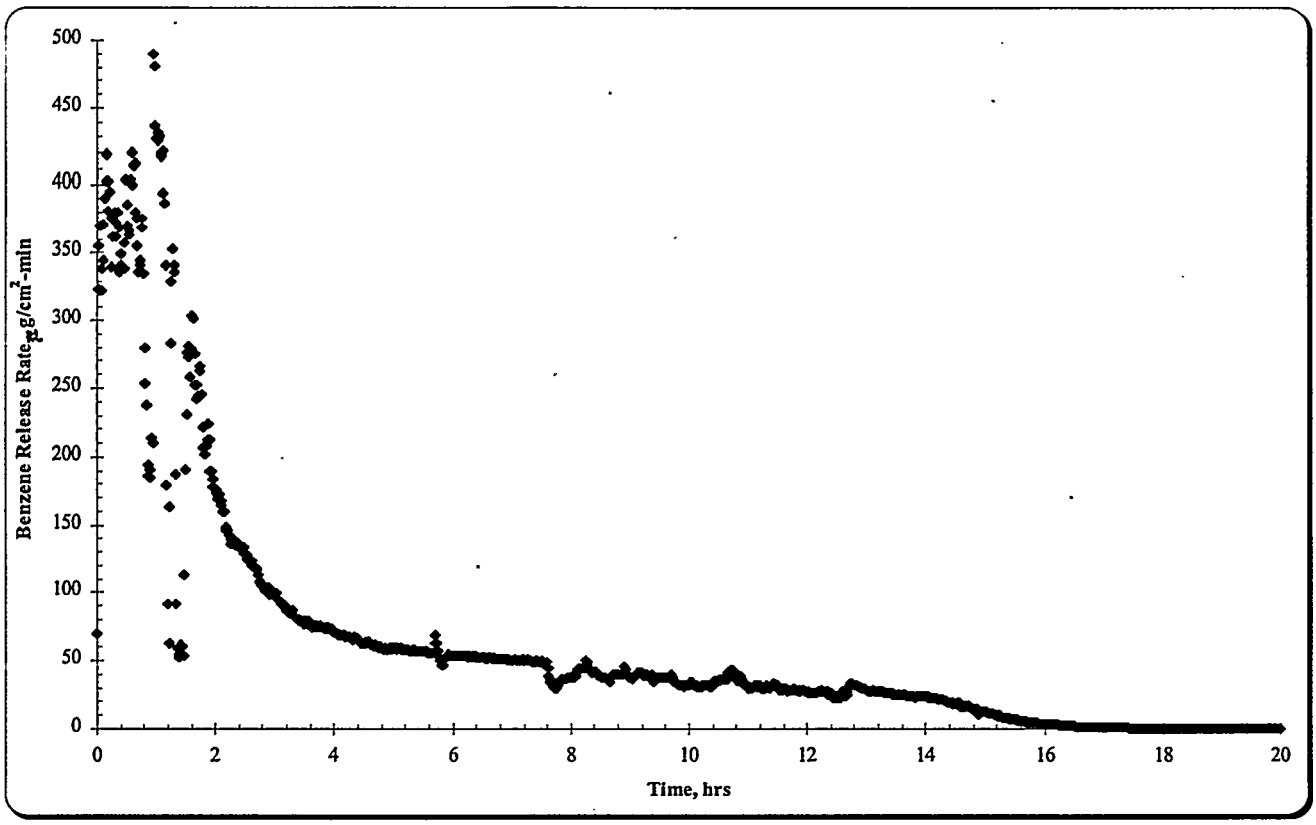

Figure 5b. Benzene Release from Agitated Slurry Containing 15,730-ppm Freshly Added Benzene

Figures 6a and 6b show the benzene release data from one 90.34-g sample of KTPB slurry prepared by freshly adding benzene at approximately 16,105-ppm (by weight) and gently premixing. Once again, Figure 6a shows the initial release rate data obtained without agitation, and Figure 6b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 6a.

Figure 6a shows that the release rate of benzene from the quiescent slurry surface declines rapidly once the initial headspace is purged, and begins to level off at approximately 10-µg benzene/cm^2-min after 0.2 hours and become fairly level at approximately 4-µg benzene/cm^2-min after 1 hour of release. Once agitation was started, Figure 6b shows that the release rate of benzene remains fairly constant at about 500-µg benzene/cm^2-min for approximately 1¼-hours. After 2 hours the release rate rapidly decreases to approximately 130-µg benzene/cm^2-min, where it begins to level out somewhat and decline slower from about 86-µg benzene/cm^2-min to 48-µg benzene/cm^2-min from the 3rd to the 7th hour of agitation, respectively. After 7 hours the benzene release rate declines rapidly to zero, reaching 3.0-µg benzene/cm^2-min after just 8 hours of agitation.

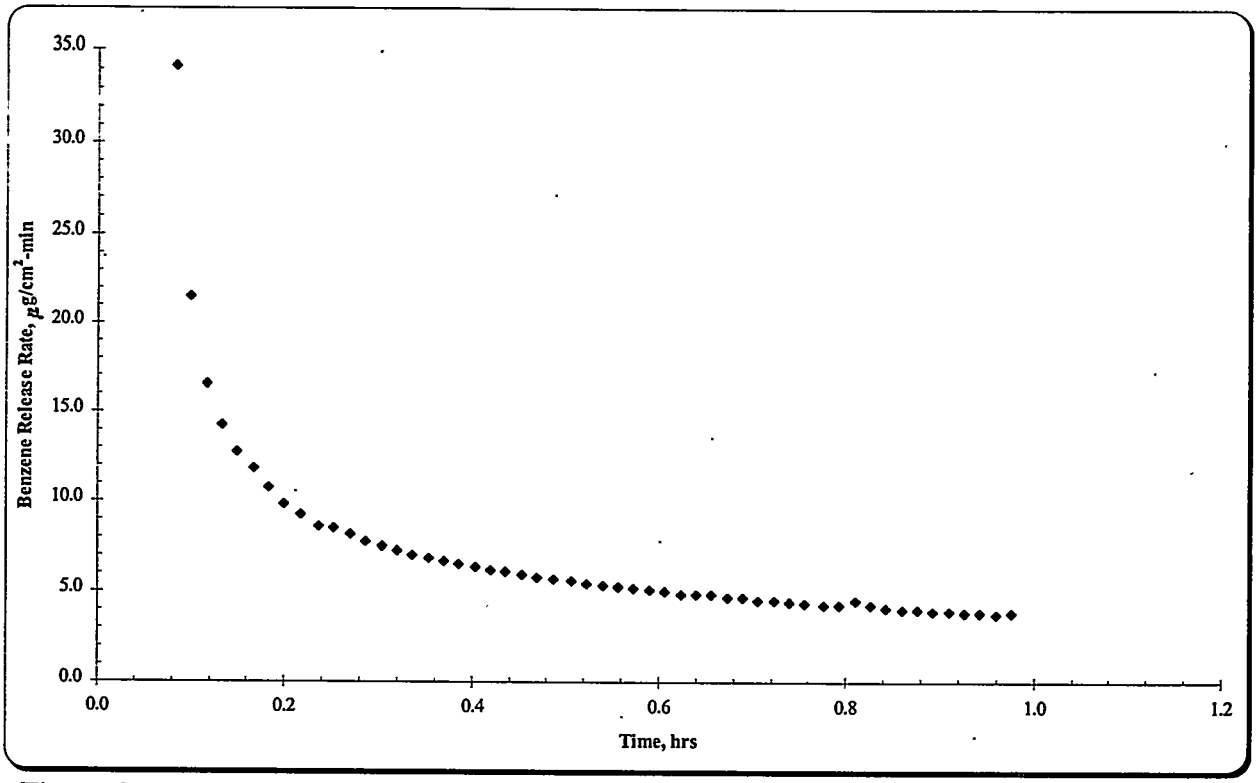

Figure 6a. Benzene Release from Quiescent Slurry Containing 16,105-ppm Freshly Added Benzene

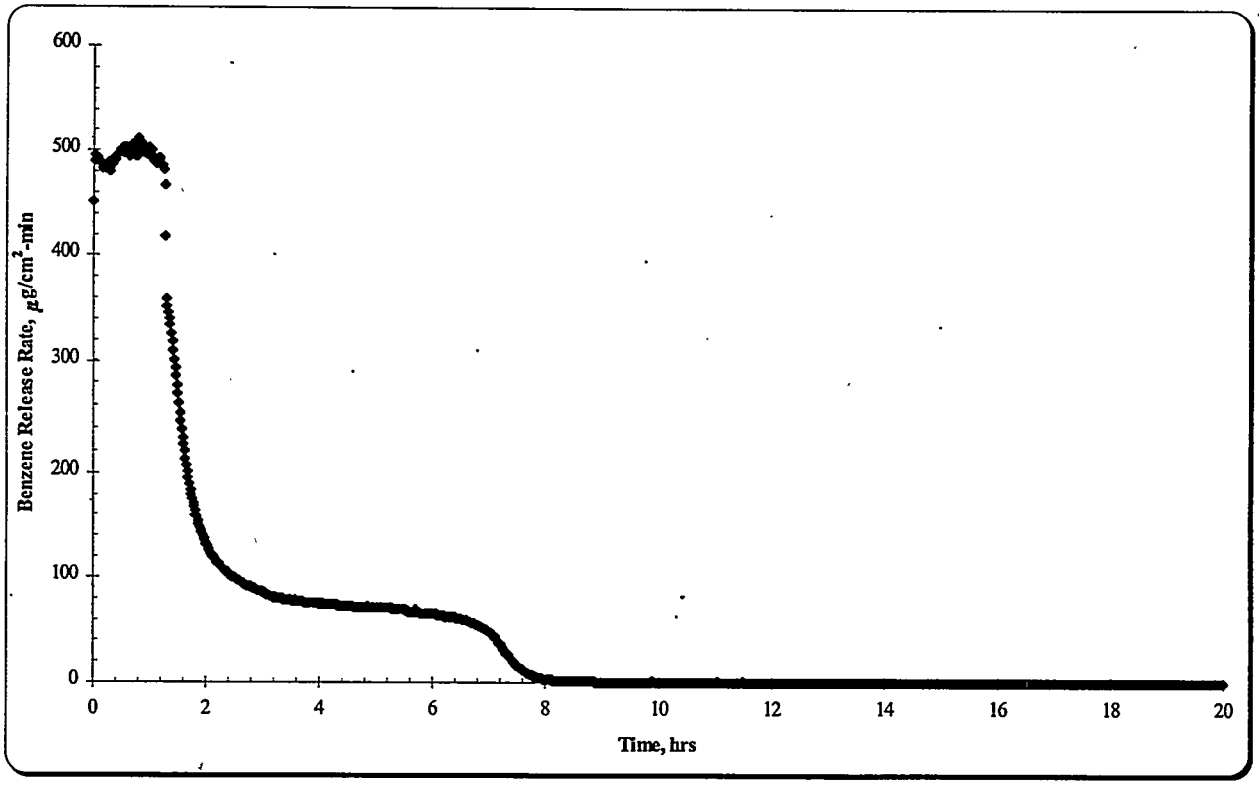

Figure 6b. Benzene Release from Agitated Slurry Containing 16,105-ppm Freshly Added Benzene

Finally, Figures 7a and 7b show the benzene release data from one 86.52-g sample of KTPB slurry prepared by freshly adding benzene at approximately 16,585-ppm (by weight) and gently premixing. Once again, Figure 7a shows the initial release rate data obtained without agitation, and Figure 7b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 7a.

Figure 7a shows again that the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged. After 0.2 hours it begins to level off at approximately 8-μg benzene/cm^2-min and become fairly level at approximately 4-μg benzene/cm^2-min after 1 hour of release. Once agitation was started, we see from Figure 7b that the release rate of benzene varies at around 450-μg benzene/cm^2-min for approximately 1¼-hours. After 1½ hours of agitation the release rate again rapidly decreases to approximately 86-μg benzene/cm^2-min, where it begins to level out somewhat and decline slower from about 57-μg benzene/cm^2-min to 13-μg benzene/cm^2-min between the 3rd and the 20th hour of agitation, respectively. Following the 20th hour of agitation, the benzene release rate declines rapidly to zero, reaching 4.9-μg benzene/cm^2-min after 22 hours of release with agitation.

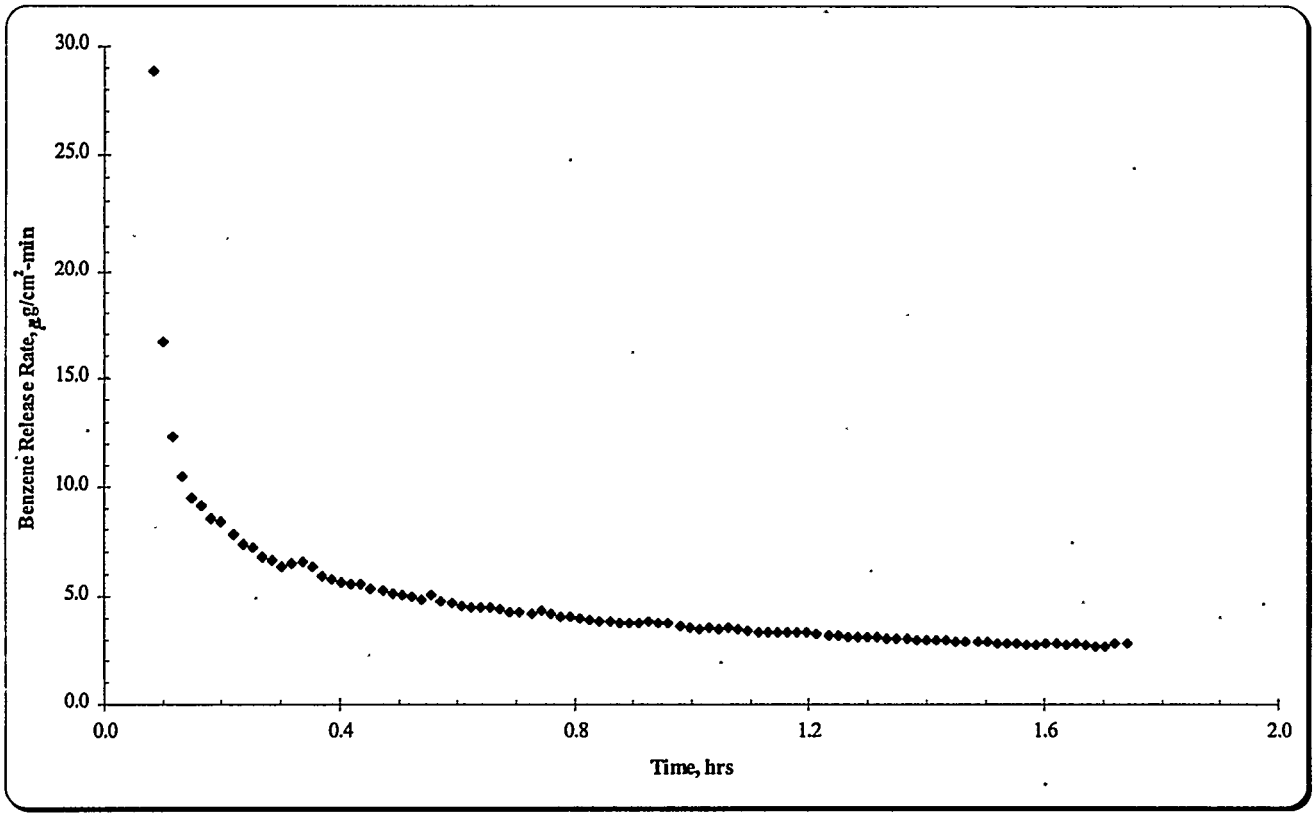

Figure 7a. Benzene Release from Quiescent Slurry Containing 16,585-ppm Freshly Added Benzene

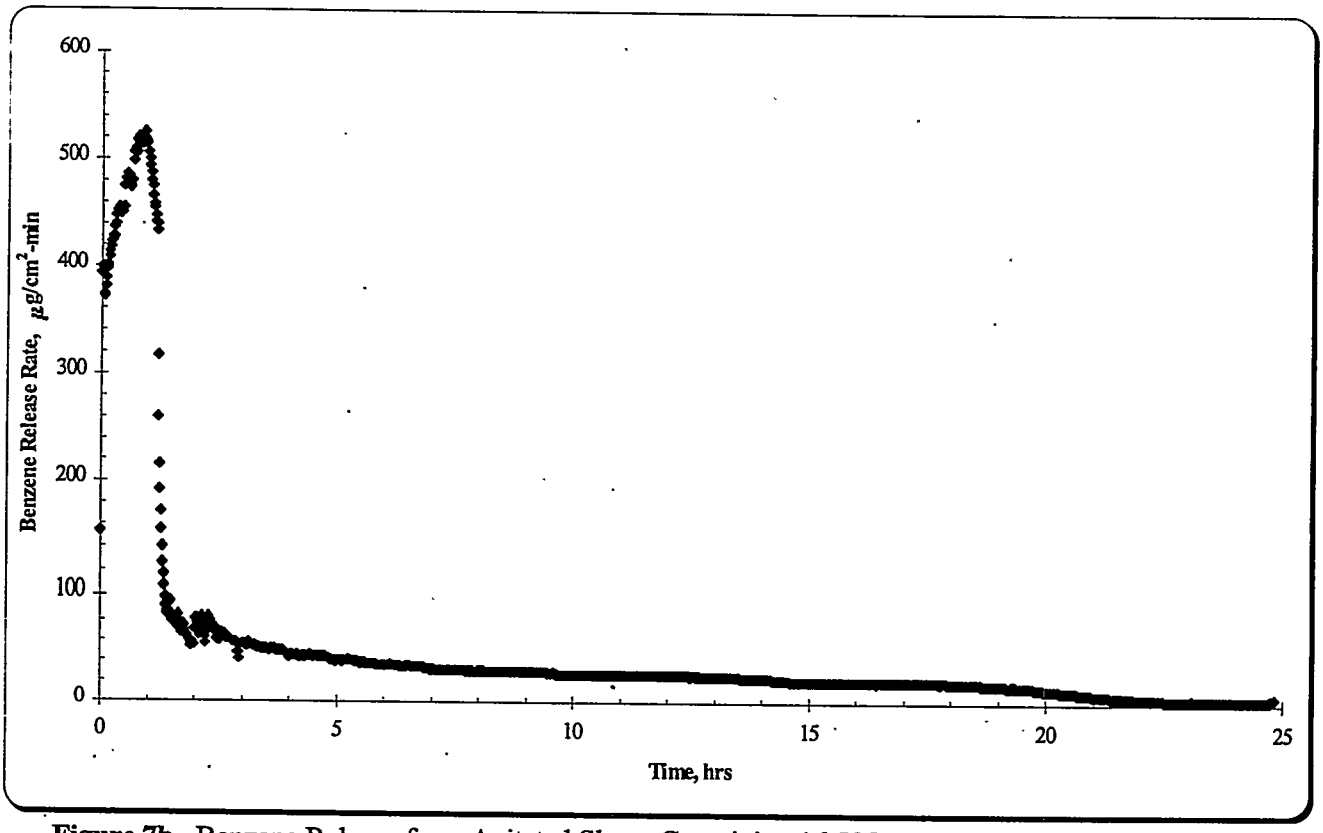

Figure 7b. Benzene Release from Agitated Slurry Containing 16,585-ppm Freshly Added Benzene

Figures 5a through 7b reveal interesting results. As we saw in earlier tests (Rappé and Gauglitz 1997), the release rate of benzene from quiescent slurry is significantly lower than the release rate from agitated slurry. Quiescent slurry released benzene about two orders of magnitude slower than initial agitated slurry. Figures 5b, 6b, and 7b show that the benzene release from the corresponding samples at ~16,000-ppm benzene exhibited an initial peak release of about 500-µg benzene/cm^2-min, which is essentially the same as a floating benzene layer. The magnitude and duration of extended release rates varied significantly amongst the samples. This is believed to be the result of slight agitation differences.

Figures 8a and 8b show the benzene release data from one 90.32-g sample of KTPB slurry prepared by freshly adding benzene at approximately 8,109-ppm (by weight) and gently premixing. Figure 8a shows the initial release rate data obtained without agitation, and Figure 8b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 8a. Figure 8a shows that the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged, after 0.2 hours it begins to level off at a bit over 1-µg benzene/cm^2-min and becomes fairly level at approximately 0.7-µg benzene/cm^2-min after 1 hour of release. Once agitation was started, Figure 8b shows that the release rate of benzene steadily increases to over 100-µg benzene/cm^2-min. After a little over an hour, the release rate of benzene then declined from ~80-µg benzene/cm^2-min to ~25-µg benzene/cm^2-min after 7 hours of agitation. At that point, the rate of decline of the benzene release rate decreases, and the release rate falls to just 20-µg benzene/cm^2-min after 13 hours of agitation. At this point, the benzene release rate falls quickly to zero, reaching just over 3-µg benzene/cm^2-min after 16 hours of agitation and 0.6-µg benzene/cm^2-min after 17 hours.

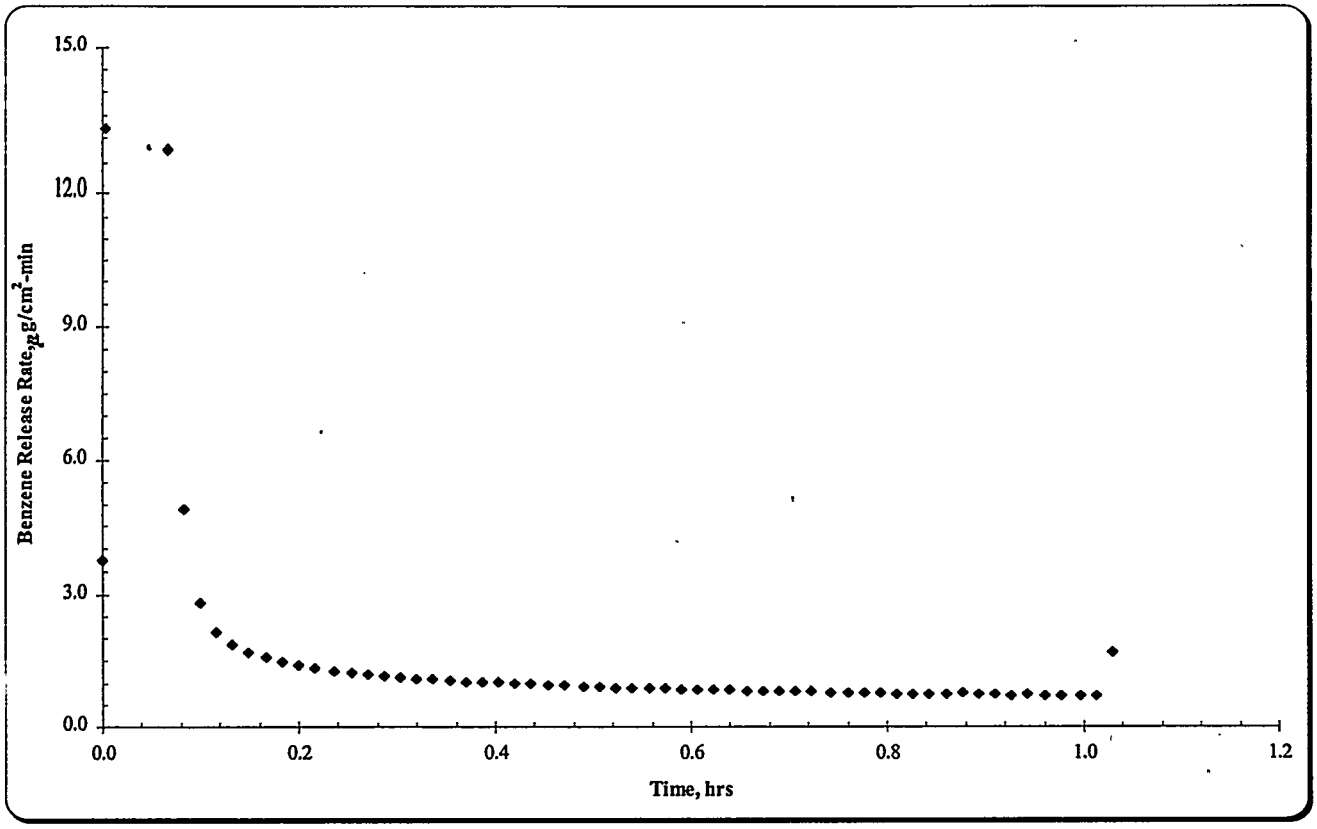

Figure 8a. Benzene Release from Quiescent Slurry Containing 8,109-ppm Freshly Added Benzene

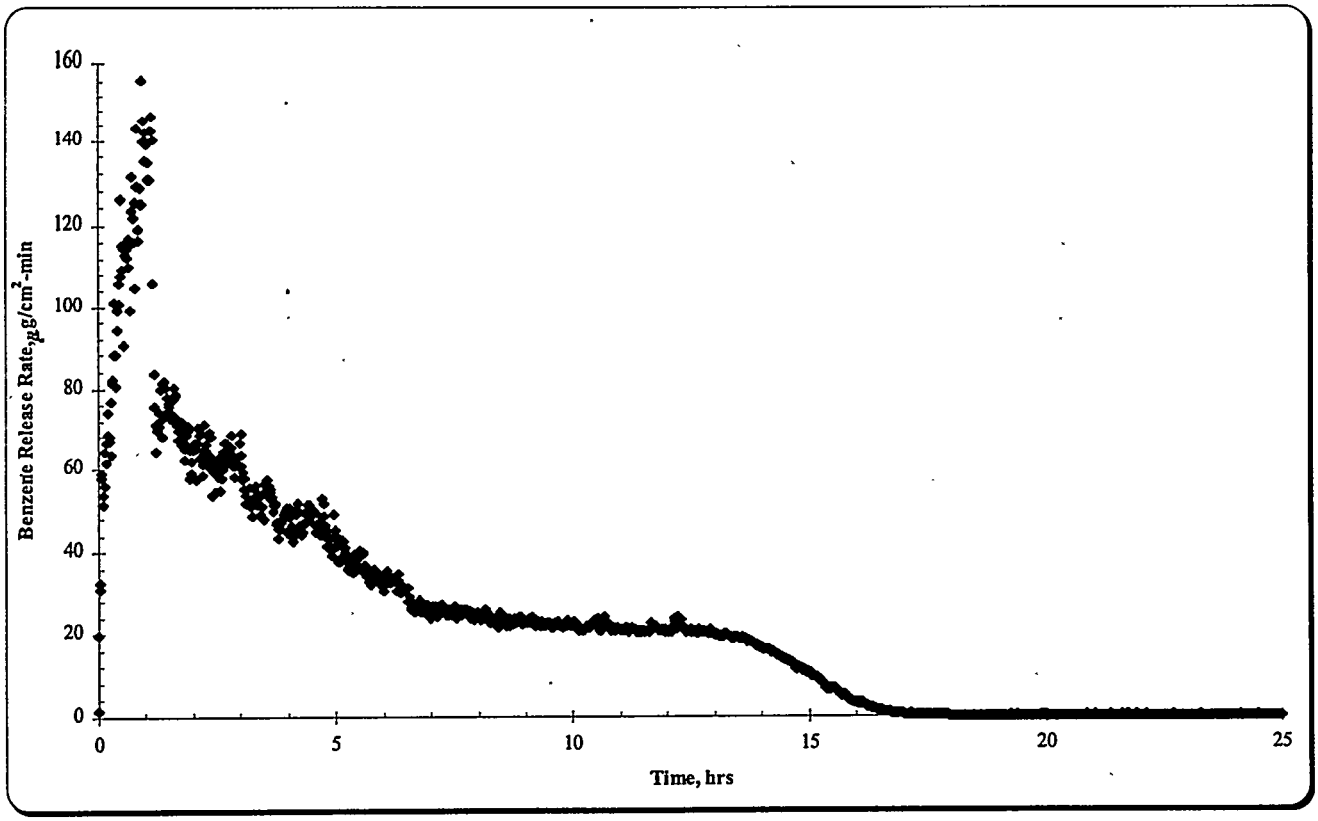

Figure 8b. Benzene Release from Agitated Slurry Containing 8,109-ppm Freshly Added Benzene

Slurries Homogenized with Added Benzene

The following four sets of data (Figures 9a, 9b, 10a, 10b, 11a, 11b, 12a and 12b) show benzene release rate data from slurry samples prepared by homogenizing added benzene with stock KTPB slurry and analyzing at room temperature. Experiments in Figures 9a,b and 10a,b are replicates, while Figures 11a,b and 12a,b show results for lower benzene concentrations.

Figures 9a and 9b show the benzene release rate data from one 79.28-g sample of KTPB slurry prepared by homogenizing with approximately 16,624-ppm (by weight) benzene. Figure 9a shows the initial release rate data obtained without agitation, and Figure 9b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 9a. Figure 9a shows the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged. After 0.2 hours it begins to level off at just over 14-μg benzene/cm^2-min, and become fairly level at over 5-μg benzene/cm^2-min after 1 hour of release. Once agitation was initiated, Figure 9b shows that the release rate of benzene varies significantly over the 24-hour test period. Initially, the benzene release rate rose to almost 93-μg benzene/cm^2-min. However, this rate immediately fell to ~56-μg benzene/cm^2-min after just 1 hour of agitation, where it remained fairly constant for the next 3-¾ hours. The benzene release rate fell to ~22-μg benzene/cm^2-min after 6½ hours of agitation. After 9-¾ hours of agitation it immediately rose again to ~50-μg benzene/cm^2-min and fell to ~24-μg benzene/cm^2-min after 12 hours of agitation. At this point, the benzene release rate slowly rose to ~38-μg benzene/cm^2-min after 16-½ hours of agitation, where it remained fairly constant for the remainder of the experiment.

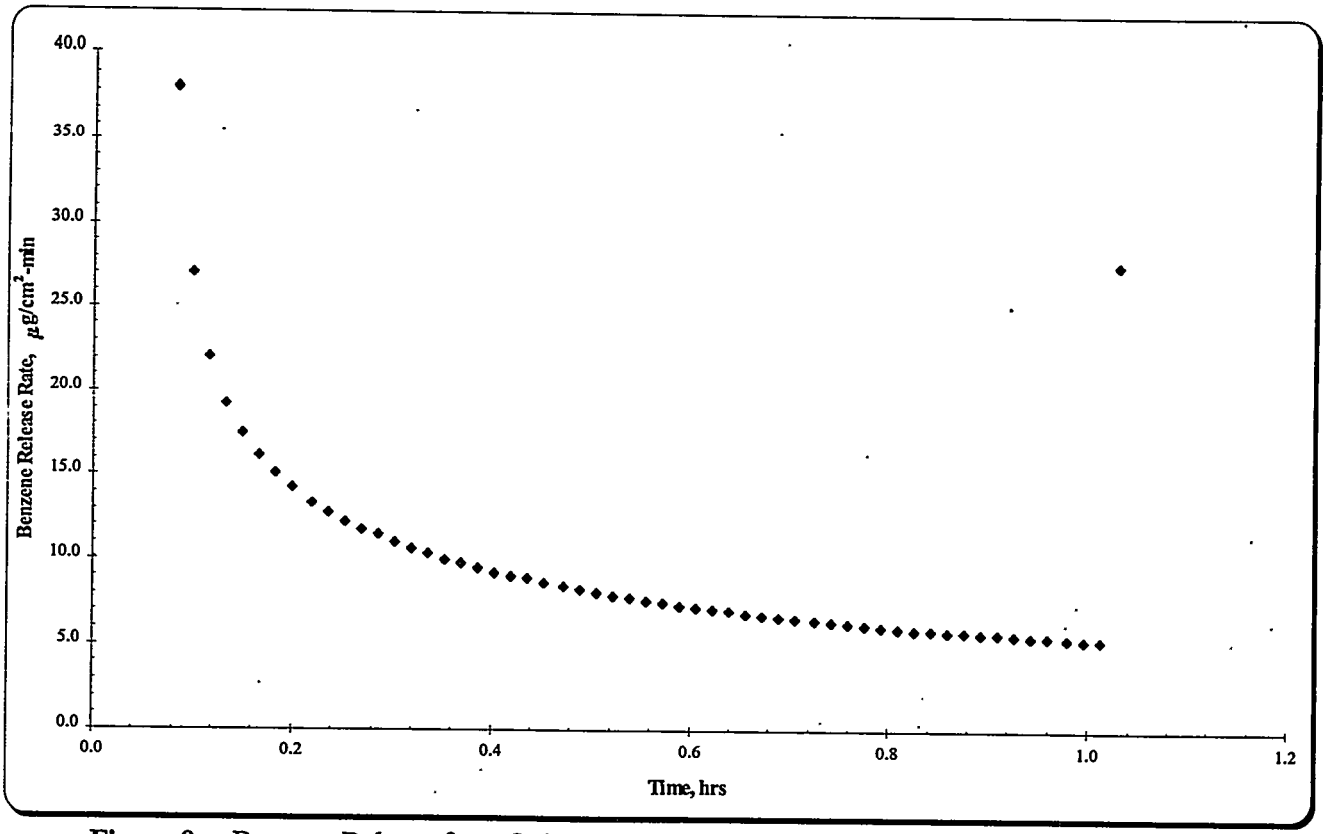

Figure 9a. Benzene Release from Quiescent Slurry Homogenized with 16,624-ppm Benzene

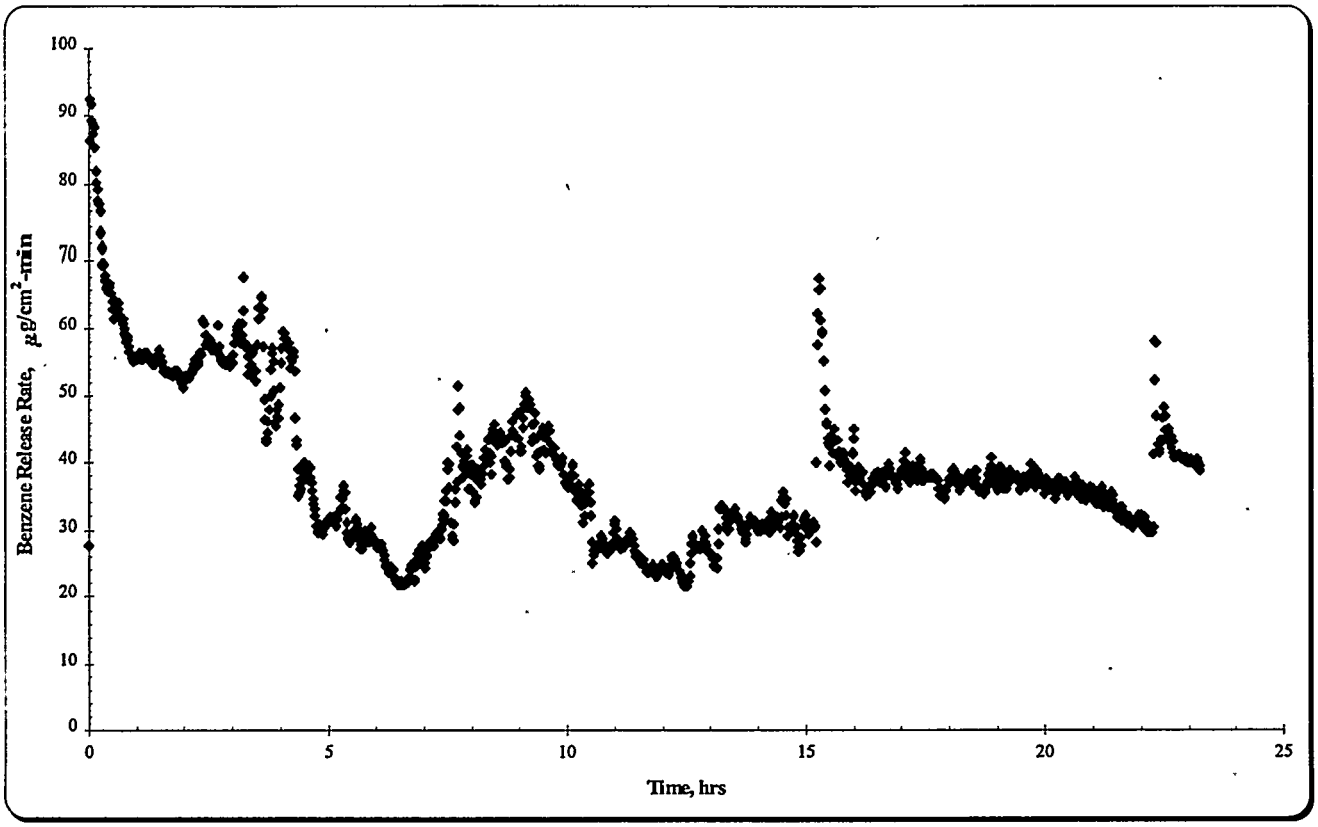

Figure 9b. Benzene Release from Agitated Slurry Homogenized with 16,624-ppm Benzene

Figures 10a and 10b show the benzene release rate data from one 74.45-g sample of KTPB slurry prepared by homogenizing with approximately 17,068-ppm (by weight) benzene. Figure 10a shows the initial release rate data obtained without agitation, and Figure 10b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 10a. Figure 10a shows that the release rate of benzene from the quiescent slurry surface decline rapidly until the initial headspace is purged. At this point the release rate began to level off after 0.2 hours at just less than 22-µg benzene/cm^2-min and become fairly level at >7-µg benzene/cm^2-min after 1 hour of release. Once agitation was initiated, Figure 10b shows that the first two hours of release rate data are fairly low and sporadic, varying anywhere from 0 to 18-µg benzene/cm^2-min. This initial region is believed to be the result of a problem with the agitation of the slurry sample, and it is, therefore, inconclusive. After this initial region, the release rate of benzene is 51-µg benzene/cm^2-min and fell rapidly to 32-µg benzene/cm^2-min in a span of about 2 hours. The benzene release then fell slower, dropping to just 25-µg benzene/cm^2-min after 16-½ hours of agitation. From this point to the 24th hour of agitation, the benzene release rate varied between 23-µg benzene/cm^2-min and 30-µg benzene/cm^2-min. After 24 hours of agitation, the release rate of benzene began a quick and steady drop to zero, reaching well over 4-µg benzene/cm^2-min after 34 hours of agitation and just over 1-µg benzene/cm^2-min after 38 hours of agitation.

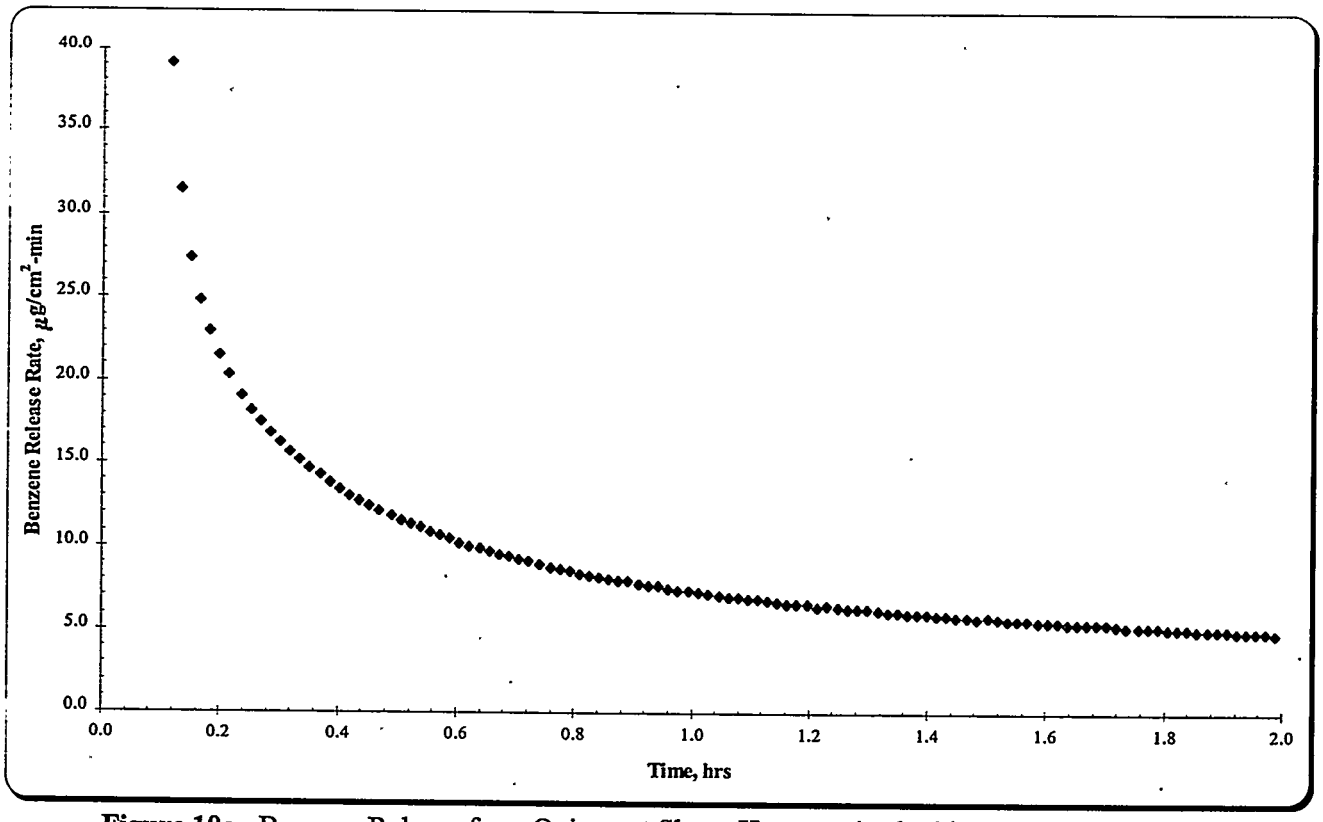

Figure 10a. Benzene Release from Quiescent Slurry Homogenized with 17,068-ppm Benzene

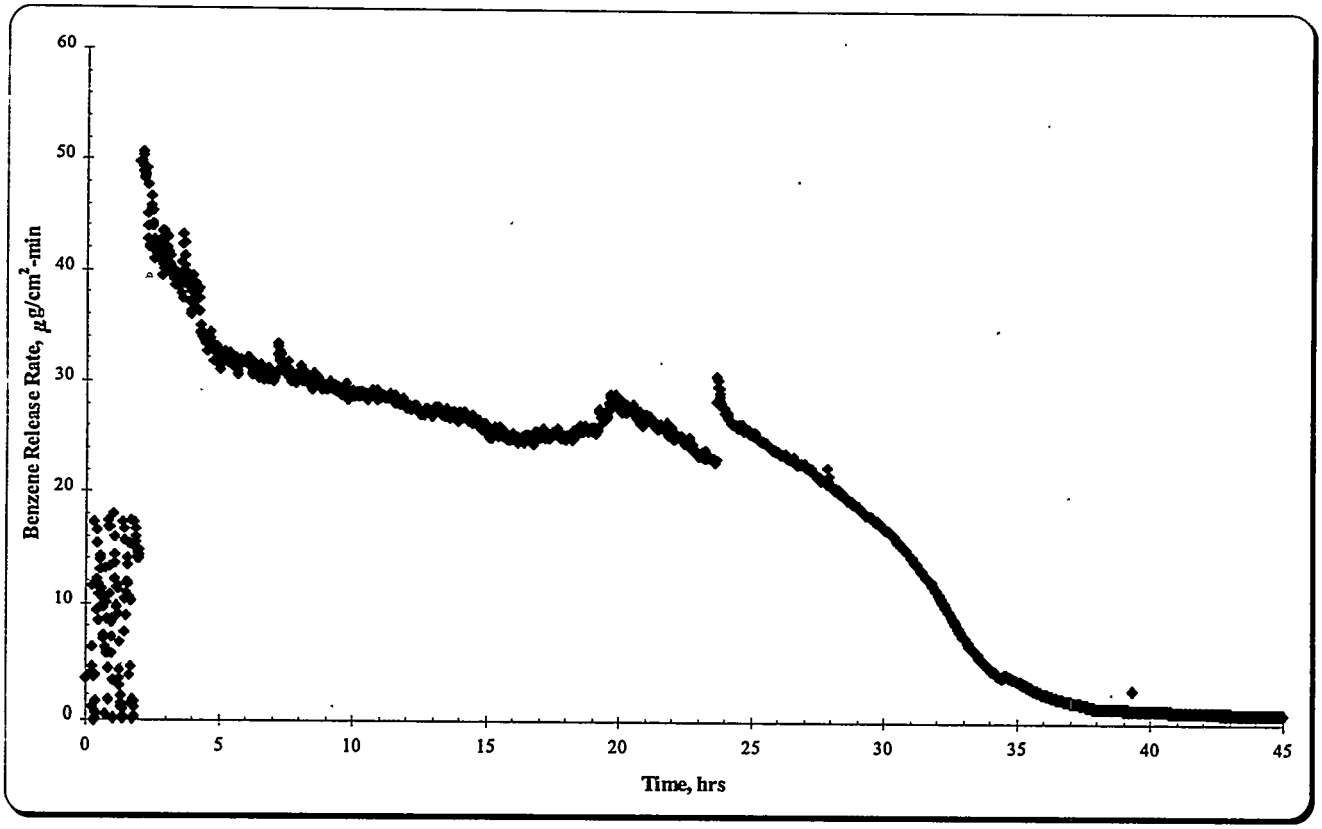

Figure 10b. Benzene Release from Agitated Slurry Homogenized with 17,068-ppm Benzene

Figures 11a and 11b show the benzene release rate data from one 77.89-g sample of KTPB slurry prepared by homogenizing with approximately 8,535-ppm (by weight) benzene. Figure 11a shows the initial release rate data obtained without agitation, and Figure 11b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 11a. Figure 11a shows that the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged. After 0.2 hours the release rate begins to level off at just less than 16-μg benzene/cm^2-min, and after 1 hour of release it becomes fairly level at just over 5-μg benzene/cm^2-min. Once agitation was initiated Figure 11b shows the release rate of benzene immediately rise to 42-μg benzene/cm^2-min and remained there for about 0.75 hours. The release rate then quickly falls to 30-μg benzene/cm^2-min after just 1-½ hours of agitation. At this point, the release rate of benzene becomes fairly stable, falling to between 22 and 23-μg benzene/cm^2-min after 16 hours of agitation. The release rate then falls much more rapidly, reaching 5.0-μg benzene/cm^2-min after 25 hours of agitation. It should be noted that the shape of the corresponding curves in Figures 10b and 11b are very similar. The sporacidy of the data in Figure 9b allows no general shape to be defined.

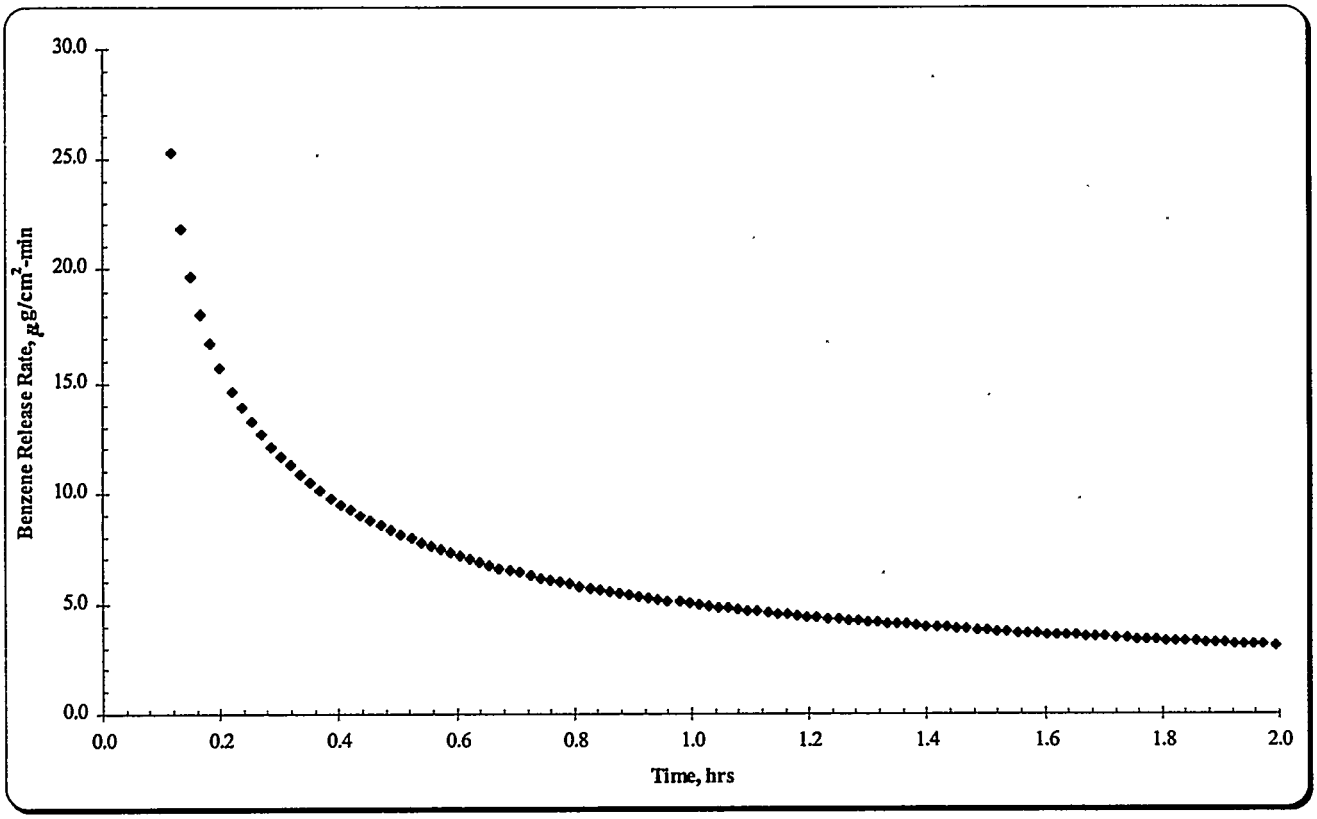

Figure 11a. Benzene Release from Quiescent Slurry Homogenized with 8,535-ppm Benzene

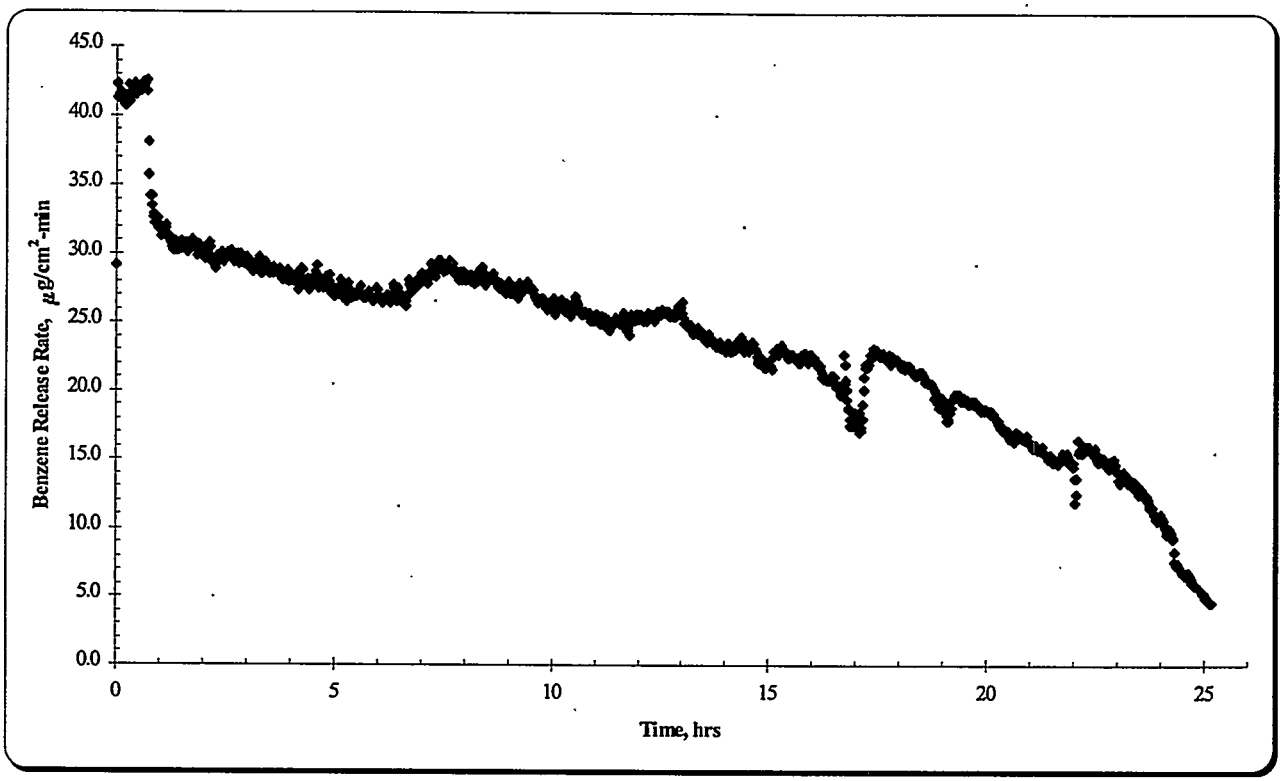

Figure 11b. Benzene Release from Agitated Slurry Homogenized with 8,535-ppm Benzene

Figures 12a and 12b show the benzene release rate data from one 77.13-g sample of KTPB slurry prepared by homogenizing with approximately 5,408-ppm (by weight) benzene. Figure 12a shows the initial release rate data obtained without agitation, and Figure 12b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 12a. Figure 12a shows that the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged. After 0.2 hours the release rate begins leveling off at well over 9-µg benzene/cm^2-min and become fairly level at less than 4-µg benzene/cm^2-min after 1 hour of release. Once agitation was initiated, Figure 12b shows that release rate of benzene varies fairly sporadically between 20- and 29-µg benzene/cm^2-min for the first 8 hours of agitation. Over the next 8.5 hours the release rate steadily declines from 23-µg benzene/cm^2-min to 13-µg benzene/cm^2-min. After 21 hours of agitation the release rate descends more rapidly towards zero, reaching just less than 3-µg benzene/cm^2-min, and reaching 0.4-µg benzene/cm^2-min after 24 hours of agitation.

Data from the homogenized slurries (Figures 9a through 12b) indicate only a brief initial peak release rate of benzene, followed by a steadily decreasing release rate. Slurries homogenized with ~16,000-ppm benzene exhibited peak releases of less than 100-µg benzene/cm^2-min, and longer-term rates were about 50-µg benzene/cm^2-min. The benzene release rates decreased slightly with decreasing benzene concentration for slurries containing ~16,000-ppm to ~5,000-ppm benzene. It is worth noting that, although somewhat similar, the release rate of benzene from the quiescent surface of slurry homogenized with benzene was consistently higher (~75%) than the respective release of benzene from slurry containing freshly added and lightly dispersed benzene.

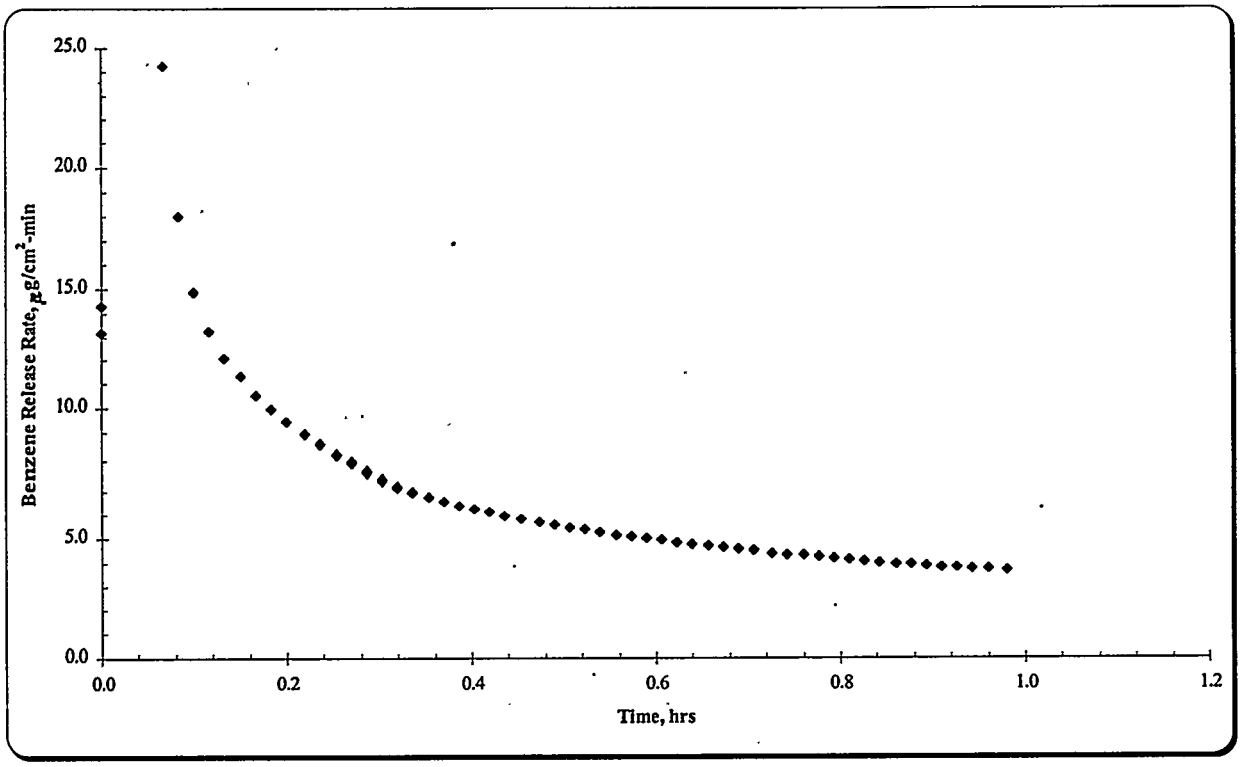

Figure 12a. Benzene Release from Quiescent Slurry Homogenized with 5,408-ppm Benzene

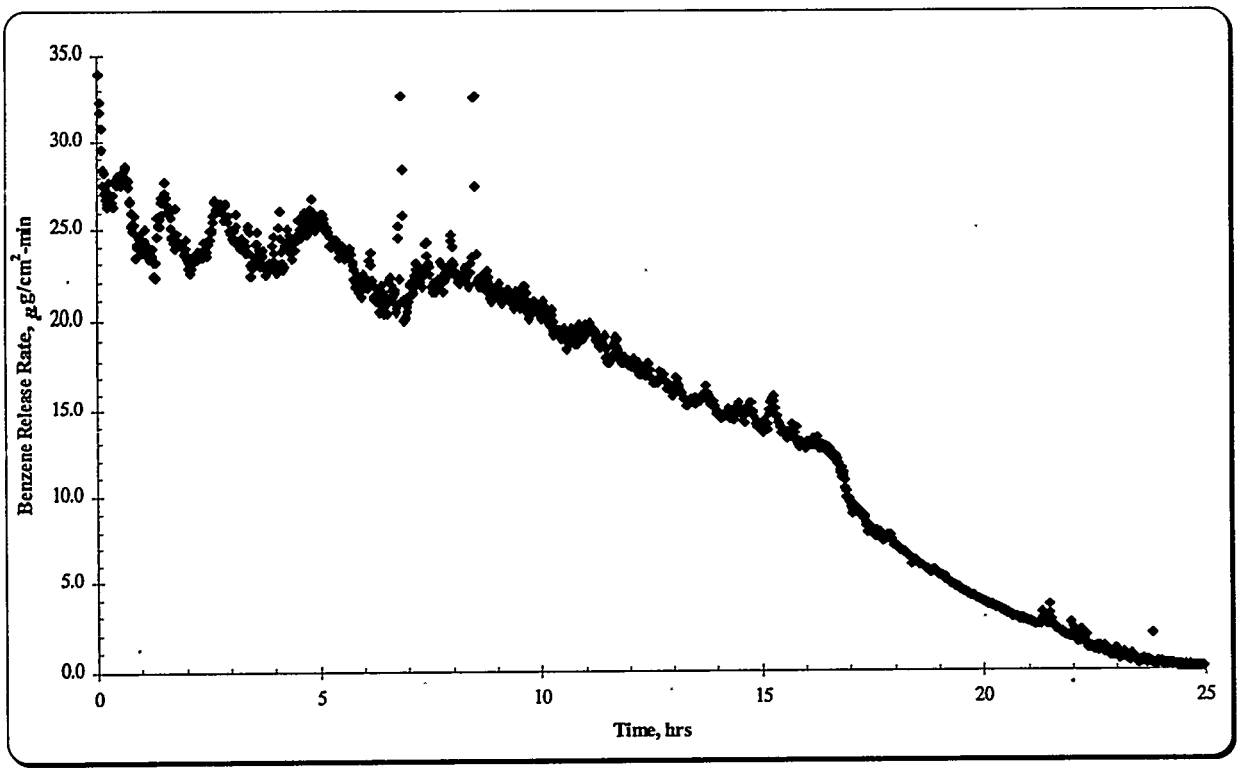

Figure 12b. Benzene Release from Agitated Slurry Homogenized with 5,408-ppm Benzene

Slurries with Both Gently Mixed and Homogenized Benzene

Figures 13a and 13b show the benzene release rate data from one 83.17-g sample of KTPB slurry prepared by homogenizing the sample with approximately 9,598-ppm (by weight) benzene, and then freshly adding an additional 8,951-ppm benzene and gently premixing, for a total of 18,212-ppm (by weight) benzene. Figure 13a shows the initial release rate data obtained without agitation, and Figure 13b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 13a. Figure 13a shows the release rate of benzene from the quiescent slurry surface decline rapidly until the initial headspace is purged. The release rate begins to level off after 0.2 hours at approximately 25-μg benzene/cm^2-min and becomes fairly level at well over 10-μg benzene/cm^2-min after 1 hour of agitation. Figure 13b shows the release rates of benzene release steadily decline from the onset of agitation. There are a few sporadic humps in the data that are probably caused by pure benzene bubbles eventually reaching the surface of the slurry. The release rate starts out at about 250-μg benzene/cm^2-min, declines to <80-μg benzene/cm^2-min after 5 hours of agitation, continues to decline to 16-μg benzene/cm^2-min after 10 hours of agitation, and was still declining when it reached ~3-μg benzene/cm^2-min after 15 hours of agitation.

The mixed slurry sample in Figures 13a and 13b had a release rate behavior intermediate to the results of the different slurries tested individually. The initial peak release rate of 300-μg benzene/cm^2-min agrees with this intermediate behavior. However, it is interesting to note that the benzene release from the quiescent slurry surface is higher than quiescent release of benzene from both the freshly added and the homogenized slurry samples.

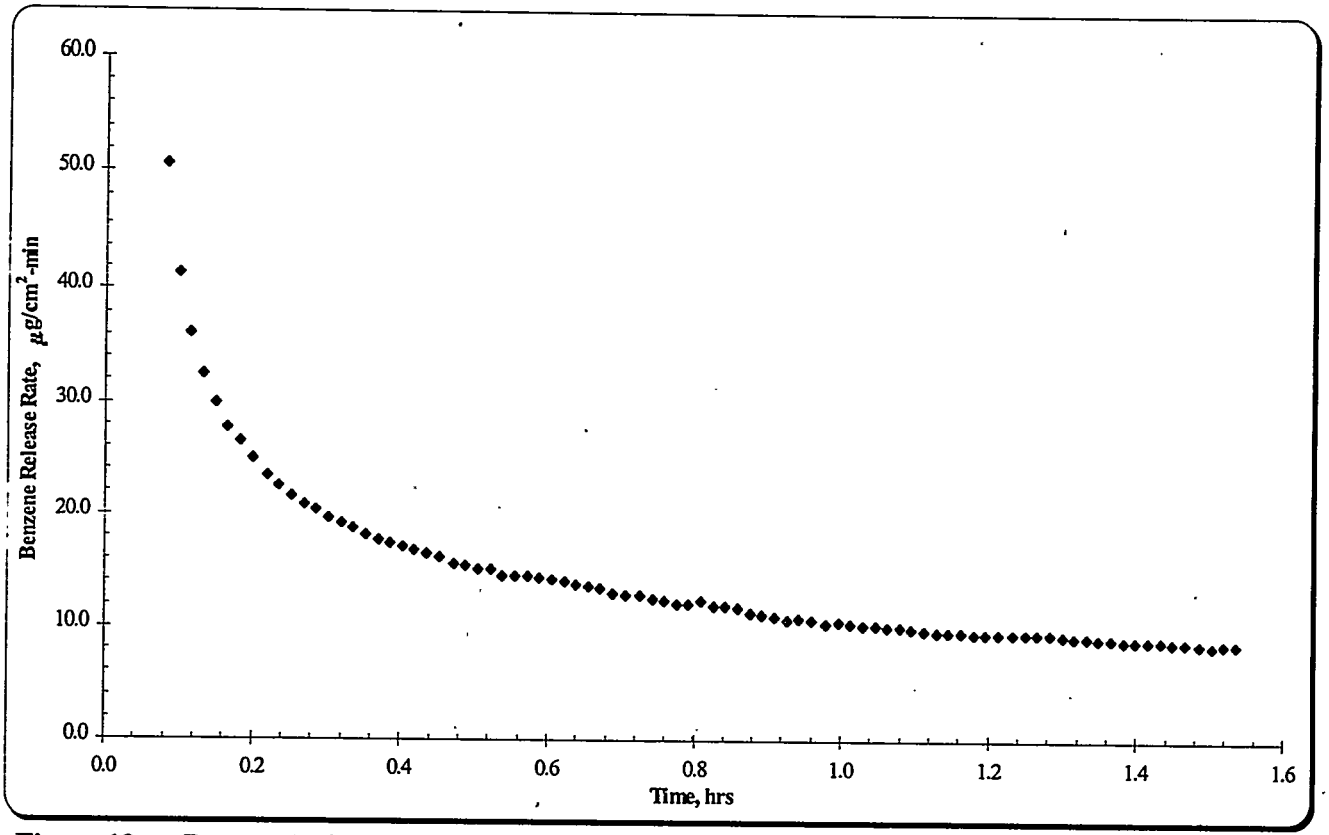

Figure 13a. Benzene Release from Quiescent Slurry Homogenized with 9,598-ppm Benzene and Containing 8,951-ppm Freshly Added Benzene

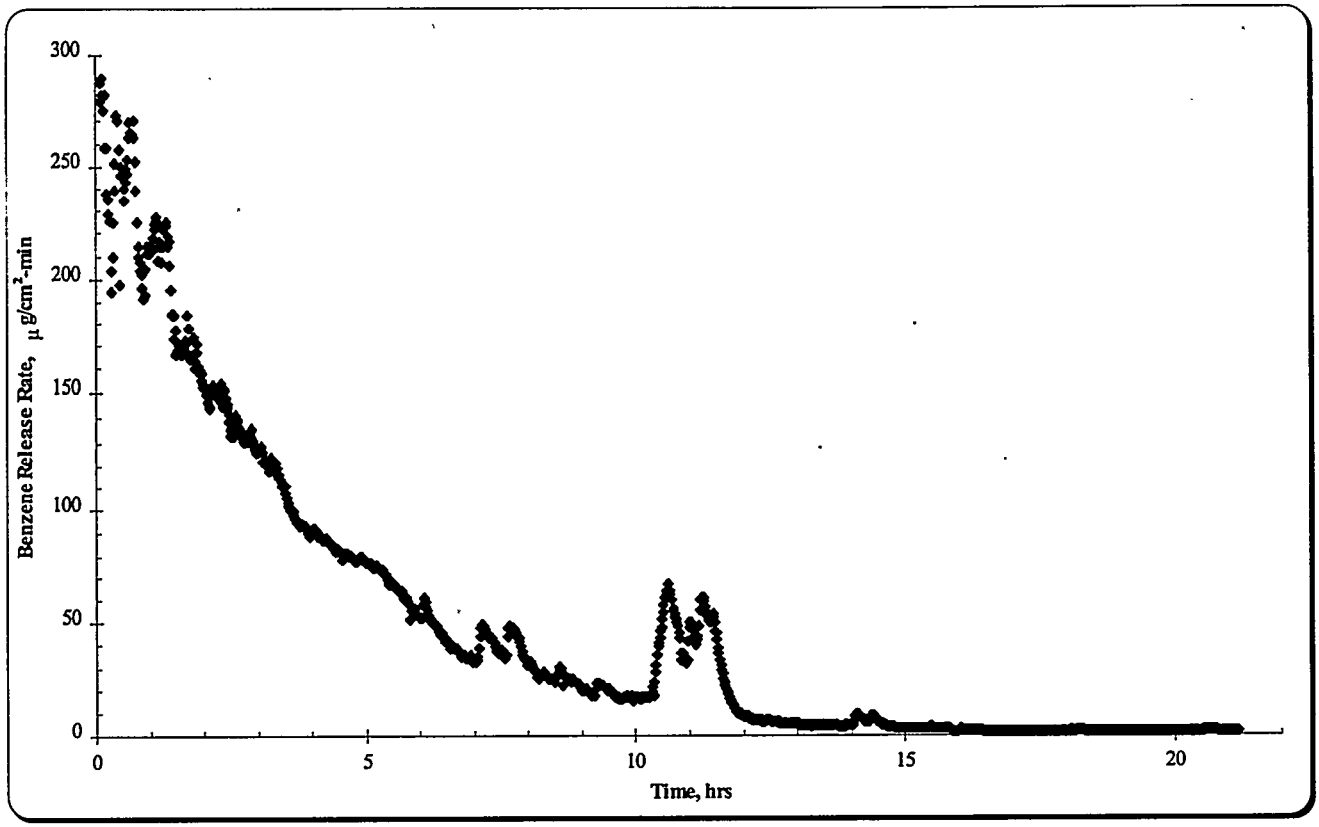

Figure 13b. Benzene Release from Agitated Slurry Homogenized with 9,598-ppm Benzene and Containing 8,951-ppm Freshly Added Benzene

We have developed a theory for the benzene release behaviors discussed above. For significant benzene release, it is hypothesized that a slurry sample must contain or be subjected to two important factors: (1) a source of readily releasable benzene, and (2) a pathway for ease of release. It is also hypothesized that benzene in the form of droplets provides a source of readily releasable benzene, and that benzene homogenized with a slurry sample, thus present as a coating on the KTPB slurry particles, provides (to some extent) a pathway for ease of release. Thus, the above benzene release behaviors can be explained using the criteria just discussed. For freshly added benzene samples, the initial peak release regime exists due to the presence of a source of readily releasable benzene (droplets) and a pathway for ease of release (agitation), at least until benzene in the form of droplets in depleted. In addition, the higher release of benzene from a quiescent surface of a slurry sample containing both homogenized and freshly added slurry is easily explained by the presence of both a source of readily releasable benzene (droplets) and a pathway for ease of release (homogenized benzene).

Slurries at Elevated Temperature

The following four sets of data (Figures 14a, 14b, 15a, 15b, 16a, 16b, 17a and 17b) show benzene release rate data from slurry samples analyzed at elevated temperatures. The initial set of data shows the release rate at 45°C of a sample prepared by adding benzene to the slurry and gently premixing (no homogenization). The remaining three sets of data show the release rate of samples prepared by homogenizing added benzene with KTPB slurry, the first two analyzed at 45°C and the final sample analyzed at 35°C.

Figures 14a and 14b show the benzene release rate data at 45°C from one 85.41-g sample of

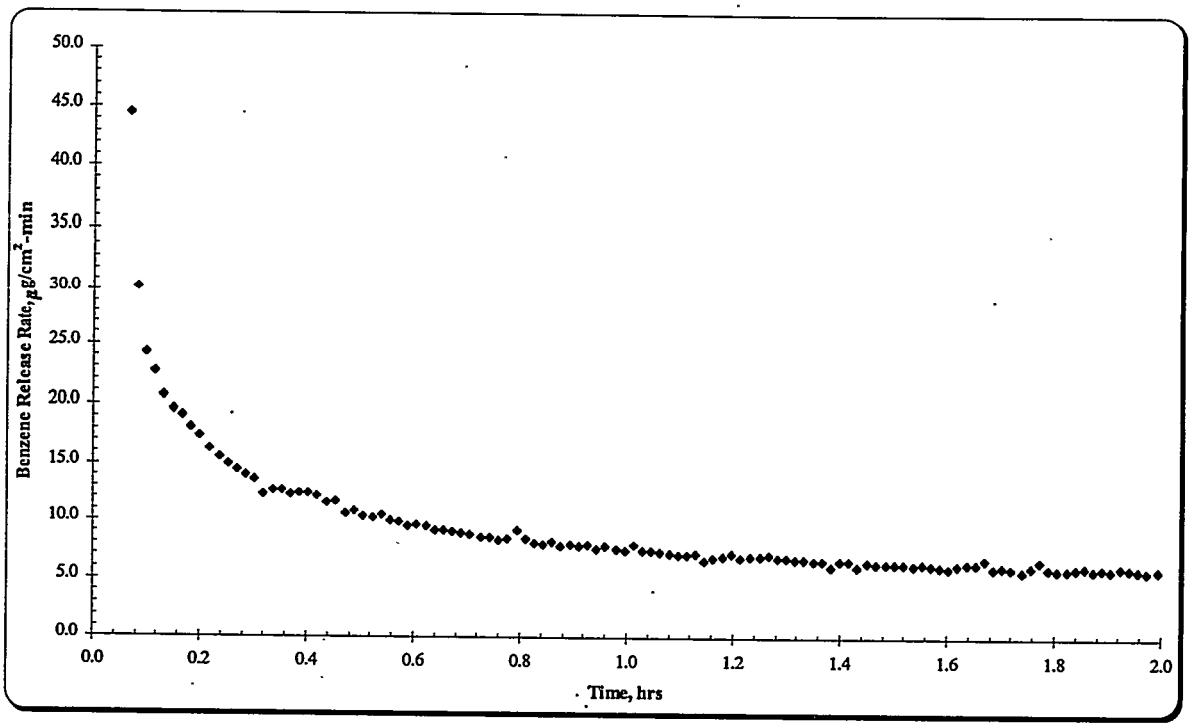

Figure 14a. Benzene Release (45°C) from Quiescent Slurry Containing 17,323-ppm Freshly Added Benzene

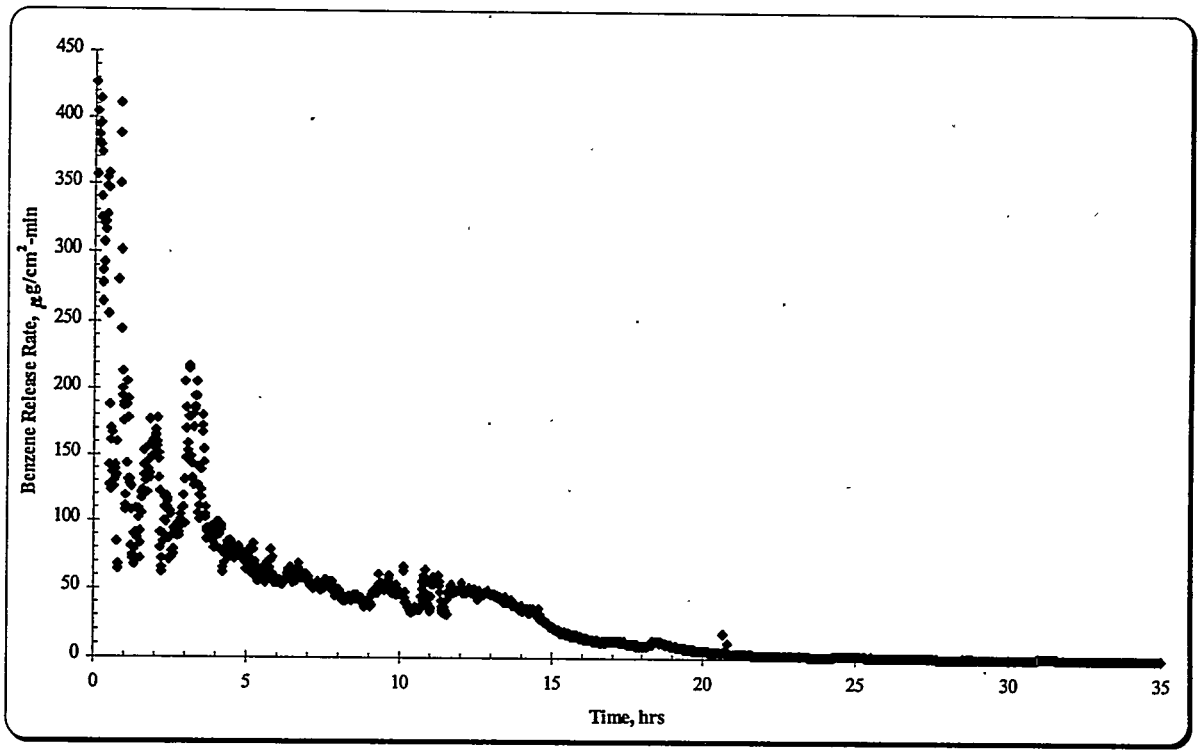

Figure 14b. Benzene Release (45°C) from Agitated Slurry Containing 17,323-ppm Freshly Added Benzene

KTPB slurry prepared by freshly adding 17,323-ppm benzene and gently premixing. Figure 14a shows the initial release rate data obtained without agitation, and Figure 14b shows the release rate data obtained with agitation, with time zero being set at the onset of agitation following the data in Figure 14a. Figure 14a shows that the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged. The release rate data begins to level off at 0.2 hours at approximately 17-μg benzene/cm^2-min and becomes fairly level at well over 7-μg benzene/cm^2-min after 1 hour of release. Once agitation was initiated, Figure 14b shows the release rate of benzene quickly plummet from ~400-μg benzene/cm^2-min to ~150-μg benzene/cm^2-min. The release rate continues to vary sporadically from ~70-μg benzene/cm^2-min to ~210-μg benzene/cm^2-min through about 3.5 hours of agitation. The data steadily declines to about 50-μg benzene/cm^2-min after almost 8 hours of agitation, and remains there over the next 5 hours of agitated release. Following a rapid decline in release rate near 12 hours, the release rate of benzene slowly and steadily declines to about zero, reaching 20-μg benzene/cm^2-min after 15 hours of agitated release, and 5-μg benzene/cm^2-min after 20 hours of release.

Figures 15a and 15b show the benzene release rate data at 45°C from one 61.19-g sample of KTPB slurry prepared by homogenizing 19,024-ppm benzene with a sample of slurry. Figure 15a shows the initial release rate data obtained without agitation, and Figure 15b shows the release rate data obtained after agitation was initiated, with time zero being set at the onset of agitation following the data in Figure 15a. Figure 15a shows that the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged, at which point it again begins to level off at just less than 16-μg benzene/cm^2-min at 0.2 hours, and become fairly level, approaching 5-μg benzene/cm^2-min, after 1 hour of release.

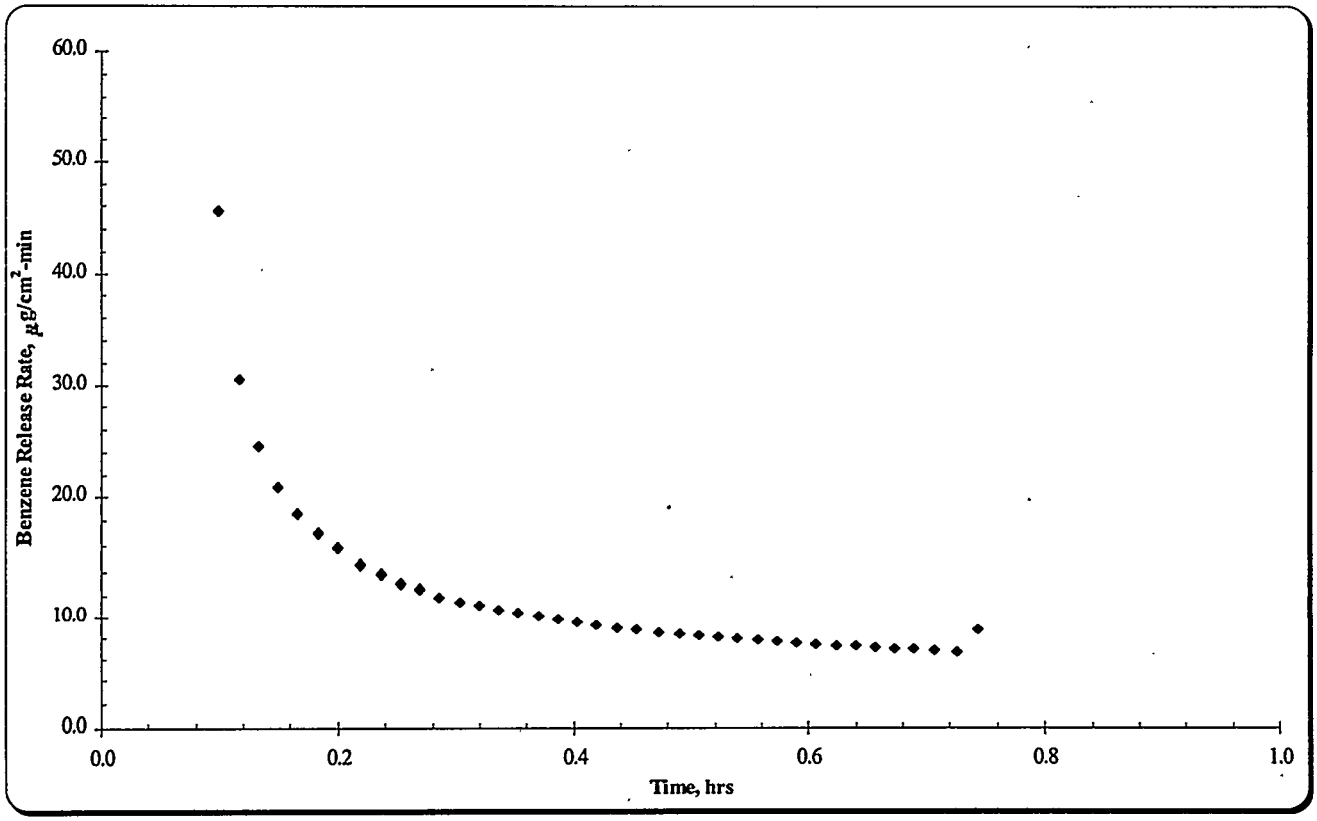

Figure 15a. Benzene Release (45°C) from Quiescent Slurry Homogenized with 19,024-ppm Benzene

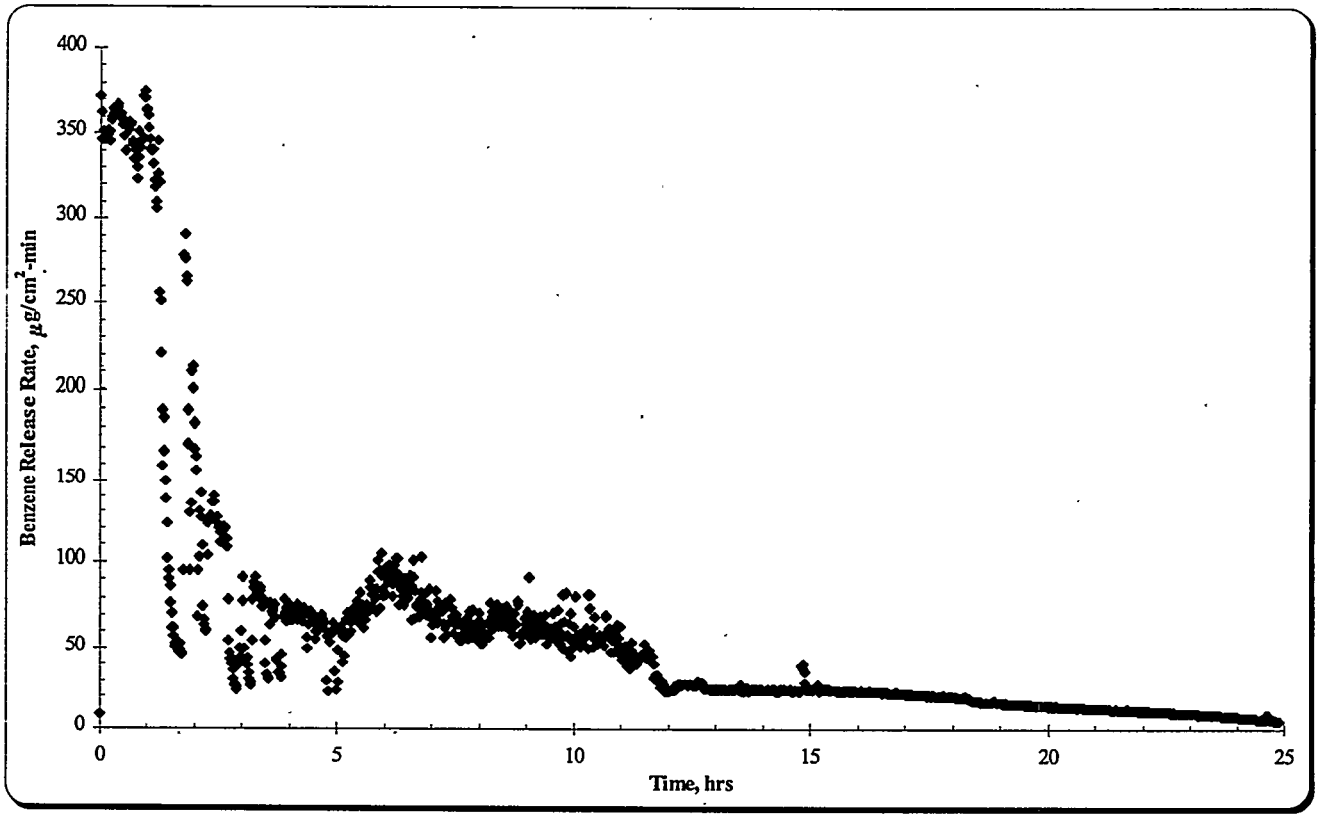

Figure 15b. Benzene Release (45°C) from Agitated Slurry Homogenized with 19,024-ppm Benzene

Referring to Figure 15b, once agitation was initiated, the slurry released benzene at a rate of approximately 350-µg benzene/cm^2-min for about 1 hour. The release rate drops quickly, varying sporadically between ~100-µg benzene/cm^2-min and ~30-µg benzene/cm^2-min until the 12th hour of agitated release. The release rate then levels out at ~24-µg benzene/cm^2-min, falling to just below 20-µg benzene/cm^2-min over the next 6 hours. Finally the data slowly and steadily falls to 5-µg benzene/cm^2-min after 25 hours of agitation.

Figures 16a and 16b show the benzene release rate data at 45°C from one 88.36-g sample of KTPB slurry prepared by homogenizing 20,653-ppm benzene with a sample of slurry. Figure 16a shows the initial release rate data obtained without agitation, and Figure 16b shows the release rate data obtained after, with time zero being set at the onset of agitation following the data in Figure 16a. In Figure 16a the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged as before, at which point it again begins to level off at 0.2 hours at just over 25-µg benzene/cm^2-min, and become fairly level after 1 hour of release at over 9-µg benzene/cm^2-min.

Figure 16b shows that upon initiating agitation, benzene is released from the slurry at a rate of approximately 90-µg benzene/cm^2-min for about 4 hours. The rate of benzene release then quickly drops and varies between 20- and 40-µg benzene/cm^2-min over the next 8 hours. Then, over the following 3 hours of agitation, the rate of benzene release gradually increases to over 65-µg benzene/cm^2-min. At that point, the benzene release rate from the slurry begins slowly and consistently declining. Over the next 25 hours of agitation, until the end of the test, the rate of benzene release from the slurry reaches

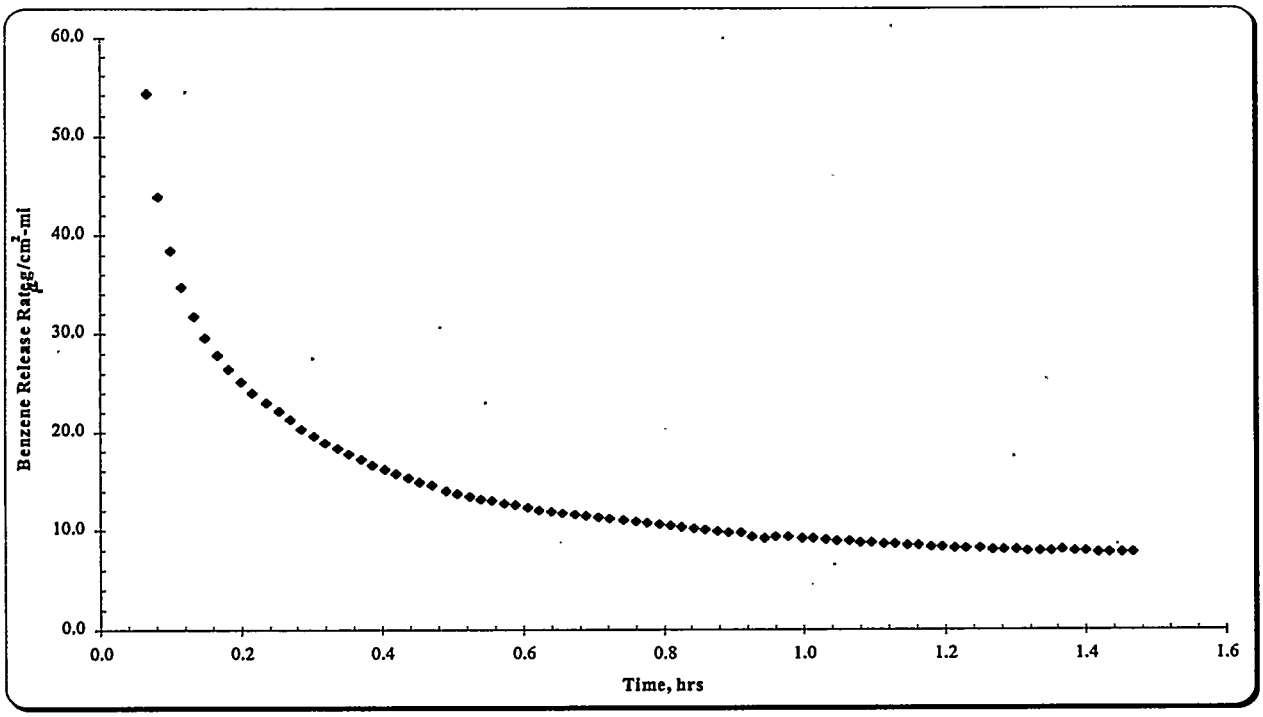

Figure 16a. Benzene Release (45°C) from Quiescent Slurry Homogenized with 20,653-ppm Benzene

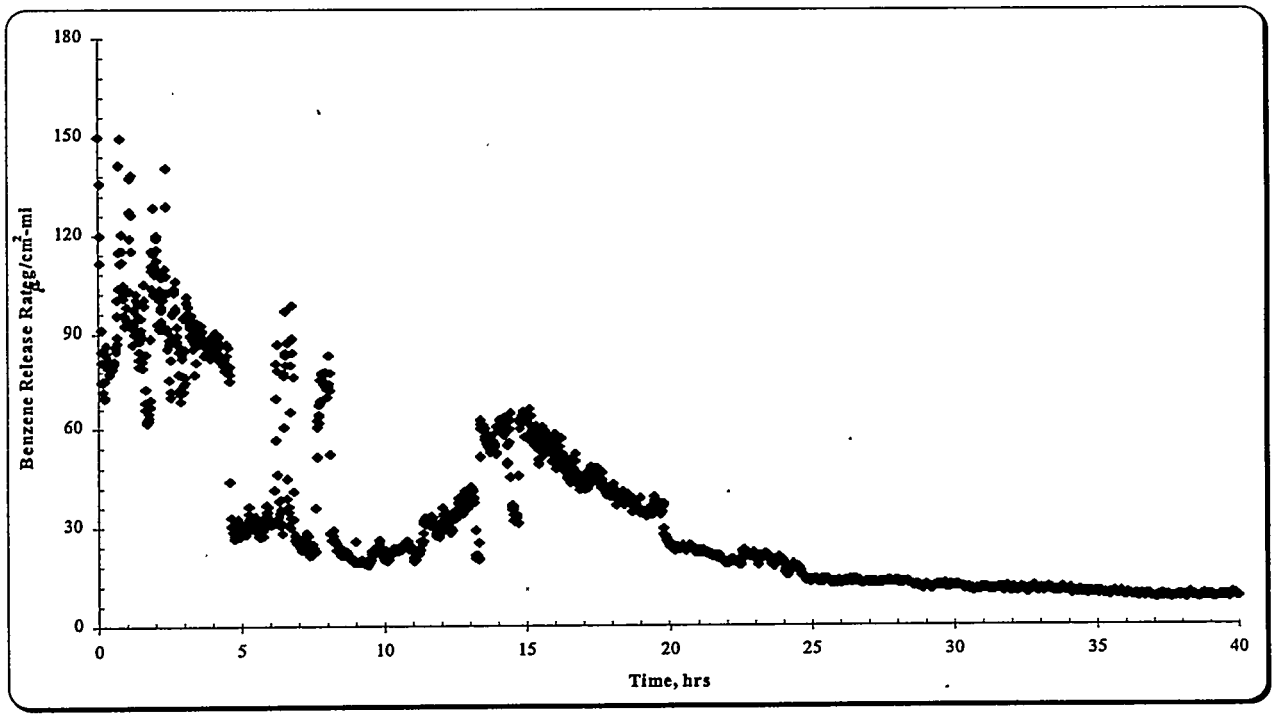

Figure 16b. Benzene Release (45°C) from Agitated Slurry Homogenized with 20,653-ppm Benzene

35–μg benzene/cm^2-min after 19 hours of agitation, 19-μg benzene/cm^2-min after 22 hours of agitation, and ~10-μg benzene/cm^2-min after 35 hours of agitation.

Figures 17a and 17b show the benzene release rate data at 35°C from one 90.71-g sample of KTPB slurry prepared by homogenizing 18,522-ppm benzene with a sample of slurry. Figure 17a shows the initial release rate data obtained without agitation, and Figure 17b shows the release rate data obtained after, with time zero being set at the onset of agitation following the data in Figure 17a. Figure 17a again shows that the release rate of benzene from the quiescent slurry surface declines rapidly until the initial headspace is purged. At that point, the release rate begins leveling off at just less than 20-μg benzene/cm^2-min after 0.2 hours of release, and becomes fairly level after 1 hour of release at just less than 8-μg benzene/cm^2-min.

Once agitation was initiated, Figure 17b shows the slurry begins to release benzene at 150 to 250-μg benzene/cm^2-min for about 2 hours. After that, the benzene release rate from the slurry quickly and steadily plummets from over 150-μg benzene/cm^2-min after 1.5 hours of agitation to ~95-μg benzene/cm^2-min after 3 hours of agitation and begins to level off at ~45-μg benzene/cm^2-min after 6 hours of agitation. The rate of benzene release continues to steadily drop, but at a much slower rate, reaching 30-μg benzene/cm^2-min after 15 hours of agitation, <16-μg benzene/cm^2-min after 25 hours of agitation, and <11-μg benzene/cm^2-min after 37 hours of agitation. The increase in release rate at 19 hours is probably a result of spontaneous agitation changes.

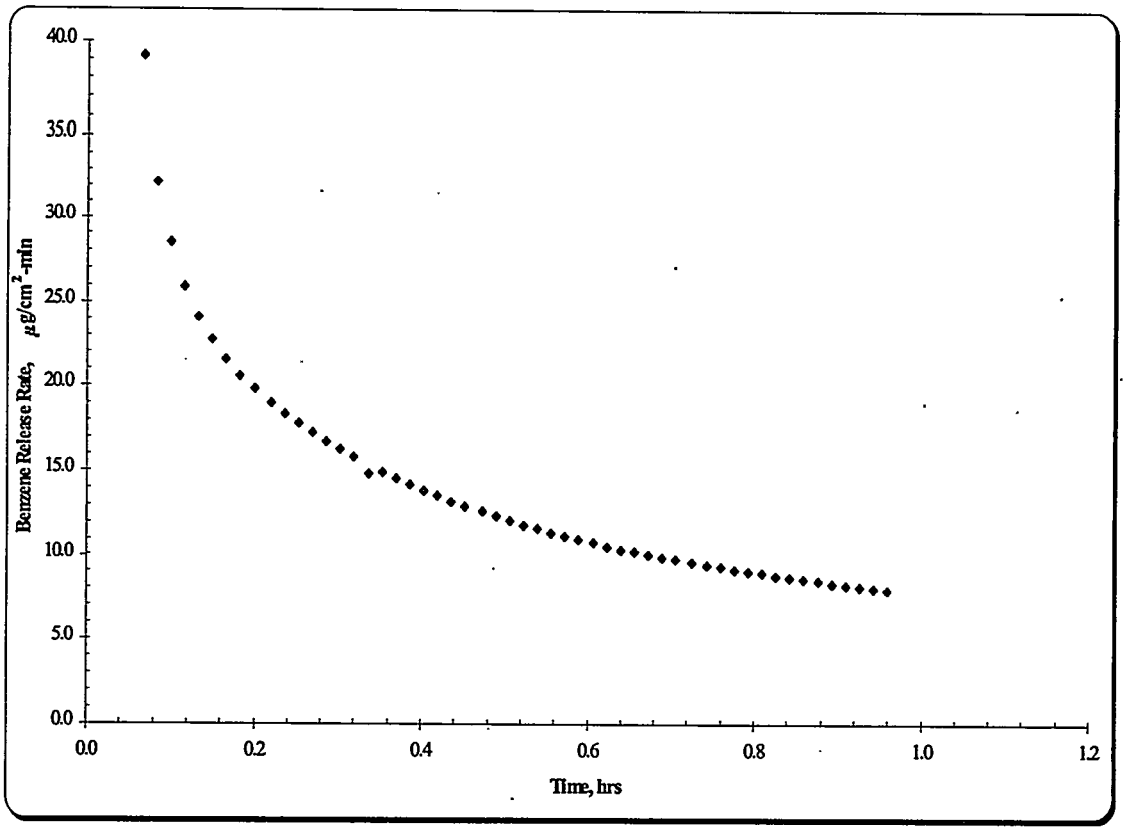

Figure 17a. Benzene Release (35°C) from Quiescent Slurry Homogenized with 18,522-ppm Benzene

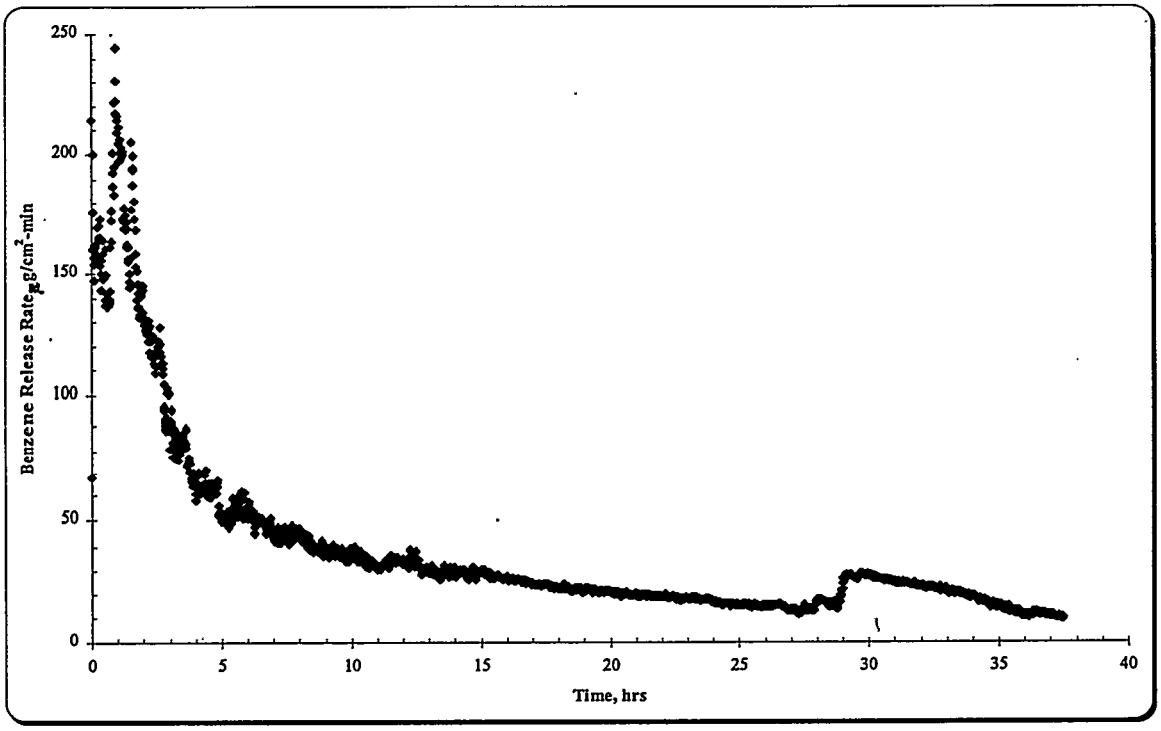

Figure 17b. Benzene Release (35°C) from Agitated Slurry Homogenized with 18,522-ppm Benzene

Temperature elevation appears to affect only the initial release of benzene from the slurry. With the samples prepared by homogenization of the benzene with the slurry, temperature elevation increases the initial release of benzene from less than 100-µg benzene/cm^2-min to well over 150-µg benzene/cm^2-min. However, after about 5 hours of agitation, there appear to be no temperature effect on the homogenized samples. With the samples prepared by freshly adding benzene to the slurry, temperature elevation appears, surprisingly, to give a slight decrease (~10%) to the rate of release of benzene from the slurry during the initial peak release period. Also with the freshly added benzene samples, temperature elevation appears to shorten the time span of the initial peak benzene release period.

Slurries from the Demo Column Experiment

Figures 18a and 18b show the benzene release rate data from one 78.77-g sample of KTPB slurry containing the DEMO column slurry with *in-situ* generated benzene. The concentration of benzene in this sample is not known. However, similar slurries have been examined at WSRC and determined to contain 4000 to 5000-ppm benzene. Figure 18a shows the initial release rate data obtained without agitation, and Figure 18b shows the release rate data obtained after initiating agitation, with time zero being set at the onset of agitation following the data in Figure 18a.

Figure 18a shows the release rate of benzene from the quiescent surface quickly decline until the initial headspace is purged. The release rate begins to level off at the 0.2-hour mark at 11.6-µg benzene/cm^2-min, and becomes fairly level after 1-hour of release at just less than 5.1-µg benzene/cm^2-min. Once agitation was initiated, Figure 18b shows that the release rate of benzene from the slurry

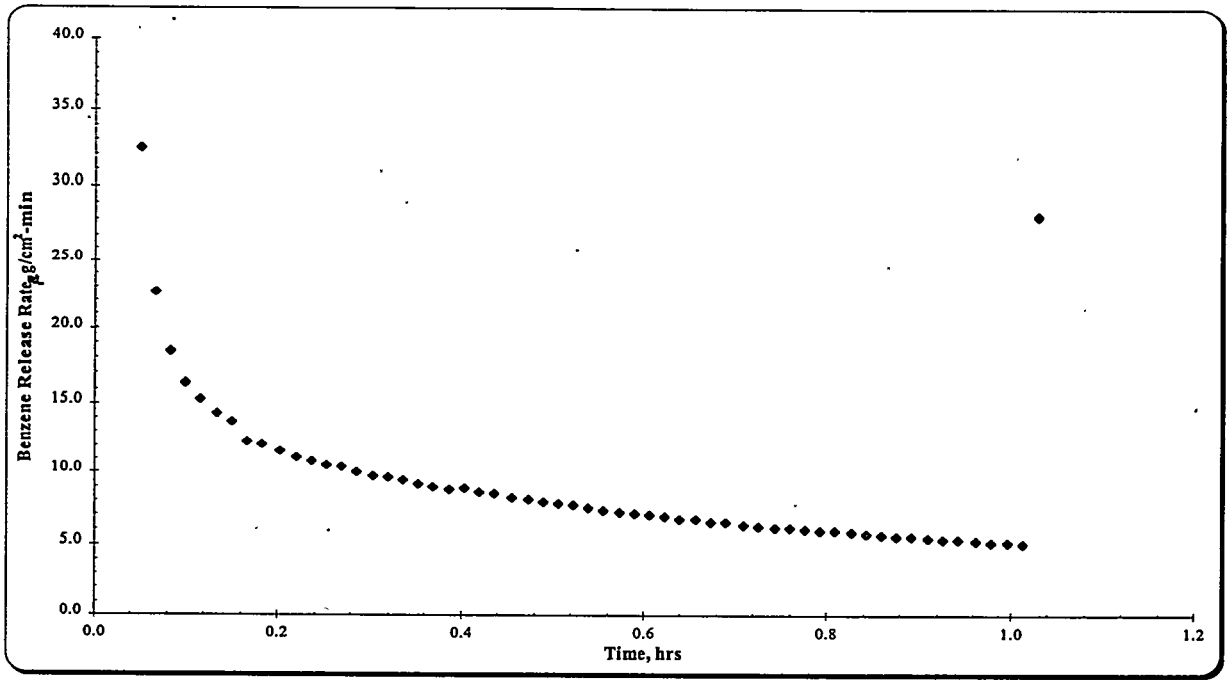

Figure 18a. Benzene Release from Quiescent DEMO Column Slurry Containing Benzene Generated *In Situ*

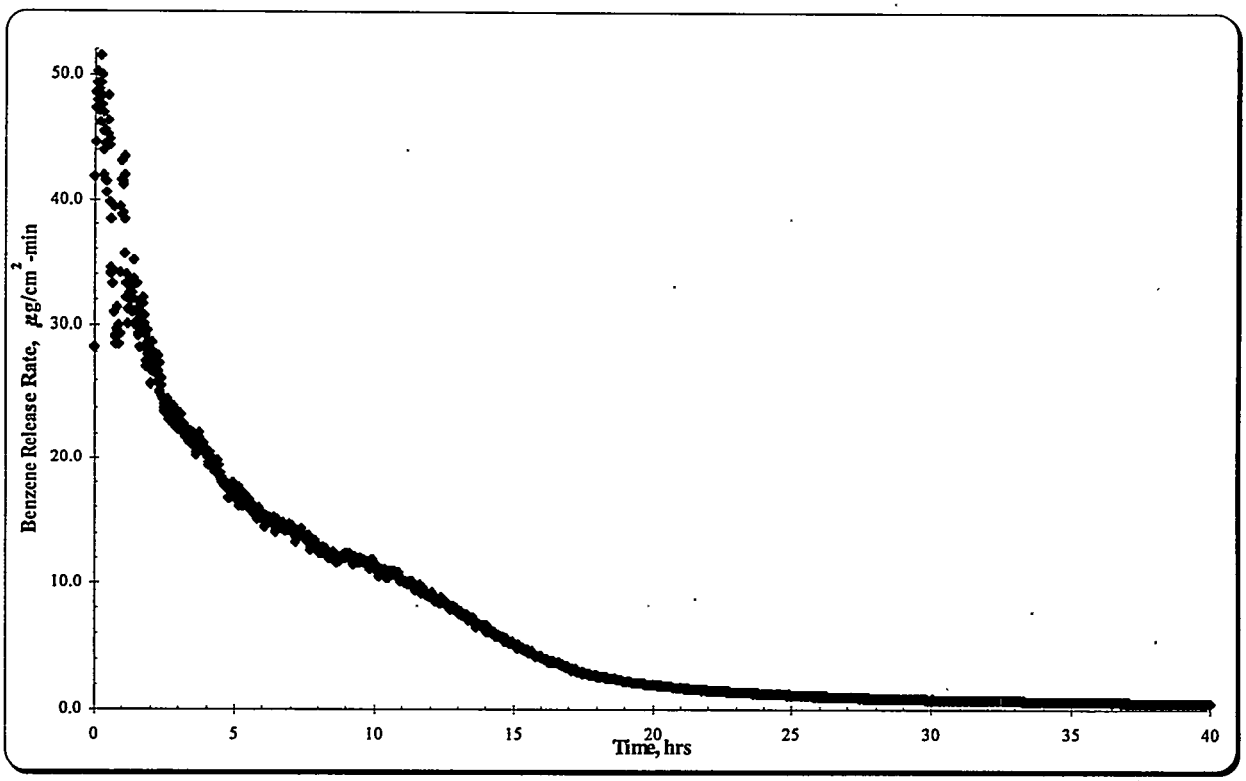

Figure 18b. Benzene Release from Agitated DEMO Column Slurry Containing Benzene Generated *In Situ*

quickly jumps up to 52-μg benzene/cm^2-min, but then immediately plummets to 24-μg benzene/cm^2-min after 2.5 hours of agitation and 17.5-μg benzene/cm^2-min after 5-hours of agitation. The rate of benzene release from the slurry continued to fall throughout the entire experiment, reaching 11.5-μg benzene/cm^2-min after 10 hours of agitation, 2-μg benzene/cm^2-min after 10 hours of agitation, and finally 0.5-μg benzene/cm^2-min after 40 hours of agitation.

The data in Figures 18a and 18b suggest that the DEMO column slurry sample (*in-situ* generated benzene) behaves like it contains both freshly added benzene and homogenized benzene. The DEMO column sample exhibited a slightly higher initial release rate (50-μg benzene/cm^2-min) than homogenized slurry with the equivalent initial benzene concentration (Figure 12b, 30-μg benzene/cm^2-min). The benzene in the DEMO column sample, however, was obviously not as effectively dispersed as in the homogenized slurries. The shape of the curve in Figure 18b suggests freshly added benzene release. Initially, the curve is concave down, followed by a somewhat brief concave up region, and followed again by a final extended concave down region. If we compare this curve with other figures, we find that it resembles the curves in Figures 5b, 6b, 7b, and 8b, the freshly added benzene experiments (at ambient temperature). In comparison, if we examine the curves in Figures 10b, 11b, and 12b, we see that the curves with these homogenized samples (at ambient temperature) exhibit much more of a concave down feature, and in some cases, are entirely concave down.

However, comparing the data in Figure 18a to the data in Figures 5a, 6a, 7a, and 8a for quiescent samples, the release rates in Figure 18a are much greater than would be anticipated from a slurry sample containing only dilute freshly added benzene. Thus, following the theory of benzene release previously

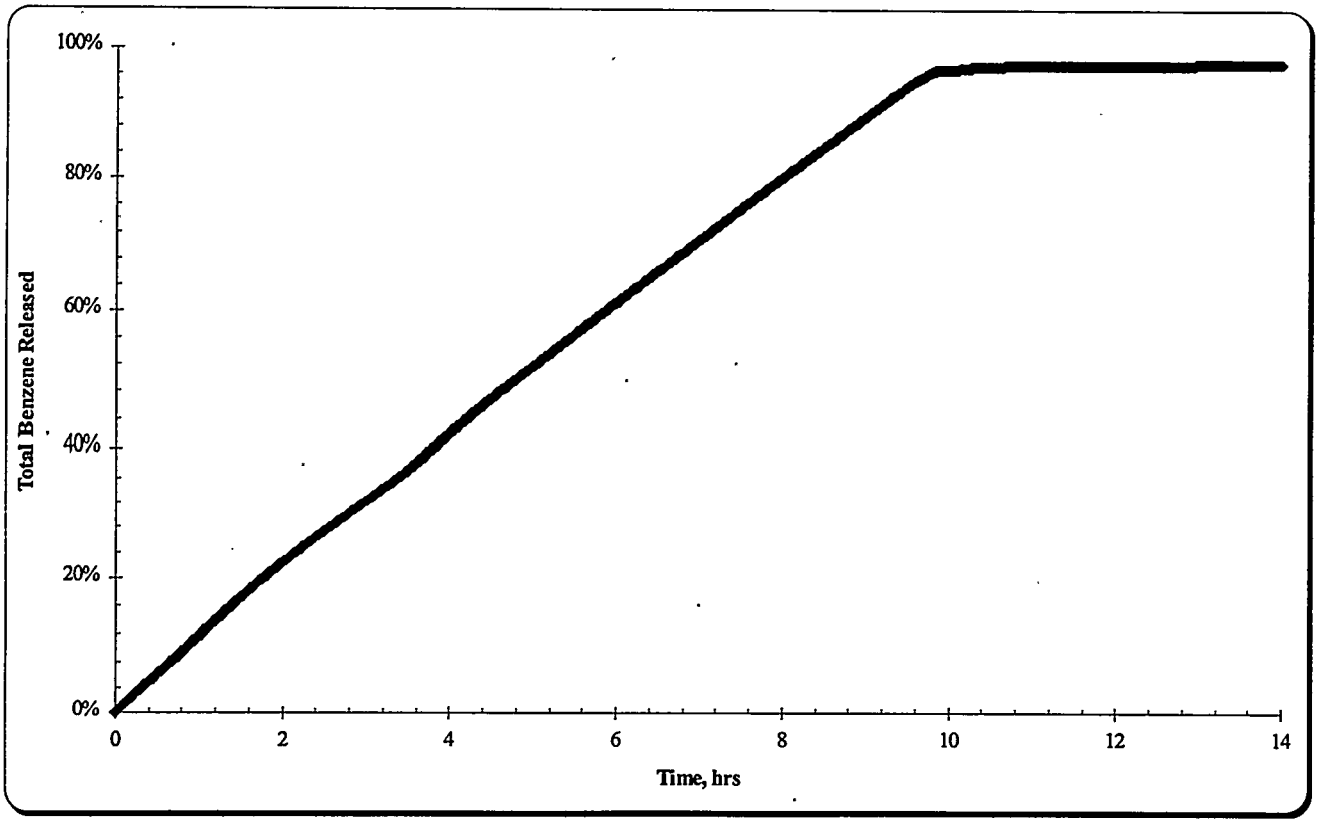

Figure 19. Total Benzene Release in Figure 4

discussed regarding the two important factors for significant benzene release, we believe that benzene is present fairly significantly in homogenized form.

Cumulative Benzene Release Results

The data from the samples prepared and tested by PNNL were integrated for total benzene release (all experiments except for the DEMO column sample). In addition, the data in Figure 4 was integrated for total benzene release as well and compared to the total amount of benzene placed on top of the slurry sample during preparation. This result is found in Figure 19 expressed as a percentage of the total benzene in the sample released versus time, and was used as a check on the accuracy of data generated with the slurry samples.

The following 13 figures (Figure 20 through Figure 32) show the integrated data for each of the experiments performed with slurry samples prepared by PNNL. These results confirm the high quality of rate data previously discussed in this report. The data generated from the first two samples prepared and tested gave what appeared to be about 120% to 140% release of benzene over the course of the experiment. This was one of the reasons for performing the release calibration experiment shown in Figure 4. As a result of the data found in Figure 4 and Figure 19, it was determined that the elevated release of benzene in those initial samples was the result of a GC calibration error (or calibration out of range). Thus, Figures 4 and 19 reflect the corrected benzene release values to give ~100% release of the benzene added to each sample. All other data were analyzed using properly calibrated GC results.

The data in Figures 20 through 32 show that almost all samples prepared by PNNL gave an

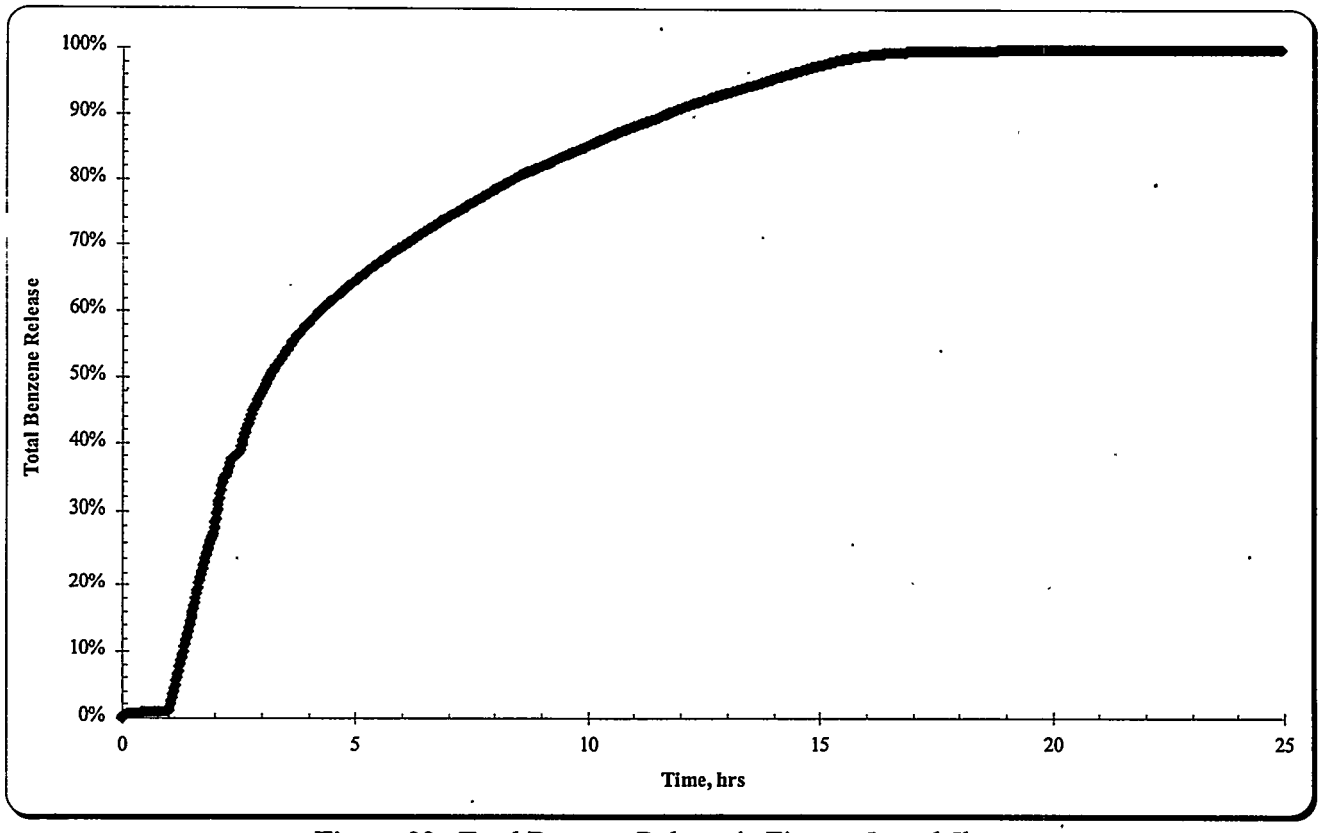

Figure 20. Total Benzene Release in Figures 5a and 5b

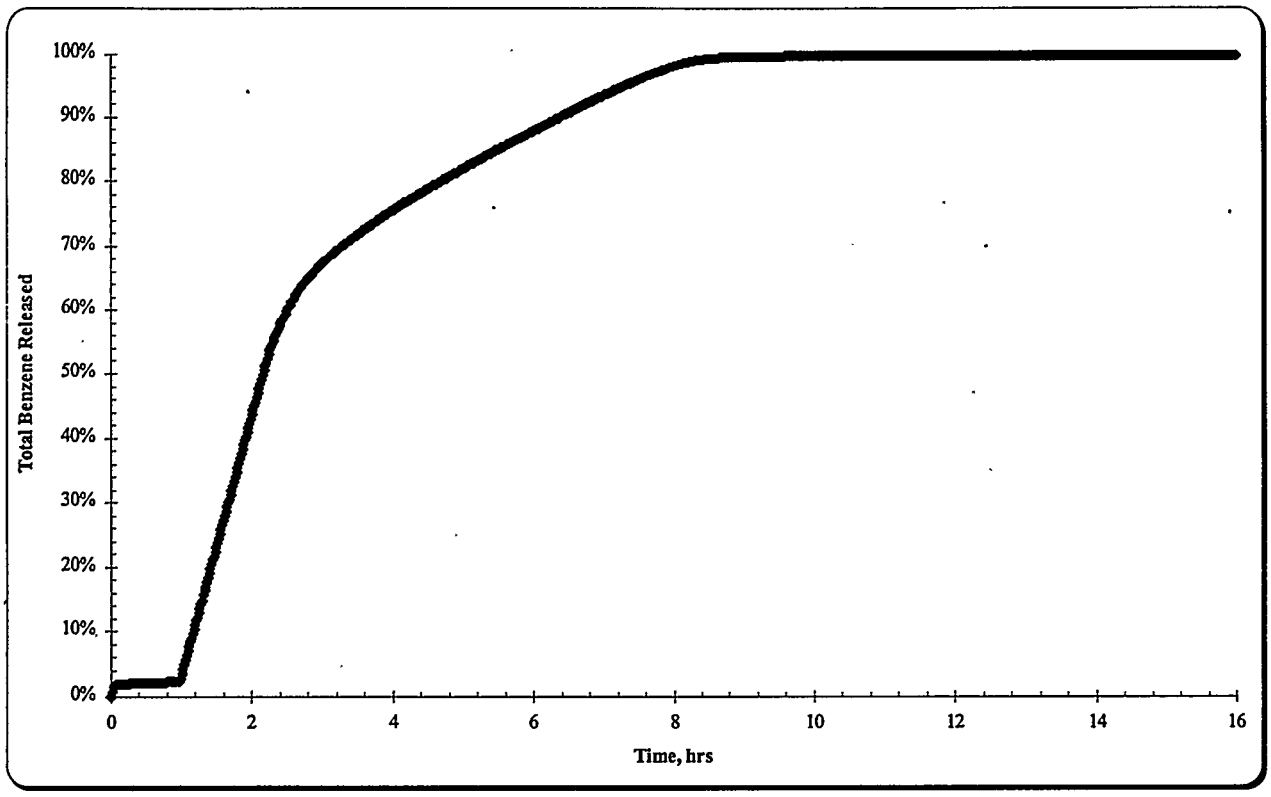

Figure 21. Total Benzene Release in Figures 6a and 6b

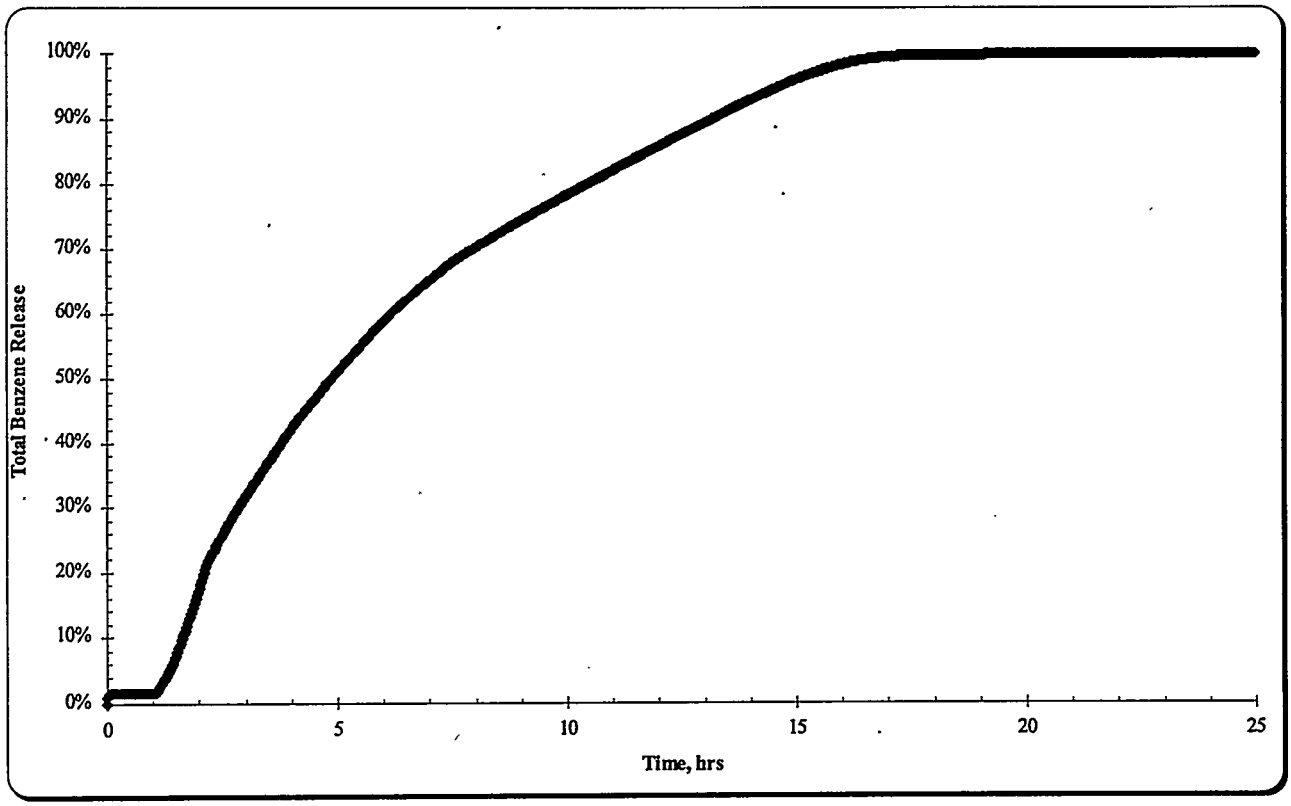

Figure 22. Total Benzene Release in Figures 7a and 7b

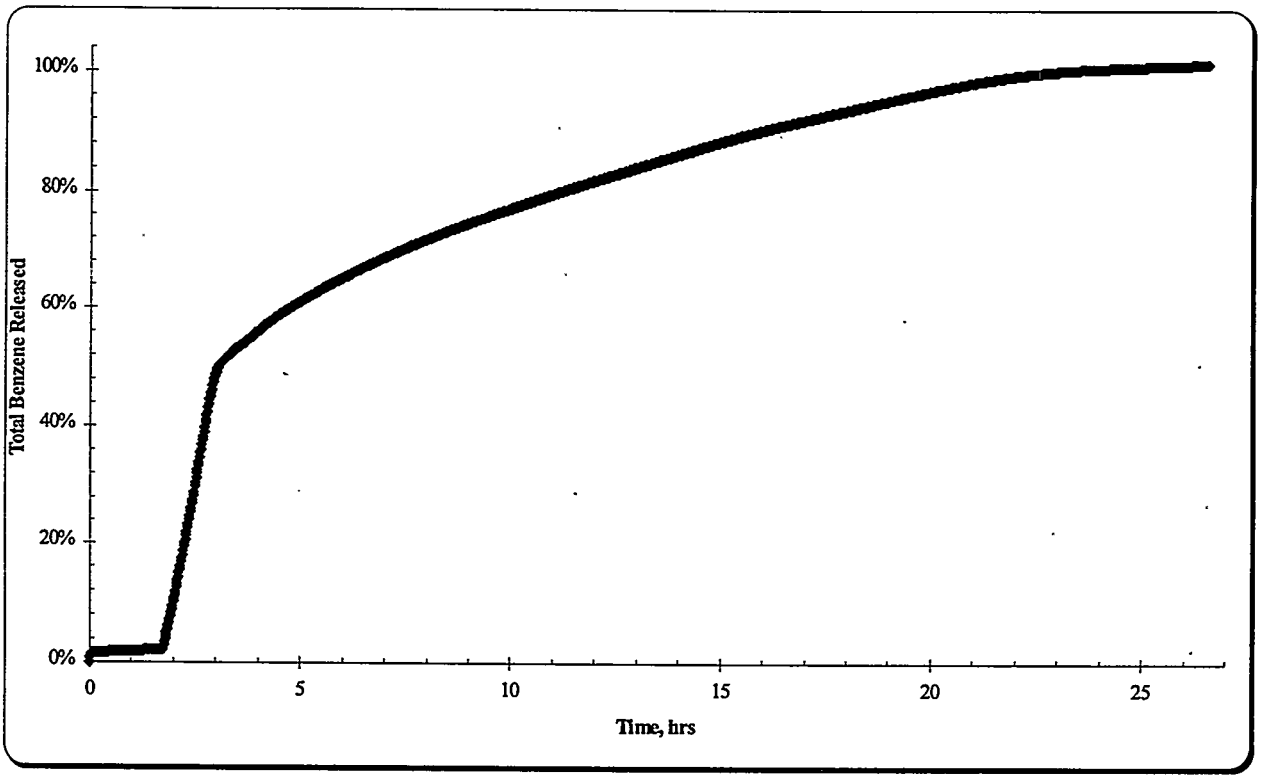

Figure 23. Total Benzene Release in Figures 8a and 8b

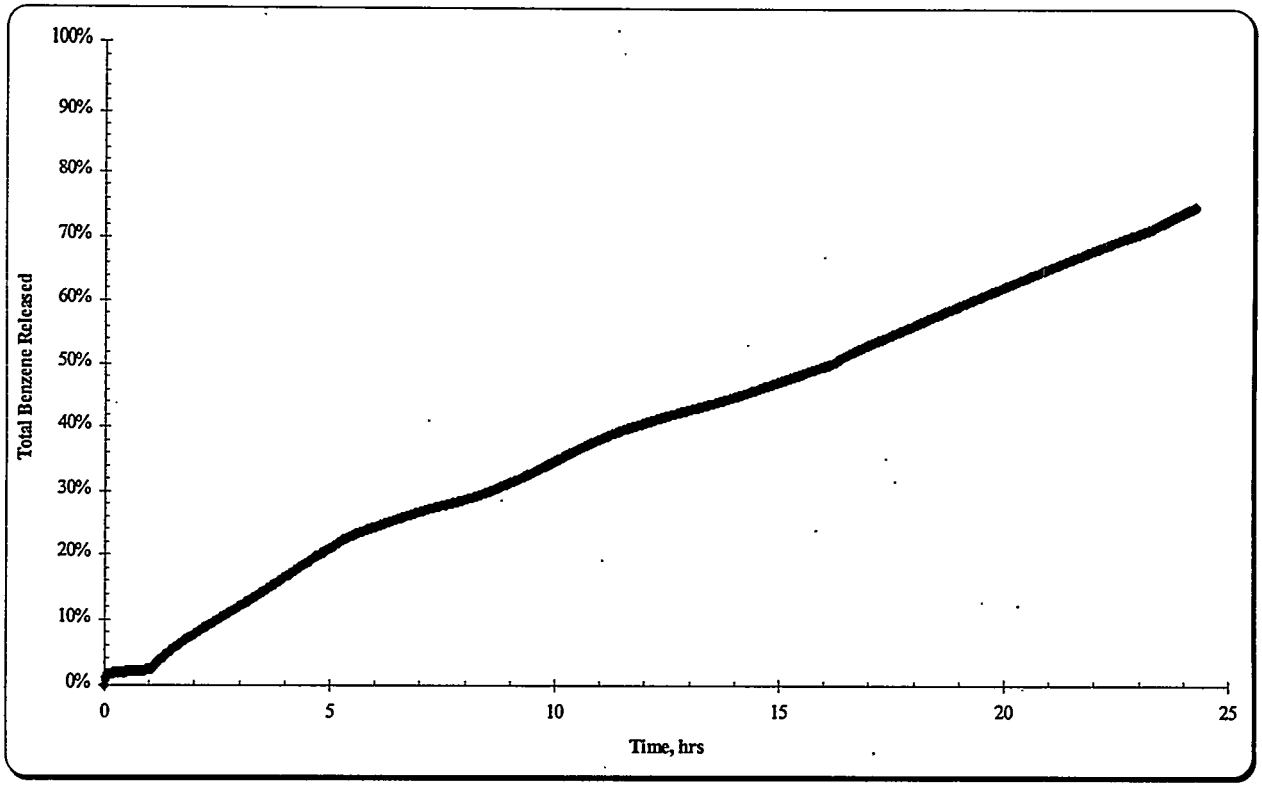

Figure 24. Total Benzene Release in Figures 9a and 9b

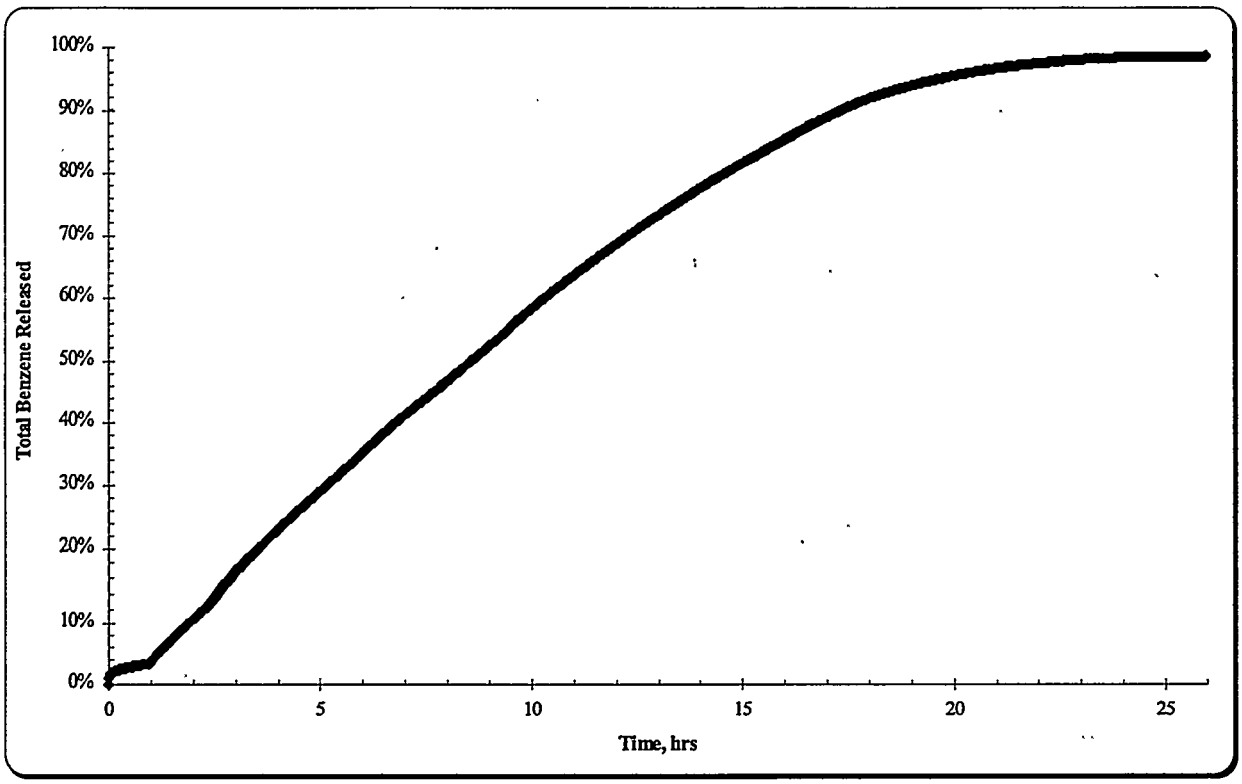

Figure 25. Total Benzene Release in Figures 10a and 10b

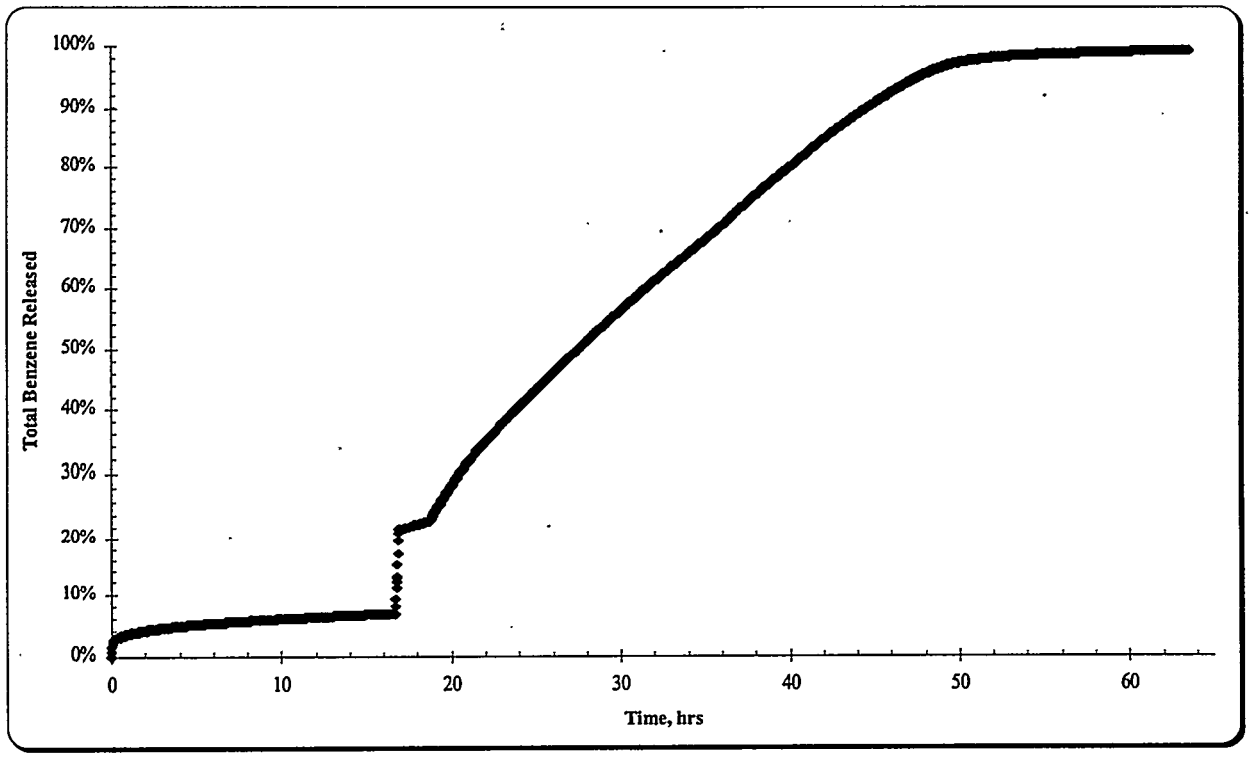

Figure 26. Total Benzene Release in Figures 11a and 11b

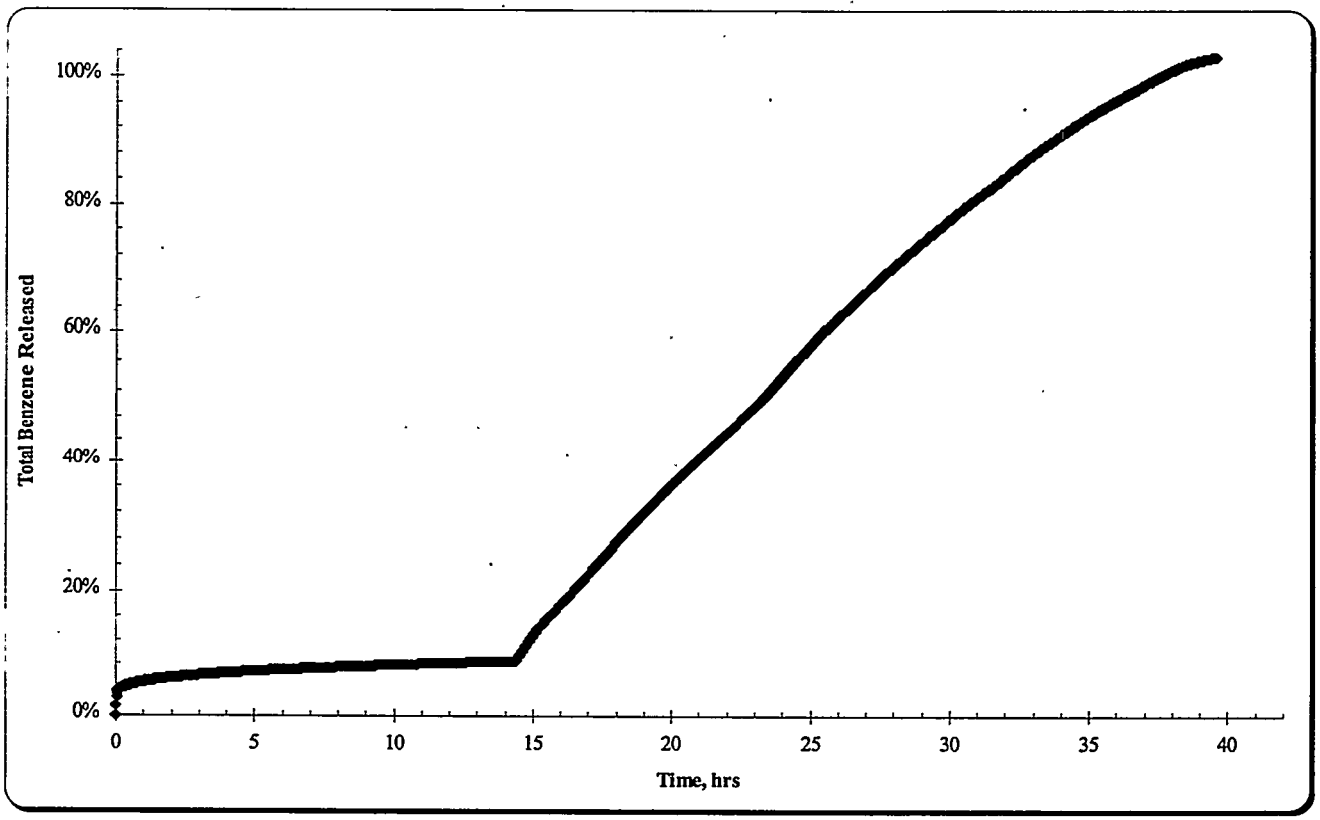

Figure 27. Total Benzene Release in Figures 12a and 12b

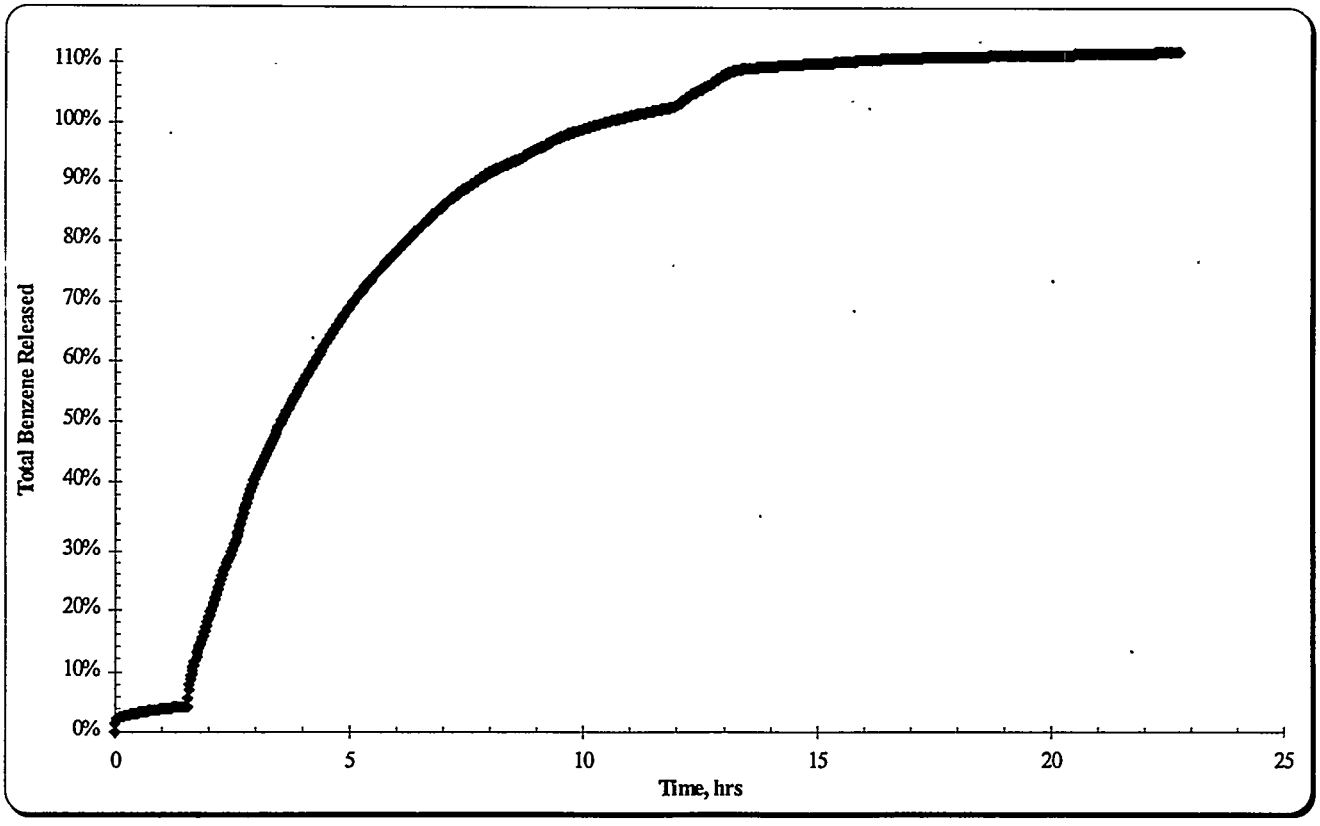

Figure 28. Total Benzene Release in Figures 13a and 13b

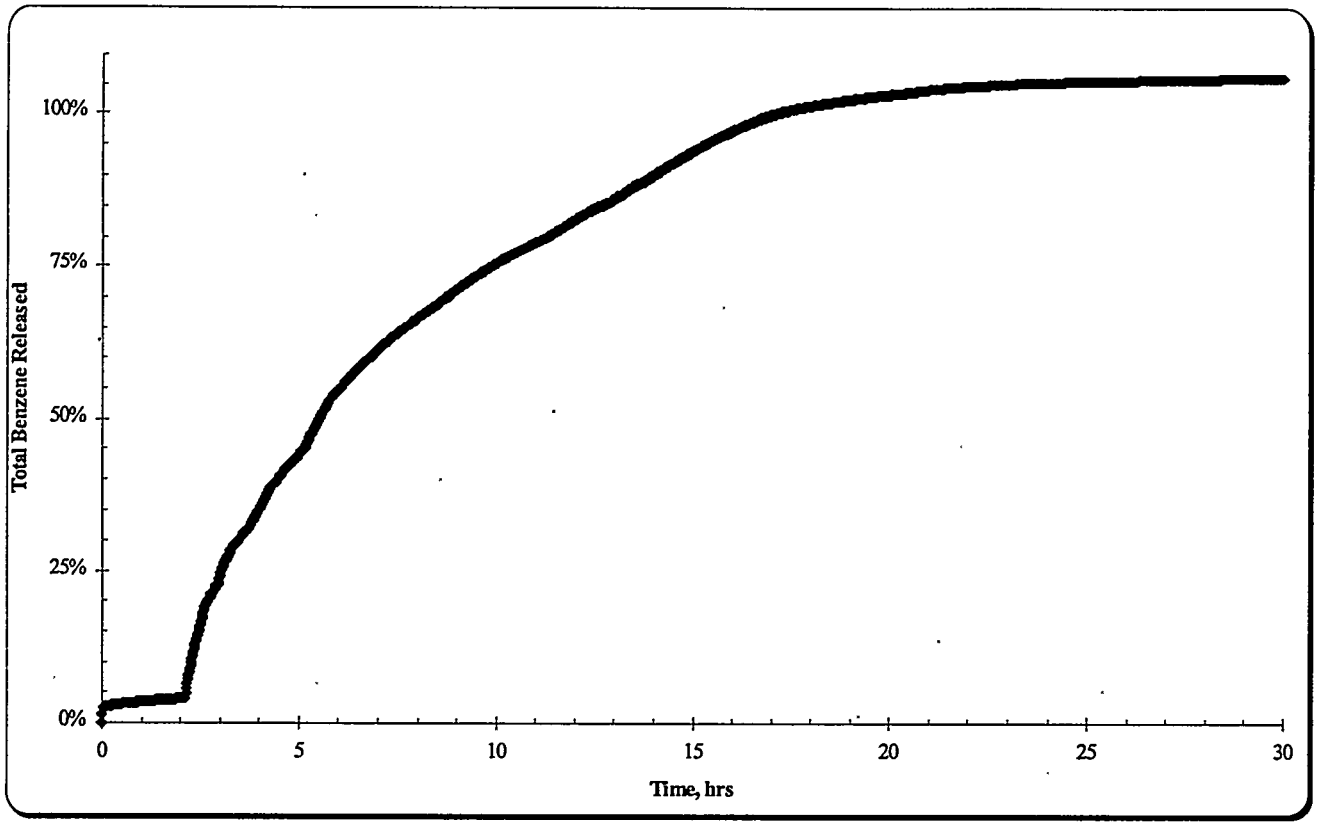

Figure 29. Total Benzene Release in Figures 14a and 14b

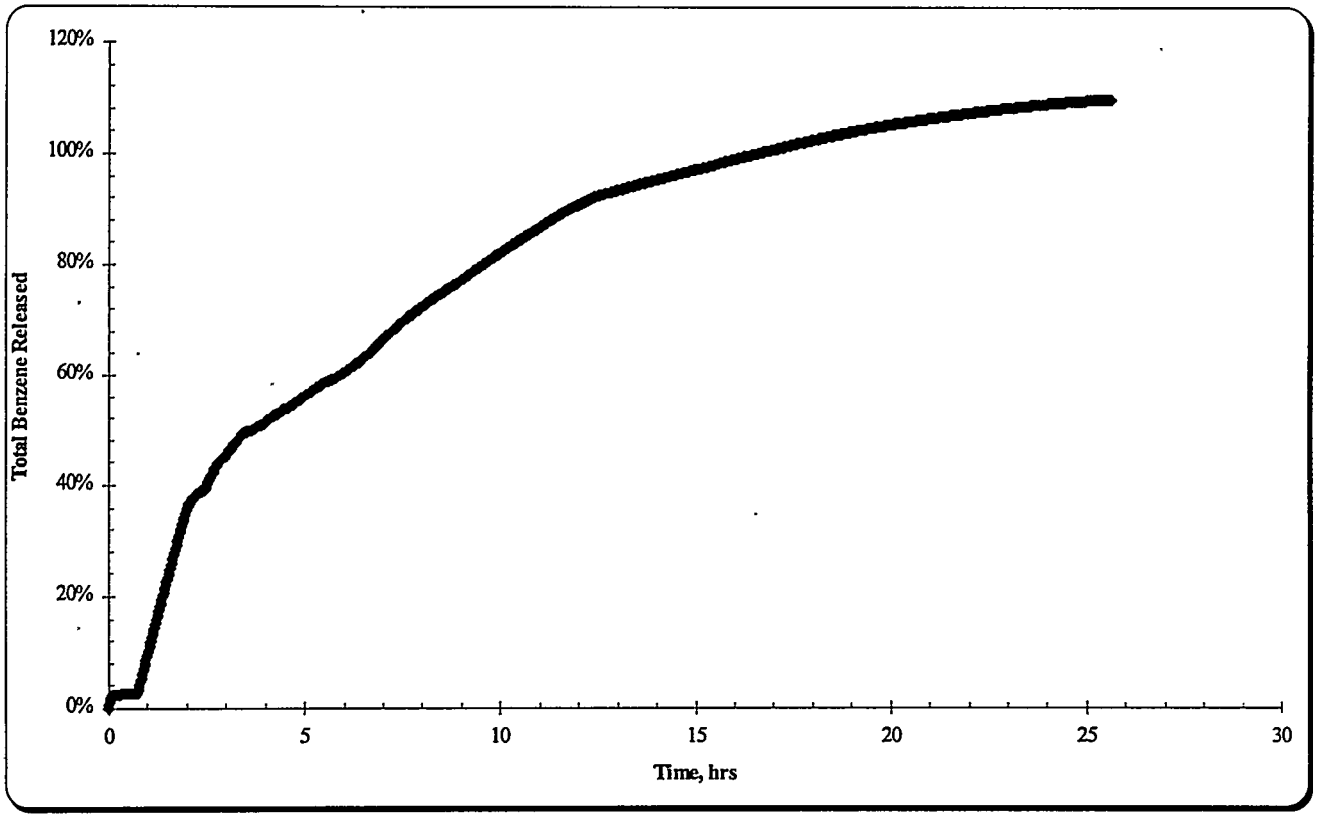

Figure 30. Total Benzene Release in Figures 15a and 15b

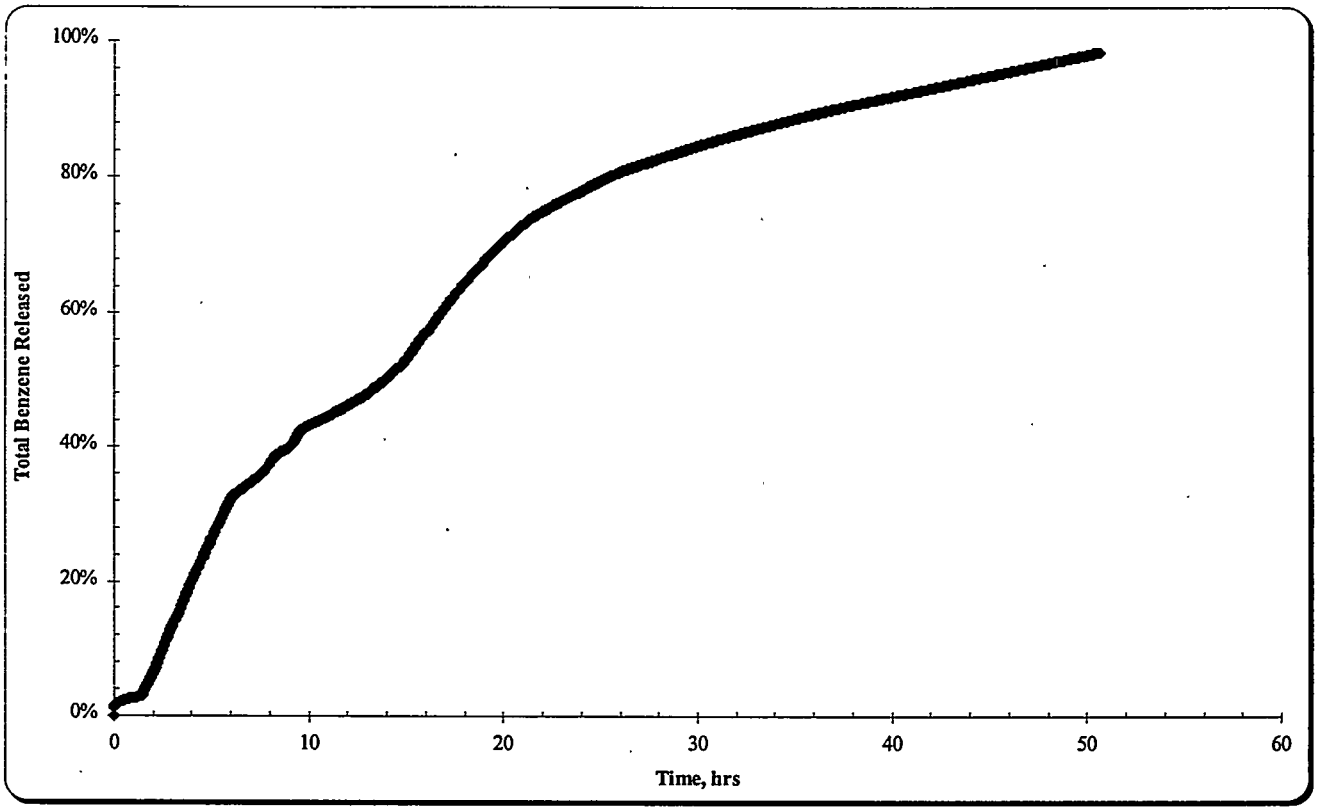

Figure 31. Total Benzene Release in Figures 16a and 16b

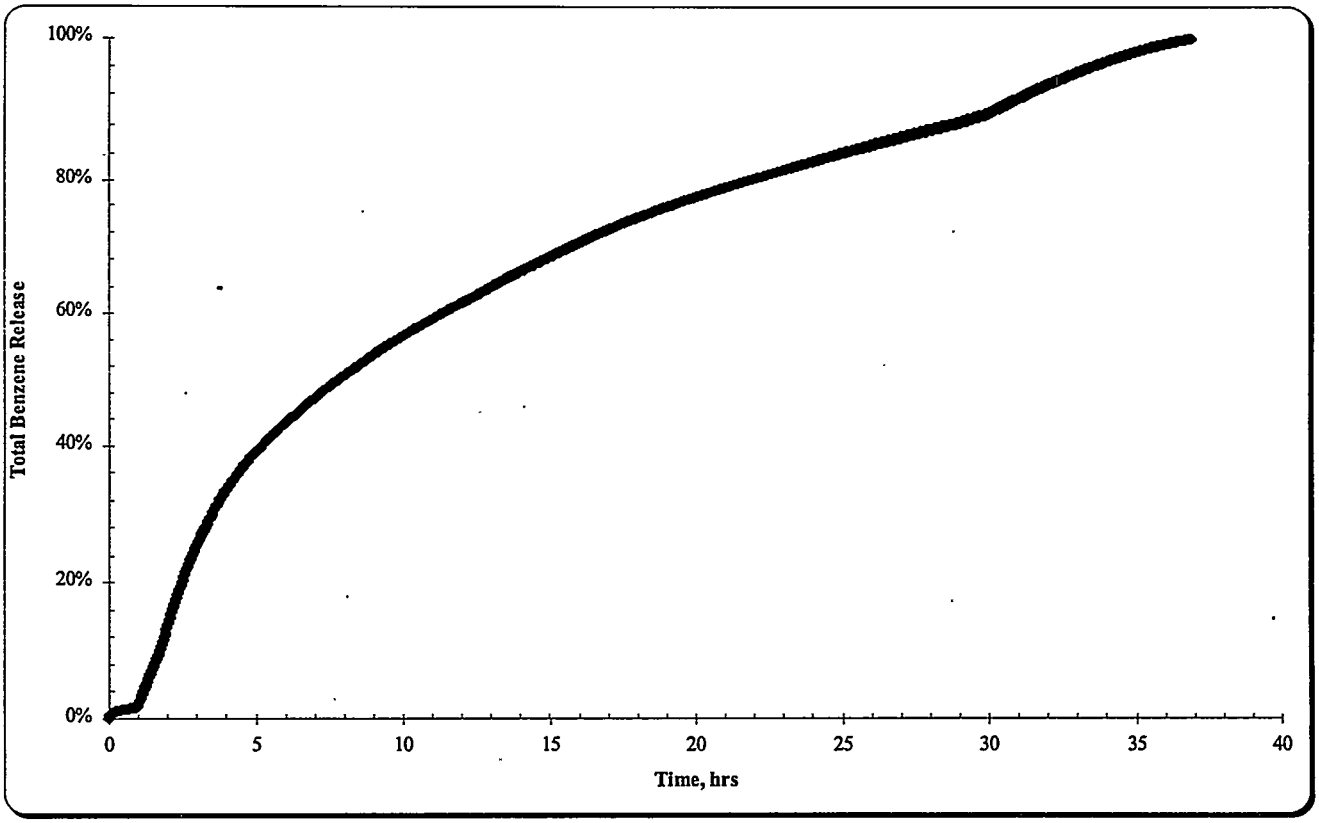

Figure 32. Total Benzene Release in Figures 17a and 17b

appropriate return of approximately 100% of the benzene added to each slurry sample. Previous studies (Rappé and Gauglitz 1997) showed that homogenized samples released very little of the benzene that was believed to be present. However, these samples had not been prepared locally (by PNNL). Therefore, it was undetermined whether the low benzene release indicated less benzene in the sample than thought to have been present or if it was an indication of a strong interaction between the benzene and the KTPB particles. It can now be determined that the samples analyzed in previous studies (Rappé and Gauglitz, 1997) did not contain nearly as much benzene as expected. Thus, it is believed that all slurry samples, given enough time, will release their entire benzene inventory, regardless of the configuration of the benzene within the slurry.

Summary and Conclusion

Experiments were performed on a variety of slurries prepared in various manners for the purpose of quantifying the release rate of benzene under various conditions. Tables 2 through 5 summarize the results of those tests discussed in the preceding sections.

Table 2. Agitated Ambient Temperature Release Rates of Benzene

Preparation Technique	Benzene Concentration	Initial Peak Benzene Release μg benzene/cm²-min		Long Term Release μg benzene/cm²-min
	(ppm)	magnitude	duration, hrs	
Freshly Added	15,730	375	1.0	40 - 60
Freshly Added	16,105	500	1.25	60 - 80
Freshly Added	16,585	450	1.2	20 - 40
Freshly Added	8,109	110	1.0	20 - 60
Homogenized	16,624	80	0.25	30 - 50
Homogenized	17,068	none	n/a	25 - 40
Homogenized	8,535	42	0.75	15 - 30
Homogenized	5,408	none	n/a	13 - 27
Freshly Added & Homogenized	18,212	250	1.0	20 - 150
DEMO Column	n/a	50	1.0	10 - 20

Table 2 summarizes the benzene release rates exhibited during agitation from the different slurry samples analyzed at room temperature. The release of benzene from KTPB slurry with readily releasable benzene droplets (fresh slurry) exhibits benzene release in two distinct regimes. An initial regime exists in which benzene is released from the slurry for about one hour at 400- to 500-μg benzene/cm²-min as if it is present as a freestanding layer on top of the slurry. Table 2 shows that as the concentration drops in the freshly added slurry, so does the magnitude of release from the slurry during this initial regime. A second regime exists in which benzene is released at a lower rate (about an order of magnitude lower) until the slurry becomes depleted of benzene. The magnitude of benzene release during this second regime seems to be independent of initial benzene concentration in the slurry at anywhere from 20- to 80-μg benzene/cm²-min. It is believed that the magnitude and duration of benzene release in the second regime is heavily dependent, though, on the agitation characteristics of the experiment. In comparison to earlier results (Rappé and Gauglitz 1997), these releases discussed are higher, which is expected because the gas purge flow through the apparatus was higher.

The release rates from homogenized slurry (no readily releasable droplets) had only a brief initial peak release rate (if any), followed by a steadily decreasing release rate. For slurry with ~16,000-ppm of benzene, the peak release was much less than 100-μg benzene/cm²-min but the longer-term rates were comparable to those of the fresh slurry samples. The longer-term release rates did decrease slightly with decreasing benzene concentration for homogenized slurries containing ~16,000-ppm to ~5,000-ppm benzene.

Table 3 summarizes the release rates of benzene from quiescent slurry for the different slurry samples at ambient temperature. The most interesting result in Table 3 is that the slurry prepared by homogenization yields higher releases of benzene from a quiescent sample (15- to 20-μg benzene/cm^2-min) than that of slurry prepared by gently premixing (8- to 10-μg benzene/cm^2-min). For freshly added benzene samples, as the initial concentration drops from ~16,000-ppm to ~8,000-ppm, the quiescent release drops off significantly by 75 to 80%. However, for the homogenized samples, the result is much different. The quiescent release from homogenized slurry containing ~8,000-ppm benzene is about the same as that at ~16,000-ppm benzene. And the release from slurry at ~5,000-ppm benzene is just about 33% lower.

Table 3. Quiescent Ambient Temperature Release Rates of Benzene

Preparation Technique	Benzene Concentration	Release Rate of Benzene μg benzene/cm^2-min	
	(ppm)	0.2-hours	1.0-hours
Freshly Added	15,730	9.7	4.0
Freshly Added	16,105	9.9	3.8
Freshly Added	16,585	8.4	3.6
Freshly Added	8,109	1.4	0.7
Homogenized	16,624	14.3	5.4
Homogenized	17,068	21.5	7.4
Homogenized	8,535	15.7	5.1
Homogenized	5,408	9.5	3.7
Freshly Added & Homogenized	18,212	25.0	10.5
DEMO Column	n/a	11.6	5.1

A theory to explain the observed benzene release behavior has been hypothesized. A slurry sample must contain or be subjected to two important factors for significant benzene release. These two factors are (1) a source of readily releasable benzene, and (2) a pathway for ease of release. The most common form of readily releasable benzene in these experiments is benzene in the form of droplets. The most common benzene release pathways would be benzene homogenized with slurry resulting in wetted particle surfaces and agitation.

Release rates during agitation from a test slurry blended from the two separate slurries containing readily releasable benzene droplets (fresh slurry) and homogenized slurry (no readily releasable droplets) has a release rate behavior intermediate to the results of the different slurries tested individually. The release rate began at roughly 250-μg benzene/cm^2-min and dropped off steadily to zero. However, quiescent benzene release from the blended sample was greater than both homogenized and freshly added samples. The quiescent release behavior of this blended sample makes sense in light of the proposed benzene release mechanisms.

Tables 4 and 5 summarize the benzene release rates both from quiescent slurry and during agitation, respectively, from the different slurry samples analyzed at elevated temperatures (35°C and 45°C). Two results are worth noting. First, results in Table 4 show that temperature elevation appears to slightly enhance the transport of benzene droplets towards the slurry surface, resulting in an increased release from quiescent slurry samples prepared by freshly adding benzene. The benzene release from quiescent slurry also slightly increased from homogenized samples, but only by very little. Secondly, results in Table 5 show that temperature elevation appears to provide homogenized slurry samples with more readily releasable benzene, resulting in an increased initial peak benzene release upon agitation.

Table 4. Quiescent Varying Temperature Release Rates of Benzene

Preparation Technique	Benzene Concentration (ppm)	Temperature of Analysis	Release Rate of Benzene µg benzene/cm²-min	
			0.2-hours	1.0-hours
Freshly Added	15,730	ambient	9.7	4.0
Freshly Added	16,105	ambient	9.9	3.8
Freshly Added	16,585	ambient	8.4	3.6
Freshly Added	17,323	45°C	17.4	7.4
Homogenized	16,624	ambient	14.3	5.4
Homogenized	17,068	ambient	21.5	7.4
Homogenized	19,024	45°C	15.9	5.5
Homogenized	20,653	45°C	25.1	9.2
Homogenized	18,522	35°C	19.8	7.8

Table 5. Agitated Varying Temperature Release Rates of Benzene

Preparation Technique	Benzene Concentration (ppm)	Temperature of Analysis	Initial Peak Benzene Release µg benzene/cm²-min		Long Term Release µg benzene/cm²-min
			magnitude	duration, hrs	
Freshly Added	15,730	ambient	375	1.0	40 - 60
Freshly Added	16,105	ambient	500	1.25	60 - 80
Freshly Added	16,585	ambient	450	1.2	20 - 40
Freshly Added	17,323	45°C	350	0.5	40 - 100
Homogenized	16,624	ambient	80	0.25	30 - 50
Homogenized	17,068	ambient	none	n/a	25 - 40
Homogenized	19,024	45°C	350	1.25	20 - 100
Homogenized	20,653	45°C	90	4.5	10 - 60
Homogenized	18,522	35°C	175	1.4	15 - 70

Comparing the benzene release theory with the data in Figures 18a and 18b, it is believed that the DEMO-column slurry sample generating benzene *in situ* behaves like it contains dilute amounts of benzene in both droplet (freshly added) and wetted (homogenized) form. The magnitude of benzene release during agitation was most similar to that of the homogenized slurry samples. However, the curve generated by the data from the experiment resembled that from freshly added benzene samples.

The level of agitation appears to strongly affect the release rate. While experiments had essentially the same agitation, it was set by visual observation of slurry surface recirculation. We believe that some variation in the release rates for duplicate experiments is largely due to small differences in the agitation rate.

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