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

K.G. Rappé
P.A. Gauglitz

September 1997

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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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 a 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 both 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 3 minutes. The following 75-mL samples were measured for release rates: KTPB slurry with 15,000 ppm freshly added benzene that was gently mixed with the slurry, KTPB slurry homogenized (energetically mixed) with 15,000 ppm and 5,000 ppm benzene, clear and filtered KTPB salt solution saturated with benzene (with and without a pure benzene layer on top of the solution), and a slurry sample from a large demonstration experiment (DEMO slurry) containing benzene generated *in situ*.

Benzene release rates for the KTPB slurry with 15,000 ppm freshly added benzene averaged between 100 and 300 µg benzene/cm^2-min with gentle agitation, and about 4 to 6 µg benzene/cm^2-min without agitation. For comparison, measurements showed that a floating layer of pure benzene gave about a 400 µg benzene/cm^2-min release rate. Release rates for the KTPB slurry homogenized with 15,000 ppm benzene was ~30 µg benzene/cm^2-min with gentle agitation, and about the same as above (4 to 6 µg benzene/cm^2-min) without agitation. And the release rate for KTPB slurry homogenized with 5,000 ppm benzene was ~2 µg benzene/cm^2-min with gentle agitation. Benzene release rates for the DEMO column slurry sample were generally less than 0.1 µg benzene/cm^2-min, which is much lower than all other tests. The data suggested that the DEMO slurry contained no free excess benzene, and the benzene concentration in the salt solution of the slurry was low. Additionally, agitation was shown to have a significant effect on the release of benzene from the 15,000-ppm benzene slurry samples (unhomogenized and homogenized).

Based on these results, slurries with 15,000 ppm of freshly added benzene behaved similarly to the limiting situation of a floating layer of benzene. These somewhat surprising results suggest that even though the freshly added benzene was dispersed in the slurry, the benzene evaporated like a floating free phase. As expected, the homogenized samples where the benzene was largely coating the KTPB slurry particles gave much lower release rates. The 5,000-ppm homogenized sample had about a 10-fold lower release rate than the 15,000-ppm homogenized sample. Sample preparation for these two samples was done in the same manner. Therefore this result is unexpected since the benzene configuration in the sample of coating slurry particles is expected to be somewhat the same with these two samples.

Finally, it is not clear why the release rate from the DEMO slurry sample was lower than any of the other samples, but this suggests that the slurry contained no benzene droplets. Two explanations have been hypothesized to account for this discrepancy. One, there was problem with the homogenization or shipping

effort that resulted in lower than expected amounts of benzene in the slurry samples before the release experiments. Two, the release results are real, and the the low benzene releases are due to a benzene configuration in the slurry that results in benzene not being easily released from the slurry, a phenomenon termed here as "unreleasable" benzene.

It is suggested that further benzene release testing be performed to measure benzene release on samples under different conditions, and on additional homogenized and *in situ* generated benzene samples to confirm or refute the benzene release data given in this report.

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 samples used in this study. The authors also wish to thank Stacey Kaley for her technical advice and help with various aspects of this research, namely, trouble shooting the analytical equipment.

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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 a 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 both 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.

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 high level waste (HLW) salt solution (Dworjanyn 1997). Due to the flammability and toxilogical safety concerns, ITP operations were halted to investigate the phenomena of benzene generation, retention, and release from the slurry.

This led to 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 was formed composed of benzene droplets coated by hydrophobic KTPB (Dworjanyn 1997). Upon further premixing, the benzene droplets seemed to disperse, forming a homogenized structure where the benzene has 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 when benzene is coating the slurry particles, 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. This information will be compared with release rates and retention mechanisms of slurry samples take 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 have a better understanding of the phenomena that occurred during recent ITP processes, and 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 and filtered salt solutions exhibiting different benzene retention mechanisms as a result of different benzene concentrations, extent of premixing, and the level of agitation during the release experiments. 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 *in situ* DEMO-column slurry sample that generates benzene.

The following experiments were conducted to achieve the above objectives. First, a stock KTPB slurry containing ~15,000 ppm benzene was measured for benzene release. Different samples of this same material were analyzed to examine (1) the effect of agitation on the release rate and (2) the effect of a rapid initial headspace vapor purge on the initial release rate.

Next, two KTPB slurries homogenized with ~15,000 ppm benzene and ~5,000 ppm benzene were measured for benzene release while lightly agitated (intermittently halting agitation to, again, examine the effect). Homogenization took place with a hand-held shaft homogenizer and was performed by WSRC before shipment of the samples to PNNL.

Then, the benzene release of a clear, filtered KTPB slurry salt solution saturated with benzene and filtered with a 0.20-μm Teflon filter (filtered by WSRC before shipment of the samples to PNNL) was examined multiple times once with continuous agitation, once with a standing layer of pure benzene on top of the continuously agitated saturated salt solution, and once with no agitation.

And finally, the benzene release rate of an *in situ* generated benzene (DEMO column) sample was examined with continuous light agitation.

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 0-100 standard cubic centimeter per minute (sccm) mass flow controller. The flow throughout these tests was set at 15.1 sccm unless otherwise noted (e.g., headspace purging).

Flow from the Brooks flow controller passes through a 0 to 100 psia Digiquartz pressure transducer 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's 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 initernal 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, which includes the total headspace in the flat bottom flask over the liquid (35.7-mL) plus 1.83-meters (6-ft.) of 3.175-mm diameter (1/8-in.) stainless steel tubing with a 0.89-mm-thick (0.035-inch-thick) wall (0.467 mL/ft).

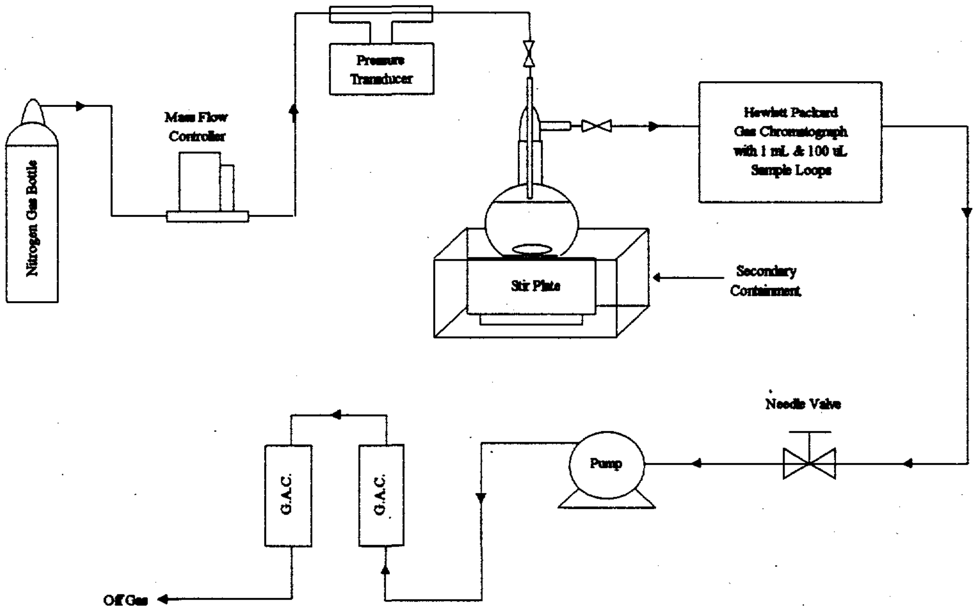

Figure 1: Flow System Diagram

The purged headspace from the sample vessel flows out through an exiting on/off throttle valve 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.

When in operation, the sample vessel was kept on a stir plate for agitation purposes. When agitation was necessary, it was supplied 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. In front of the bin, a plexiglass shield was in place to shield the user and any others in the laboratory should the glass vessel pressurize and rupture.

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

Sample Preparation

Local (PNNL) sample preparation took place in the fume hood in Laboratory 108 of 324/300. A stock slurry simulant was provided by WSRC to prepare freshly added benzene slurry samples. A detailed chemical make-up of that simulant can be found in Table 1. WSRC provided homogenized samples of benzene in KTPB slurry at approximately 5,000 and 15,000-ppm benzene, a clear salt solution from the slurry prefiltered with a 0.2 Teflon filter, and an *in situ* sample from the DEMO columns at Savannah River.

For each sample preparation using WSRC stock slurry and freshly added benzene, the amount of slurry necessary would be estimated by sight volumetrically. The corresponding amount of benzene to be used would then be estimated by site volumetrically and quantified gravimetrically. One-half of the slurry would be added to the test flask, then the benzene would be added, and then the remaining slurry would be added. The entire sample would then be weighed to confirm the amount of slurry used. Concentration units in the slurry phase are reported as parts per million (ppm) on a weight basis.

The clear salt solution provided by WSRC was placed in a small mouth bottle sealed by a cap with septum, with sufficient benzene added to saturate it. The solution was agitated for an extended period of time, and then allowed to sit, cap and septum downward, to allow complete phase separation of the benzene-saturated salt solution (bottom) and the pure benzene (top). After phase separation, the saturated solution was removed from the bottom through the septum with a needle and syringe and placed in a separate sealed vessel. After sufficient sample had been acquired, the amount of solution necessary for the release experiment was estimated volumetrically by sight and then determined gravimetrically.

Upon preparation, each sample in the test flask would be immediately capped, agitated by hand for approximately 1 minute, then placed inline in the flow apparatus with itself sealed off from flow by having the throttle valves at the inlet and outlet of the vessel in the "off" position. The sample would then be continuously gently agitated with a stir bar for at least 1 hour, nominally approximately 2 hours. When the sample had been sufficiently agitated, data accumulation was started and then flow of nitrogen began through the sample vessel headspace by turning the ball valves to the "on" position (while continuing to agitate unless otherwise noted). In the cases where the headspace was initially purged, the flow of nitrogen would be started at approximately 100 sccm, then decreased to 15.1 sccm after 1 minute.

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). The pictures show, for the homogenized sample, 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.

Table 1. Make-up 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. Make-up of 4.2 M Na KTPB Stock Slurry

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

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 30-meter-length, 0.5- mm-I.D. Alltech Carbograph™ capillary column with helium carrier gas flowing through the column. 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 flame ionization detector (FID) is used on the GC. An FID will record a response anytime anything comes through 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 exert no response to the permanent gases (N_2, O_2, H_2O, CO, CO_2, etc.).

An initial 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. FID response does not drift appreciably, but calibration was repeated regularly to change the range of calibration for different sets of experiments. To adjust the range as necessary, a single point calibration (multiple analyses of a single standard of known concentration) was therefore performed between every second to third experiment at a benzene concentration varying between 10,000 and 80,000 ppm. 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 would be placed in a gas sample bag, diluted if necessary, and then 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.

Through a Visual Basic™ program, generated data are stored in a text file. The data generated include GC file name, time of sample, date of sample, retention time of benzene, and FID response of benzene. These data can then be imported into an MS 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:

$$ReleaseRate_{benzene_{0,1}} = \frac{average[C_0,C_1] \times F_{avg} \times P_{avg} \times MW_{benzene}}{A_S \times R_G \times T}$$

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 (3 minutes, unless otherwise noted).

Experimental Results and Observations

A total of 10 benzene release experiments are discussed in the following. These tests can be grouped into five general categories: ~15,000 ppm benzene freshly added to KTPB slurry, ~15,000 ppm benzene homogenized with KTPB slurry, ~5,000 ppm benzene homogenized with KTPB slurry, clear, filtered salt solution from KTPB slurry saturated with benzene, and *in situ* benzene generating DEMO column slurry. The release data, as mentioned above, will be release rates presented as a flux of benzene crossing the air/liquid (air/slurry) interface, μg benzene/cm^2-min. Release rates from the homogenized and unhomogenized samples will be examined and compared. Release rates from the clear, filtered salt solution will be examined and compared with the homogenized and unhomogenized samples. And finally, release rates from the DEMO column slurry will be examined and compared to the previously discussed prepared slurries.

Figure 2 shows benzene release rate data from a clear, filtered salt solution saturated with benzene beginning with a standing layer of pure benzene on top of the solution. 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 quality of data production.

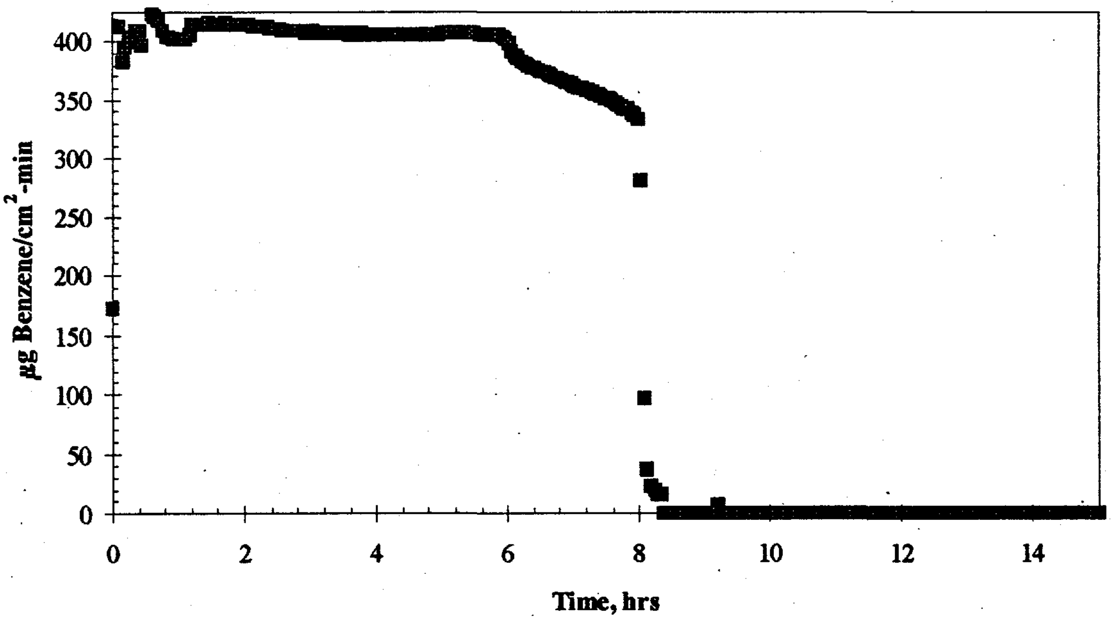

Figure 2. Benzene Release from Pure Benzene Layer on Salt Solution

The following three sets of data show benzene release rate data from slurry samples prepared by freshly adding benzene to stock KTPB slurry and gently premixing (no homogeniztion). Figure 3 shows the benzene release data from one sample of KTPB slurry prepared with freshly added benzene at approximately 16,091 ppm (by weight). Once flow was established, agitation was held constant and uninterrupted.

Although variable, the initial benzene release rates average around ~200 µg benzene/cm^2-min. At approximately 2.5 hours, release rates drop quickly to ~80 µg benzene/cm^2-min. After about an hour of consistent release at ~80 µg benzene/cm^2-min, release rates began a slow descent to ~30 µg benzene/cm^2-min, ending when data accumulation was halted at approximately 10 hours.

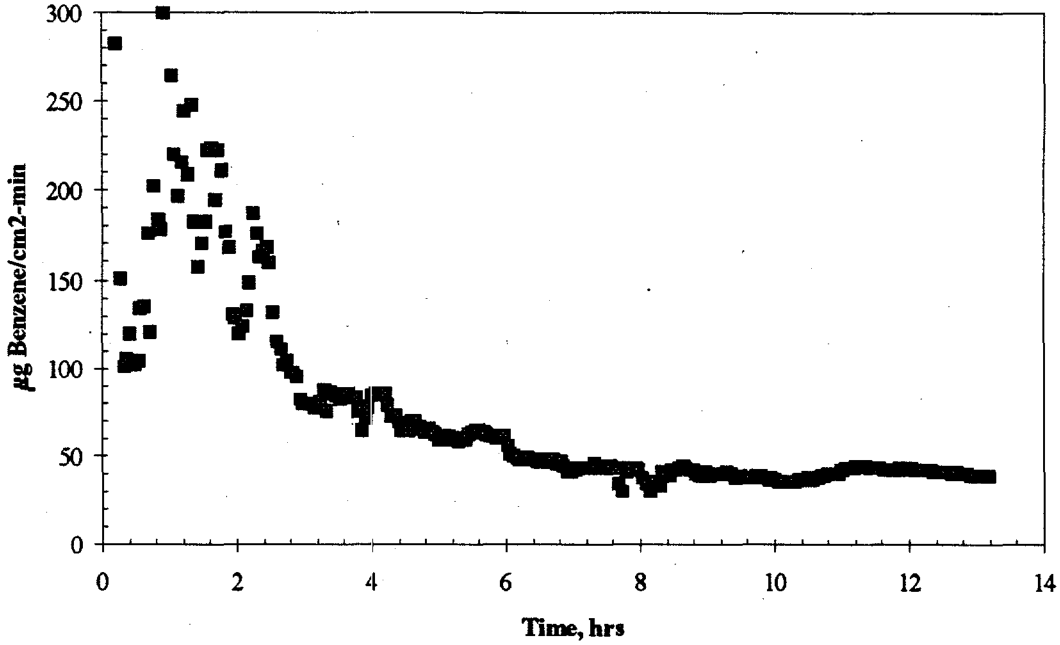

Figure 3. Benzene Release from Slurry Containing 16,091 ppm Freshly Added Benzene

Figure 4a shows benzene release data from a sample of KTPB slurry prepared with fresh benzene at approximately 14,731 ppm (by weight). Figure 4b shows this same data on a different scale to better see the data at lower release rates. This experiment began with agitation, which was decreased slightly at approximately 2.25 hours, then stopped at the point indicated on Figure 4a (approximately 4 hours). The agitation was halted to examine the effect it has on the release of benzene from the slurry. When agitation was slightly decreased at 2.25 hours, release rates significantly fell from ~300 µg benzene/cm^2-min to ~100 µg benzene/cm^2-min. And as expected, the release of benzene significantly fell upon halting agitation from ~100 µg benzene/cm^2-min (with agitation) to ~1 µg benzene/cm^2-min, as can be seen in Figure 4b. Clearly, agitation has a direct positive relationship with the release of benzene from slurries containing freshly added benzene. At the point indicated in Figure 4a (~8.25 hours), agitation was started again and held constant for the rest of the experiment. Upon restarting agitation, benzene release rates immediately rose to over 40 µg benzene/cm^2-min, then slowly but steadily dropped to zero over the next 14 hours, that descent quickening at the 20-hour mark. This suggests that the amount of benzene in the slurry also is directly related to the rate of benzene release from that slurry.

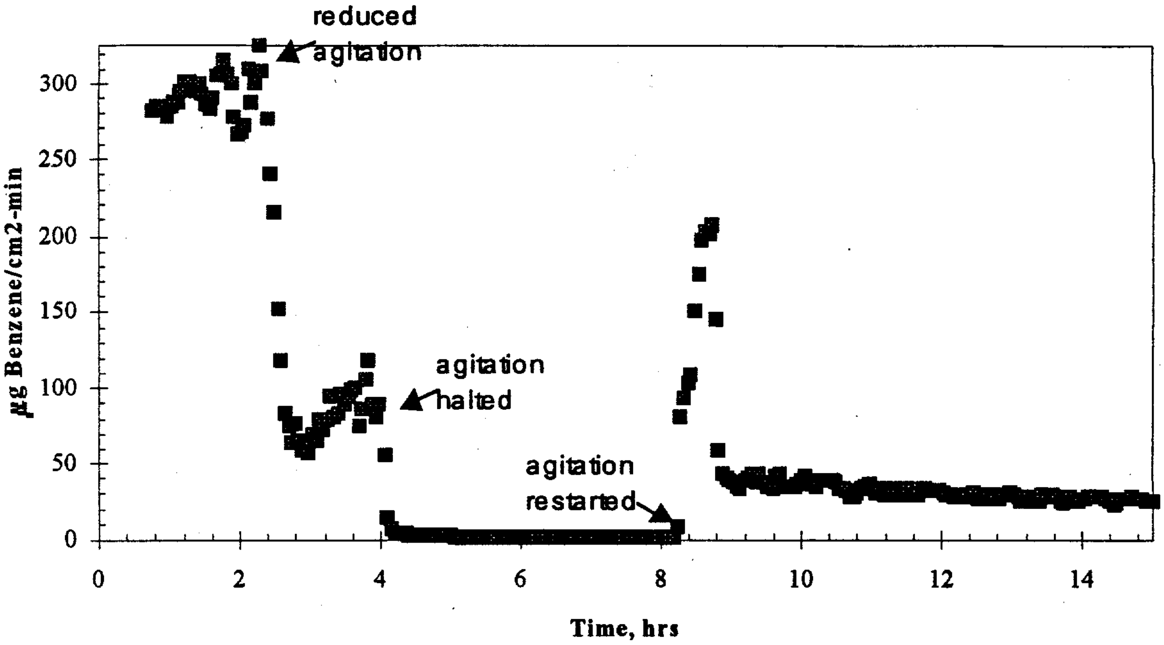

Figure 4a. Benzene Release from Slurry Containing 14,731 ppm Freshly Added Benzene

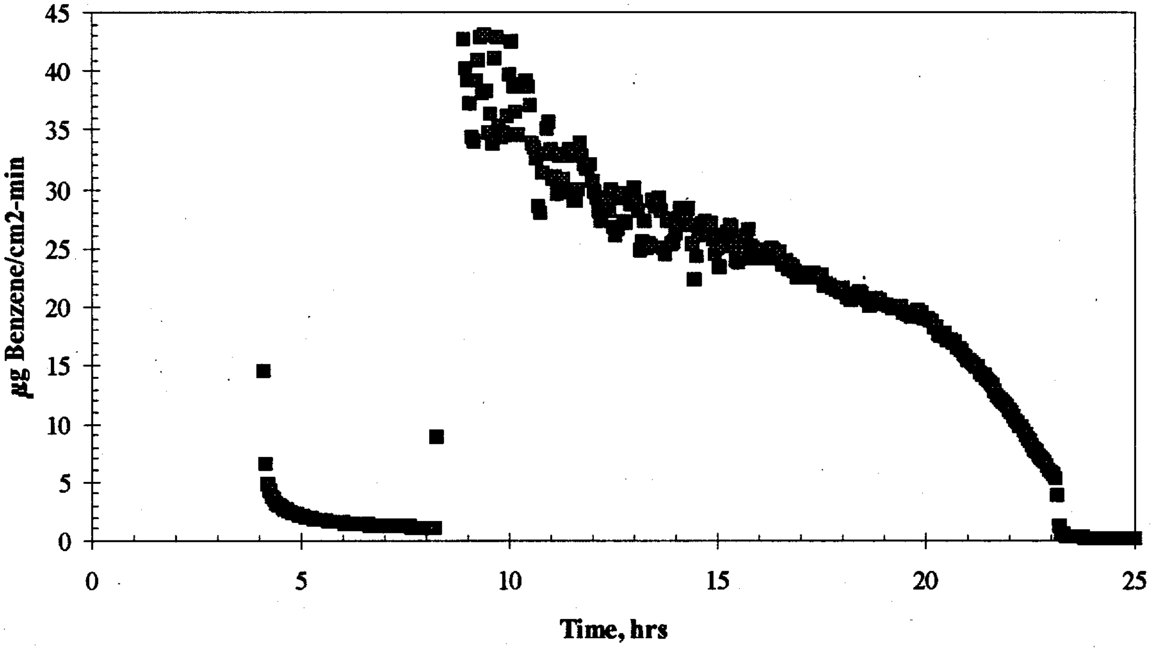

Figure 4b. Benzene Release from Slurry Containing 14,731 ppm Freshly Added Benzene

Figure 5a shows benzene release data from a sample of KTPB slurry prepared with fresh benzene at approximately 13,160 ppm (by weight). Figure 5b shows this same data on a different scale to better see the data at lower release rates. This experiment began with agitation, then agitation was halted at just under 1 hour, restarted at ~3 hours, and then halted again at ~4.5 hours, where it remained off for the rest of the experiment. Again, agitation clearly increased the release of benzene from the slurry. At the start of the test, the release rate quickly rose to ~275 μg benzene/cm^2-min, then descended to ~140 μg benzene/cm^2-min, where it remained for a short period of time before agitation was halted. Then, when agitation was restarted, the release rate steadily dropped from ~140 μg benzene/cm^2-min to ~100 μg benzene/cm^2-min. Figure 5b shows an expanded view of the benzene release rate with the agitation halted. In both cases, the reader sees the release rate quickly drop to ~2 μg benzene/cm^2-min, then steady out at between 1 and 0.5 μg benzene/cm^2-min.

We now have quality average release rates of KTPB slurry with freshly added benzene: ~100 to 200 μg benzene/cm^2-min with agitation, and ~1 μg benzene/cm^2-min without agitation. Data accumulation for Figure 5a was began by initially purging the headspace of the sample vessel at ~100 sccm nitrogen before setting a steady, constant, slower flow of 15.1 sccm. Data accumulation for Figures 3 and 4a began with no initial purge, just the beginning of a steady, constant flow rate of 15.1 sccm nitrogen. No appreciable effect of the headspace purge is evident, and it is assumed to have no significant effect on the benzene release rates once they rise, or decline, to steady values.

The release rate for pure benzene under the current conditions was at ~400 μg benzene/cm^2-min. We see from examining Figures 3, 4a, and 5a that the release of benzene from the freshly added samples is on the same order as the release of pure benzene.

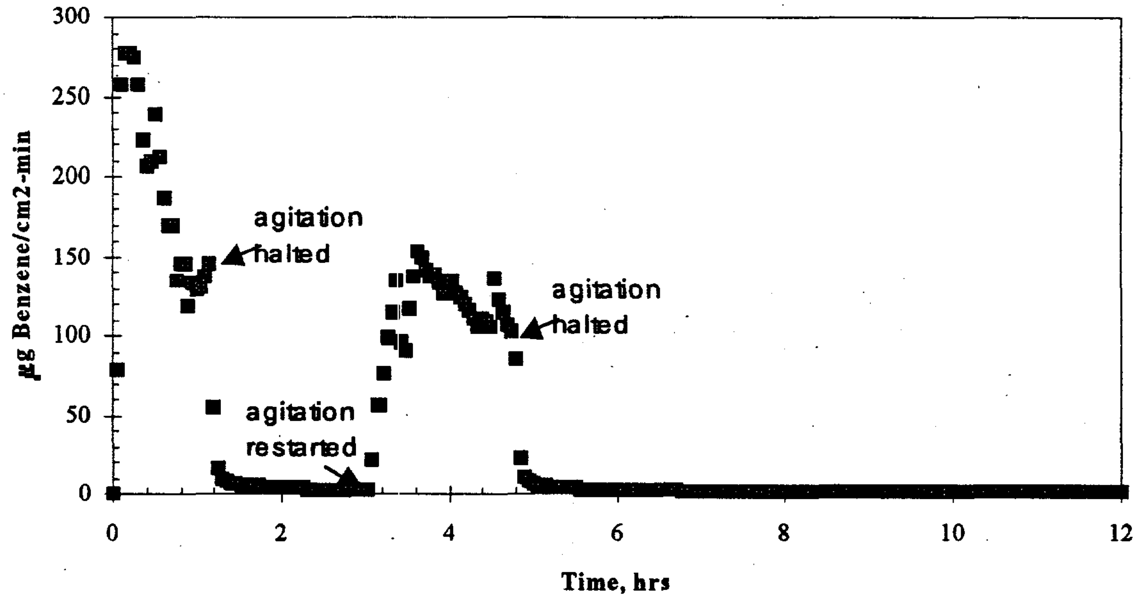

Figure 5a. Benzene Release from Slurry Containing 13,160 ppm Freshly Added Benzene

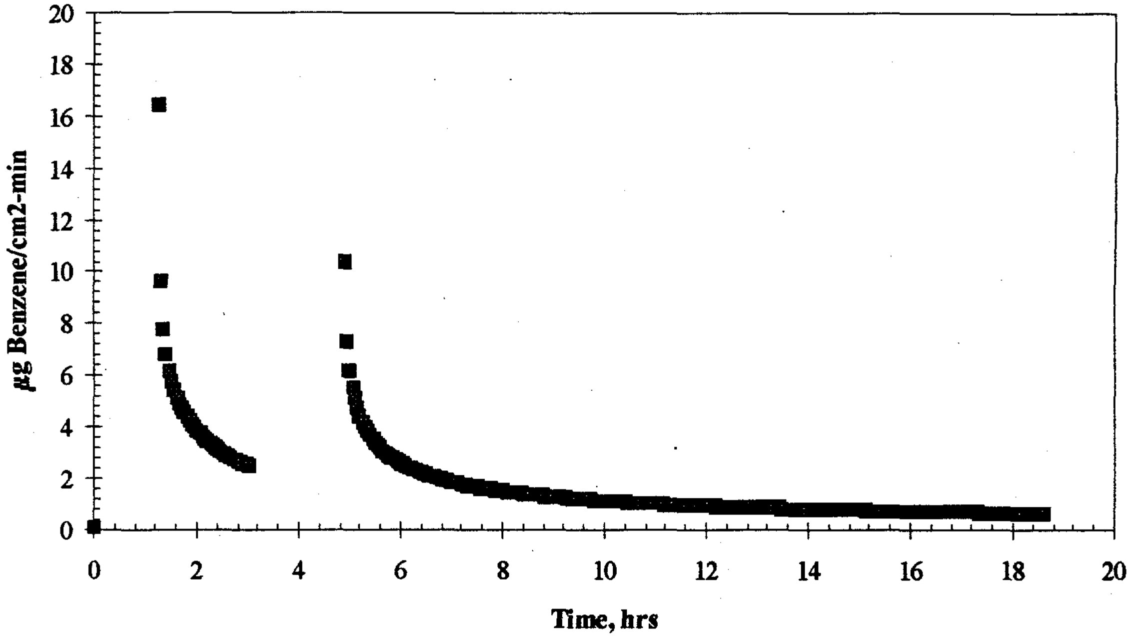

Figure 5b. Benzene Release from Slurry Containing 13,160 ppm Freshly Added Benzene

The following sets of data are benzene release rate data from slurry samples premixed with benzene by *homogenization*. Figure 6a shows benzene release data from a sample of 11,793 ppm of benzene (by weight) *homogenized* with KTPB slurry. Figure 6b shows this same data on a different scale to better see the data at lower release rates. This experiment began with agitation, which was shut off as indicated at just under 2 hours and then restarted at just over 3 hours. The initial release rate for this homogenized slurry went as high as ~40 µg benzene/cm^2-min and steadily declined to ~25 µg benzene/cm^2-min, at which point the agitation was shut off. When agitation was restarted, release rates resumed to ~30 µg benzene/cm^2-min, then reached a point (~5 hours) where they significantly and steadily dropped off. Release rates reached as low as ~0.2 µg benzene/cm^2-min when data accumulation was halted, at which point release rates were still declining.

It is clear that this *homogenized* sample has a lower benzene release rate with gentle agitation (~40 µg benzene/cm^2-min) than the samples containing freshly added benzene and gently premixed *without* homogenizing. Depending on the rate of agitation, the steady release rate of freshly added benzene at ~15,000-ppm from the slurry is on the order of 100 to 200 µg benzene/cm^2-min. Without agitation, though, both slurries with freshly added and homogenized benzene-slurry samples have approximately the same steady release rate of 1 to 2 µg benzene/cm^2-min. Upon halting agitation, even the slope and magnitude of the curve are relatively the same. This suggests relatively similar benzene-release mechanisms between the two samples in the absence of agitation.

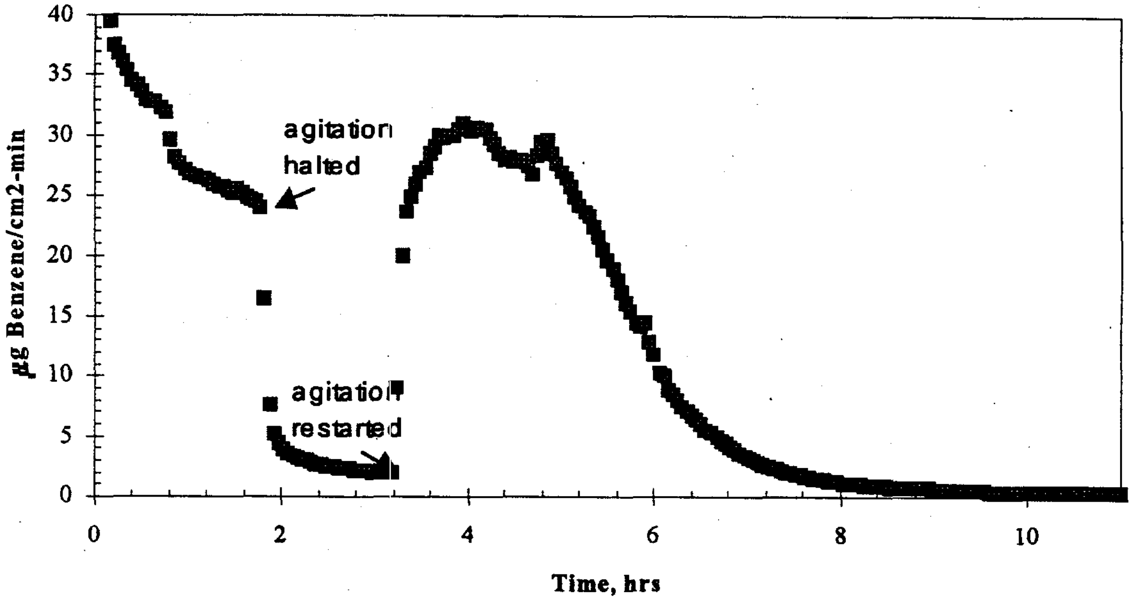

Figure 6a. Benzene Release from Slurry Homogenized with 11,793 ppm Benzene

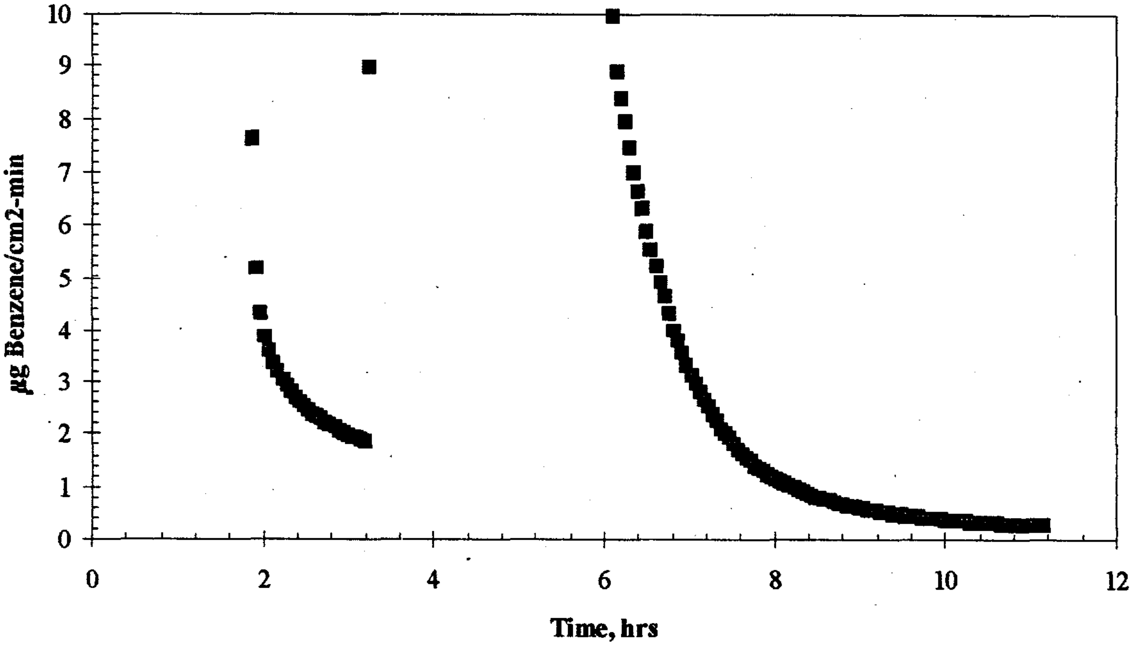

Figure 6b. Benzene Release from Slurry Homogenized with 11,793 ppm Benzene

Figure 7a shows the benzene release data from one sample of 3,897 ppm benzene (by weight) *homogenized* with KTPB slurry. Data in Figure 7b was generated simply to repeat the experiment shown in Figure 6a. Agitation was constant throughout each of the two tests. Release rates for these samples were much lower than expected, initially at or greater than 1 μg benzene/cm^2-min, rapidly decreasing to ~0.6 μg benzene/cm^2-min, and then slowly and steadily declining to <0.1 μg benzene/cm^2-min, where data generation was halted.

There is approximately an order of magnitude decrease in the release rates with gentle agitation between the freshly added benzene slurry and the 11,793 ppm benzene homogenized slurry, and another order of magnitude decrease between the 11,793 ppm benzene homogenized slurry and the 3,897 ppm benzene homogenized slurry. Reasons for these differences are not completely clear; however, it is believed, as a result of the homogenization, benzene coats the KTPB particles thus inhibiting its ability to be be released. It is also hypothesized that this different benzene configuration resulting from homogeniztion adds an additional force affecting the equilibrium controlling the amounts of benzene in the liquid phase, dissolved in solution, and in the sample vessel headspace.

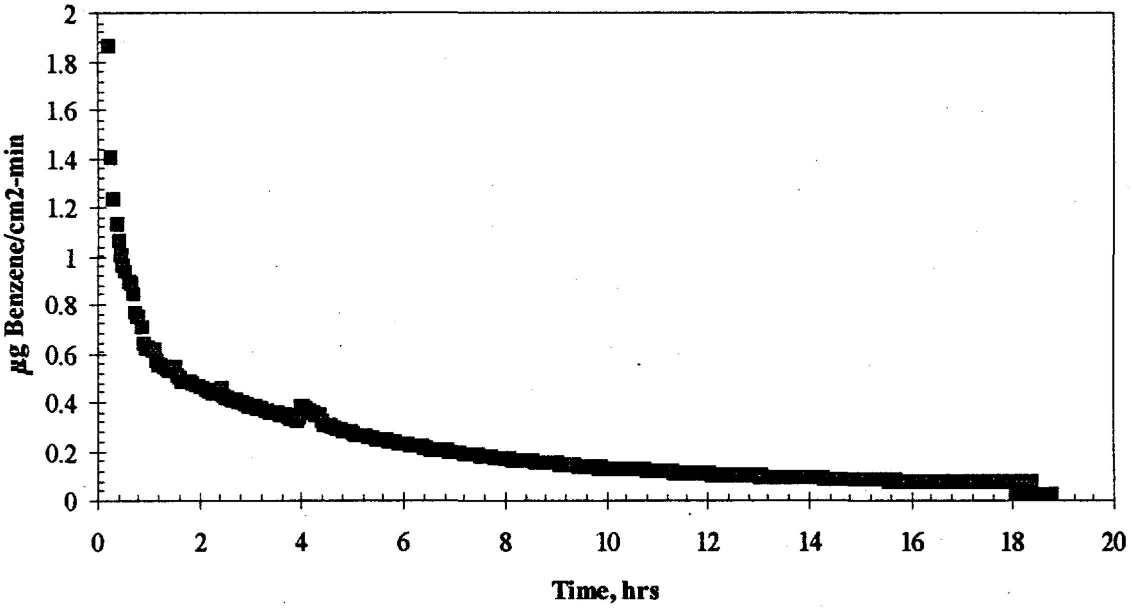

Figure 7a. Benzene Release from Slurry Homogenized with 3,897 ppm Benzene

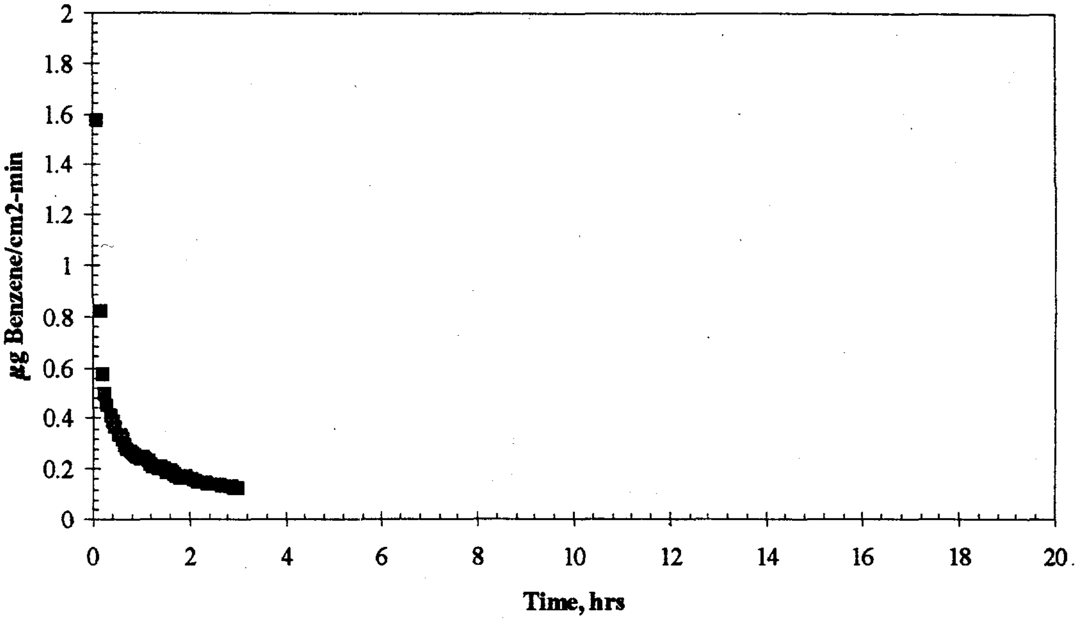

Figure 7b. Benzene Release from Slurry Homogenized with 3,897 ppm Benzene

The following two sets of data (Figures 8a and 8b) show benzene release-rate data from two separate samples of clear, filtered salt solution from KTPB slurry saturated with benzene. The data in Figure 8a were generated with agitation, and those in Figure 8b without. The benzene release rate for the agitated solution began at just over 11 µg benzene/cm^2-min and quickly declined to ~0 µg benzene/cm^2-min in a span of about 3 hours. The benzene release rate for the unagitated solution began significantly lower at just over 2 µg benzene/cm^2-min and declined much slower, reaching ~0.1 µg benzene/cm^2-min at data termination at 20 hours. These results possibly suggest two different rate-limiting steps for removing benzene from the solutions: (1) (agitated) either the transfer of benzene across the vapor-liquid interface or the removal of benzene from the sample vessel headspace, and (2) (unagitated) the diffusion of benzene in solution to the vapor-liquid interface.

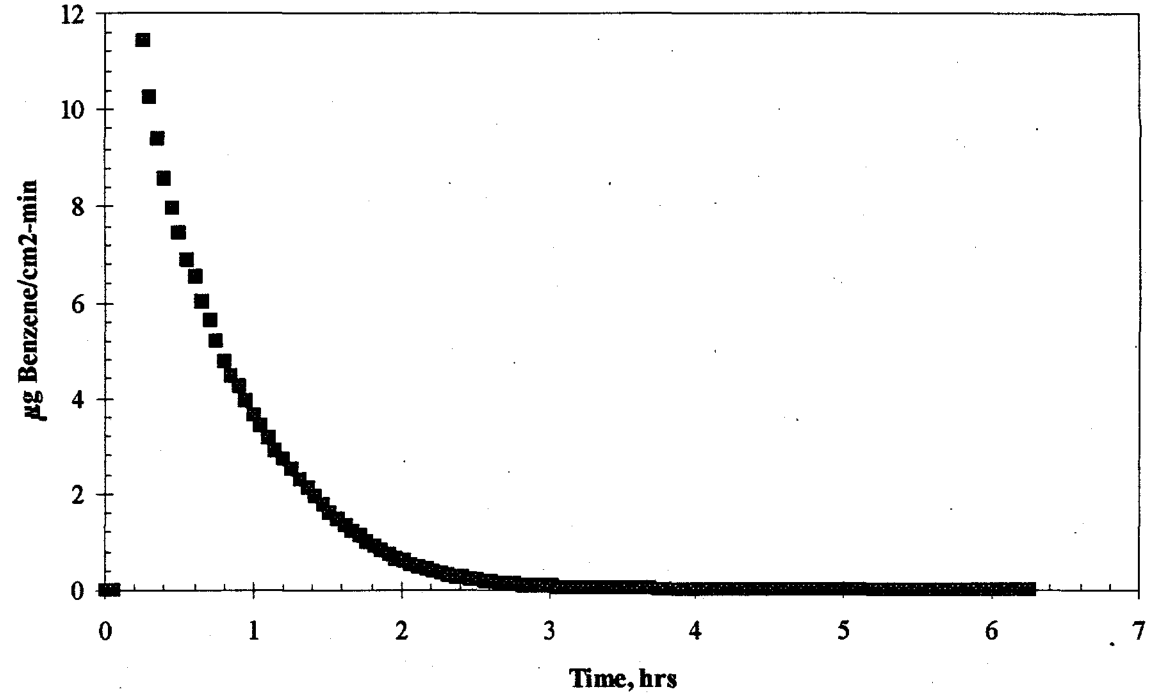

Figure 8a. Benzene Release from Clear, Filtered Salt Solution Saturated with Benzene (agitated)

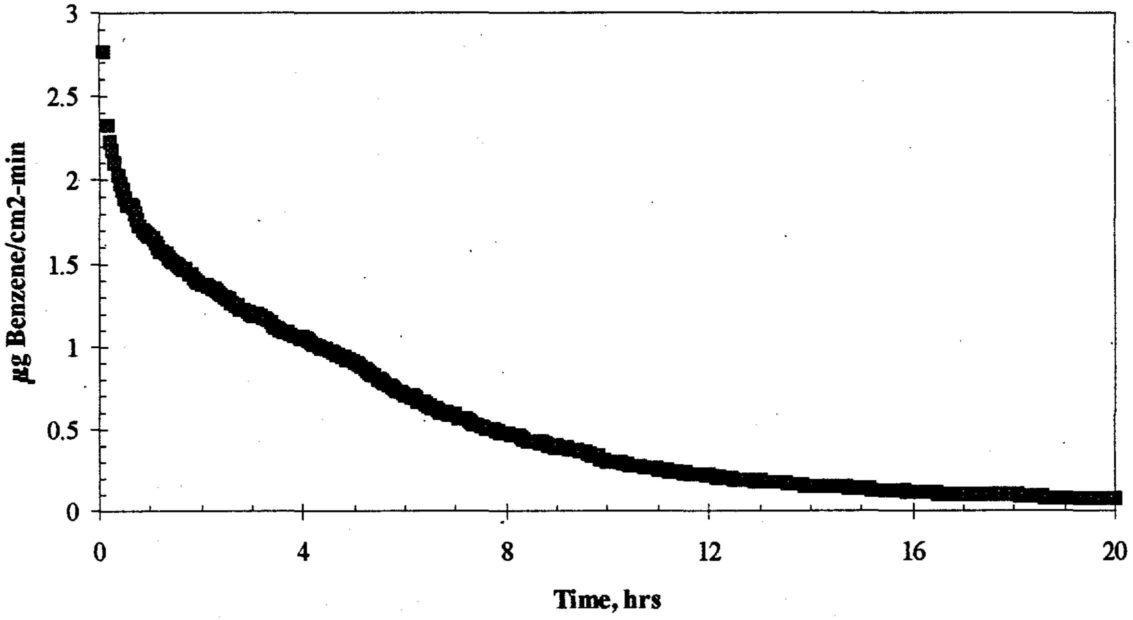

Figure 8b. Benzene Release from Clear, Filtered Salt Solution Saturated with Benzene (unagitated)

Examining Figures 6a and 7a again, exponential decays at the end of each release rate curve for the 5,000 and 15,000 ppm homogenized samples resemble the release rate of a benzene saturated clear, filtered salt solution (Figure 8a). This resemblance is not present in the release rate curves for the slurry samples with freshly added benzene. With the slurry samples containing freshly added benzene, the main retention mechanism is exposing the benzene droplets to the surface of the slurry. However, slurry samples homogenized with benzene have benzene coating KTPB particles which result in a different benzene release mechanism.

Figure 9 shows the benzene release rate for an *in situ* generated benzene (DEMO column) slurry sample. Continuous agitation was applied throughout the experiment. Since the benzene released from this sample was generated *in situ* and no chemical analyses were performed on the slurry before or after the release rate tests, it is not known how much benzene was present in the slurry during the release rate test. In addition, it should be noted that percent solids in this slurry sample was less than the percent solids in all previous slurry samples discussed.

Release rates in Figure 9 were much lower than all previous tests, beginning at approximately 0.17 µg benzene/cm^2-min and steadily declining to less than 0.04 µg benzene/cm^2-min. The curve suggests that no free excess benzene was in the slurry and very little benzene dissolved in the salt solution of the slurry. Once benzene was depleted from the sample (to ~0.04 µg benzene/cm^2-min), release rate fluctuations took place over an extended period of time, which is believed to be caused from temperature fluctions in the laboratory. It is important to note that there is a lasting residual release rate (0.03 to 0.02 µg benzene/cm^2-min) that this DEMO column slurry exhibited that was not seen in the clear, filtered salt-solution samples. It should also be mentioned that the percent solids in the DEMO column slurry was lower than that in the prepared slurries.

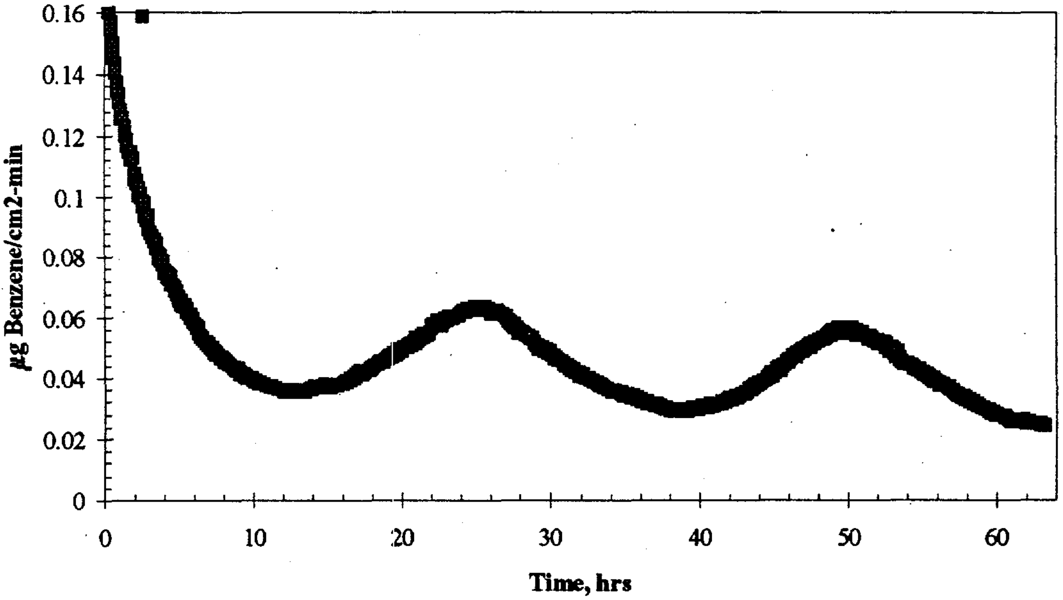

Figure 9. Benzene Release from DEMO Column Sample Containing Benzene Generated *In Situ*

The samples with benzene freshly added to slurry, with benzene homogenized with slurry, and with clear, filtered salt solution saturated with benzene were integrated for total benzene release. These data are expressed as a percentage of the total benzene in the sample released versus time. For the clear, filtered salt solutions saturated with benzene, a saturation concentration of 250 ppm is assumed.(Walker 1989). These results are found in Figures 10 through 16. The integrated data for the freshly added benzene samples (Figures 10 and 11) agreed well with the amount of benzene added. It is believed that if the third test of that group (Figure 12) had continued to be agitated, more benzene would have been released in the given time frame and recoveries much greater than 50 percent would have been expected. Examining Figures 10 and 11, it should be noted that the slope of the total benzene released upon halting data accumulation in Figure 10 gives no insight into the total amount of benzene that would have eventually been released. The slurry samples homogenized with benzene (Figures 13 and 14) did not agree well with the amount of benzene added. It is believed that this low recovery was a result of numerous unforseen factors. The low benzene release may indicate a strong interaction between the benzene and the KTPB particles due to a benzene configuration in the slurry resulting in benzene not being easily released from the slurry ('unreleasable' benzene). Alternatively, the samples may not have contained the amount of benzene thought to have been added as a result of the homogenization technique or the transfer of samples from WSRC to PNNL.

The measured total amount of benzene released from the freshly prepared salt solution samples saturated with benzene (Figures 15 and 16) agreed fairly well with the predicted amount of benzene dissolved in the salt solution. Again, not that the recovery of benzene in the unagitated salt solution (Figure 16) was lower than the agitated sample (Figure 15).

The integrated data in Figure 17 shows that the amount of benzene released from the pure benzene layer from Figure 2 agrees well with the mass of benzene used in the pure layer. It should be noted that, after the pure benzene layer is depleted (sometime between 6 and 8 hours), no definite conclusions can be made of the remaining saturated salt solution since the conditions of the test are not clearly defined.

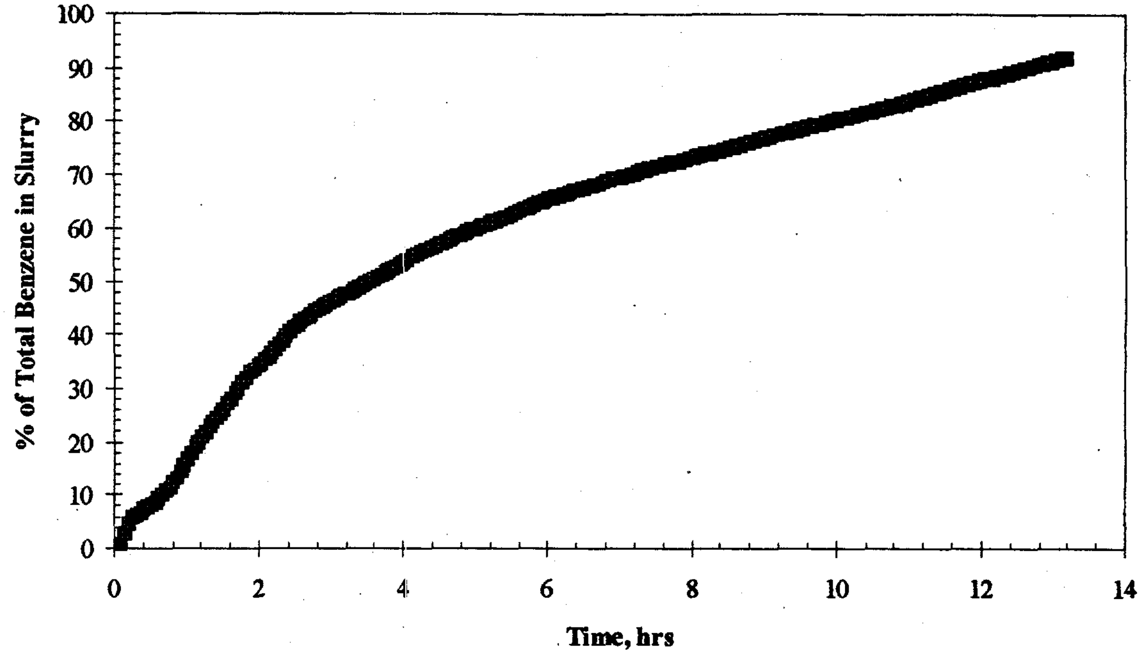

Figure 10. Total Benzene Release in Figure 3.

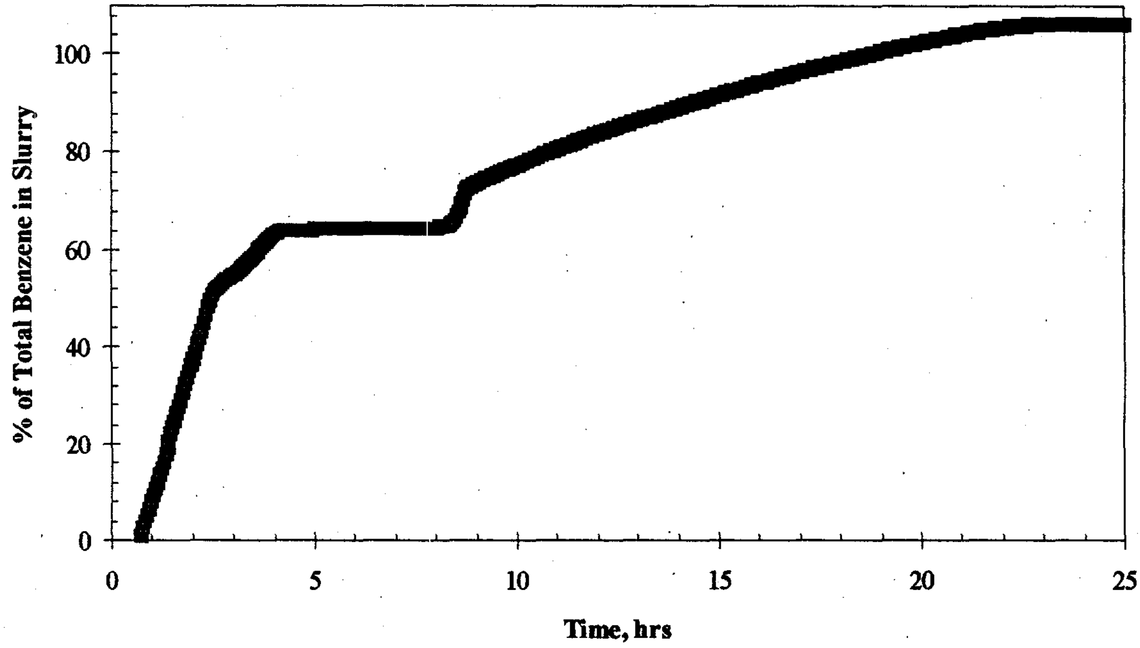

Figure 11. Total Benzene Release in Figure 4a.

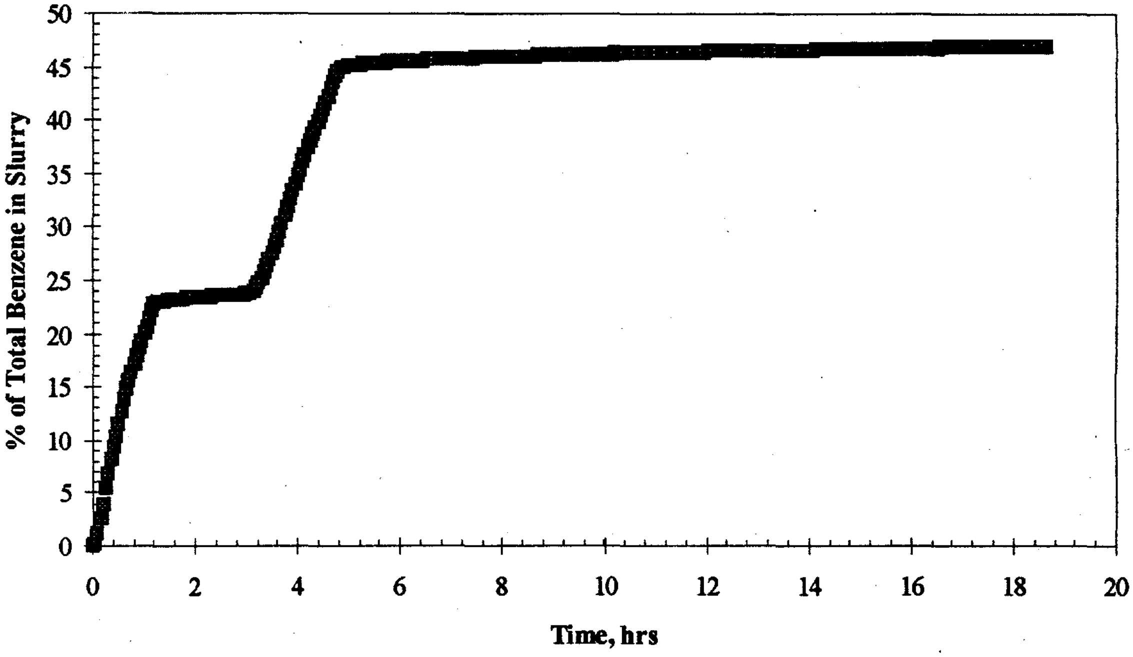

Figure 12. Total Benzene Release in Figure 5a.

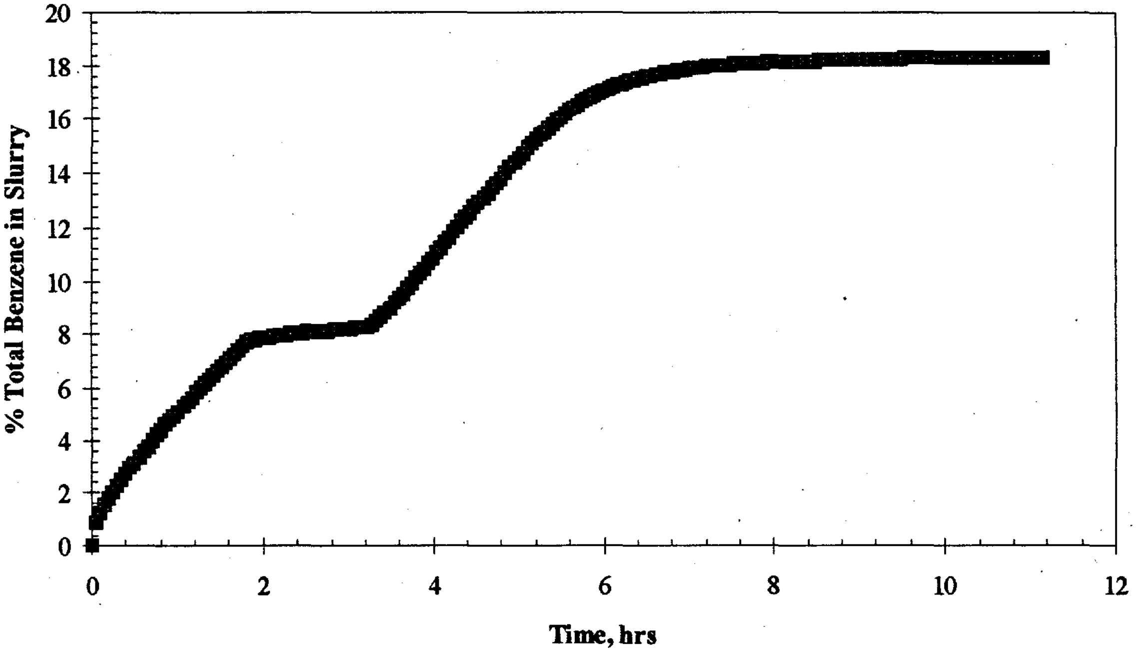

Figure 13. Total Benzene Release in Figure 6a.

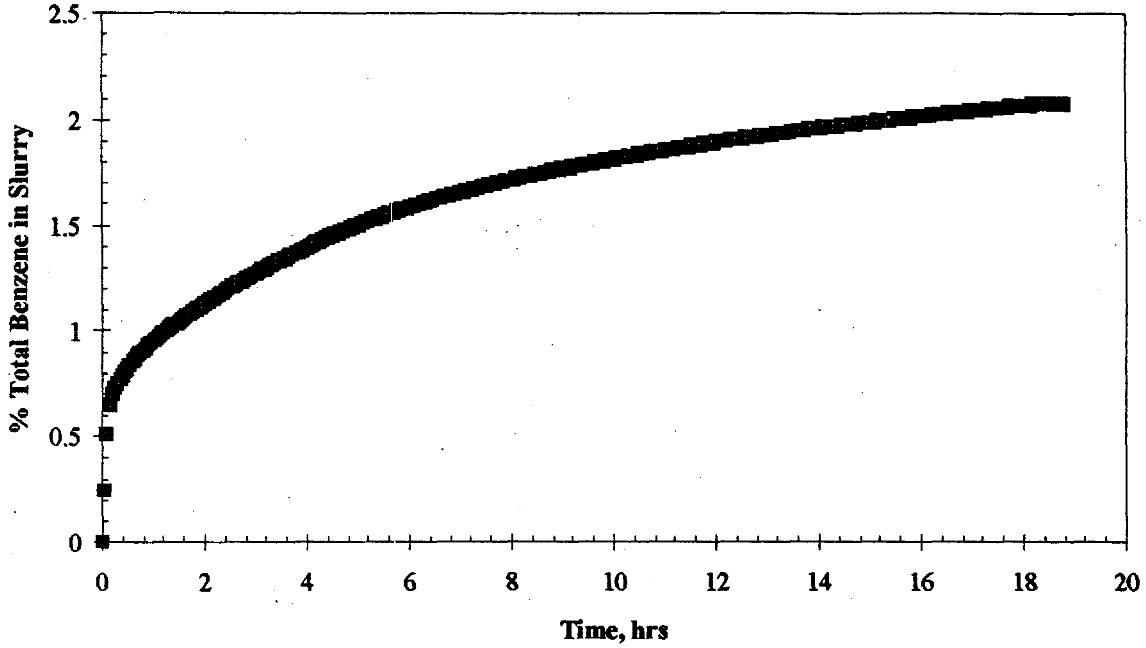

Figure 14. Total Benzene Release in Figure 7a.

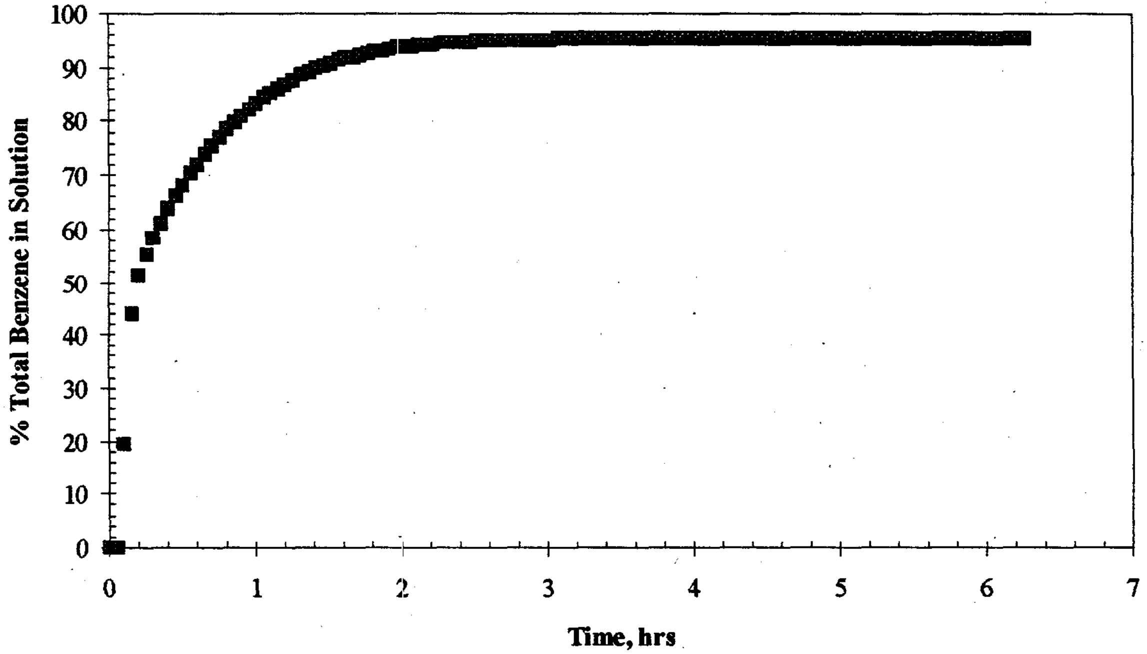

Figure 15. Total Benzene Release in Figure 8a.

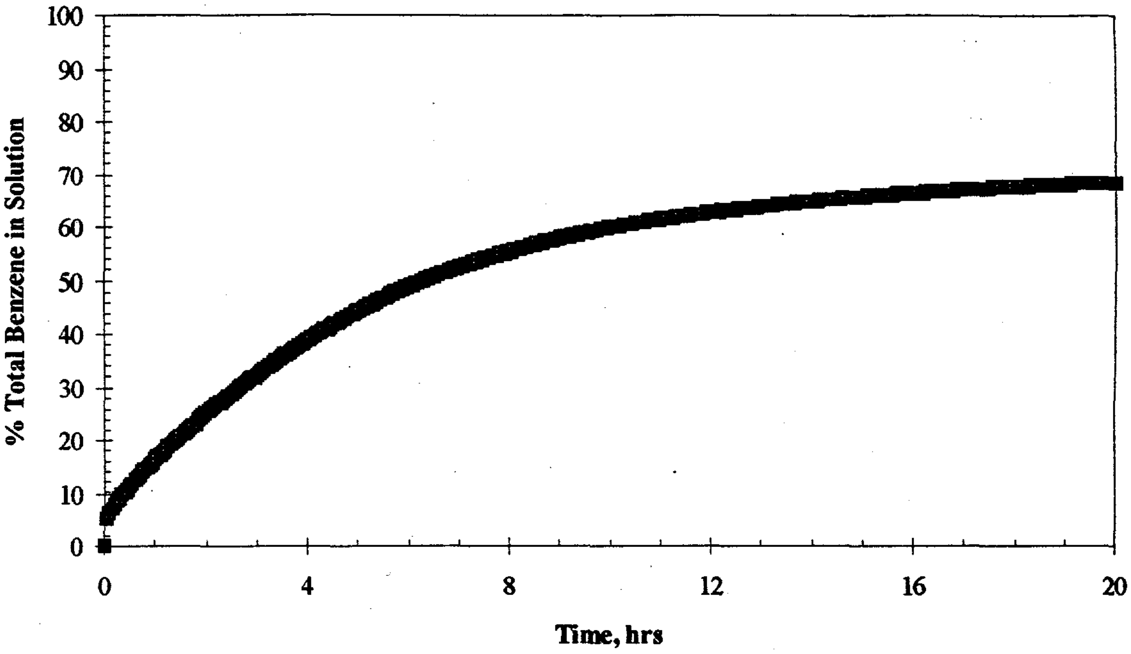

Figure 16. Total Benzene Release in Figure 8b.

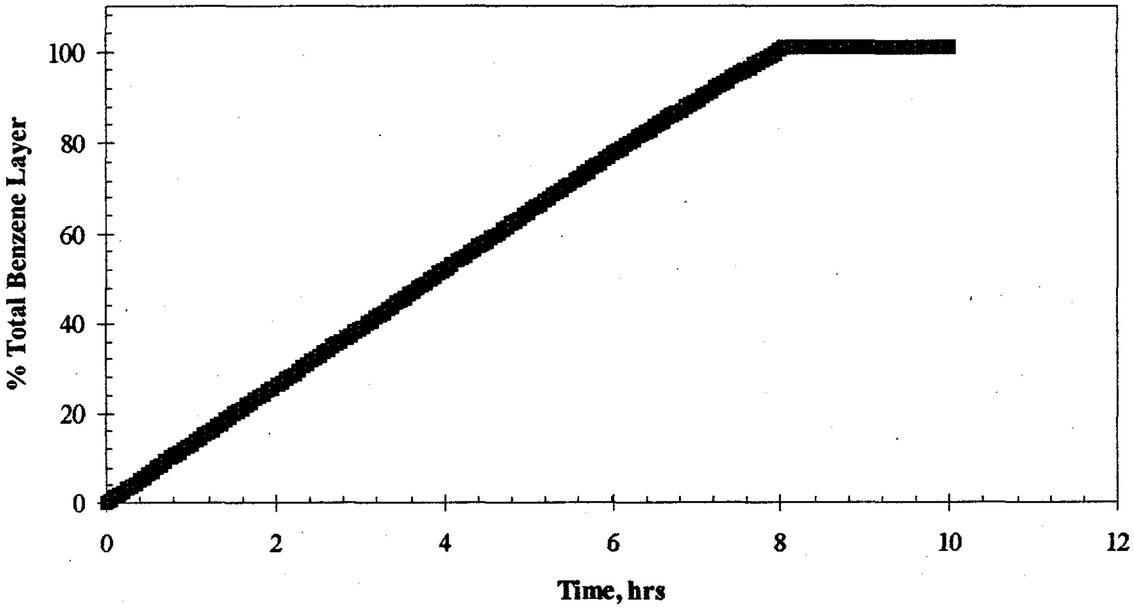

Figure 17. Total Benzene Release in Figure 2 (Pure Benzene Layer).

Conclusions

Experiments were performed on a variety of slurries and solutions (KTPB slurry with freshly added benzene and gently premixed, KTPB slurry homogenized with benzene, filtered salt solution from KTPB slurry saturated with benzene, slurry from a large demonstration experiment containing benzene generated *in situ*) to measure benzene release rates. The main conclusions are as follows:

- KTPB slurry containing ~15,000-ppm benzene (by weight) and gently premixed initially released benzene at a rate (~100 to 200 μg benzene/cm^2-min) comparable to that of pure benzene (~400 μg benzene/cm^2-min).
- KTPB slurry containing ~12,000-ppm benzene (by weight) and premixed by homogenization released benzene at a rate (~40 μg benzene/cm^2-min) much lower than that for slurry containing freshly added benzene and gently premixed. Similar slurry homogenized with ~4,000-ppm benzene released benzene much lower (~1 μg benzene/cm^2-min) than that of the ~12,000-ppm benzene sample.
- Release rates of benzene from a slurry sample from a large demonstration experiment containing benzene generated *in situ* were significantly lower than all of above slurry samples (~0.17 μg benzene/cm^2-min).

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Walker, D.D. 1989. *Vapor Pressure of Benzene, Methanol, Isopropanol over Salt Solution,* DPST-88-661, Westinghouse Savannah River Company, South Carolina.

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