

**GAS - LIQUID MASS TRANSFER IN AGITATED TANKS CONTAINING NON-
NEWTONIAN FLUIDS**

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Summary

The Savannah River Technology Center (SRTC) developed a program to investigate various operating parameters in a process to precipitate cesium from salt solution with tetraphenylborate. The effects of operating parameters, such as KTPB concentration, time, sodium molarity, temperature, salt composition, sludge concentration, and radiation dose, on benzene retention and release were studied. The benzene retention and release tests were performed in the following manner: KTPB slurries were prepared and placed in glass vessels in temperature controlled water baths. The vessels were purged with nitrogen at 10 ml/min and remained quiescent for a predetermined time. The purged vapor was sampled periodically for benzene, and slurry samples were collected weekly to measure benzene and phenylborate levels. The benzene release tests were performed by increasing the nitrogen purge rate to 1 L/min and agitating the vessels at approximately 150 rpm. The vapor benzene concentration was sampled for 2 - 5 hours. The agitation was stopped, and the purge rate reduced to 10 ml/min. The vessel remained quiescent for one week, and the agitation test was repeated.

The conclusions of the work are:

- Increasing the KTPB concentration decreases the maximum benzene release flux during agitation. As KTPB concentration increases, slurry yield stress and consistency increase and the mixing effectiveness decreases if agitation speed is constant.
- Increasing the quiescent time increases the integrated quiescent benzene release, the integrated total benzene release, and the maximum benzene flux during agitation over the range of quiescent times investigated (30 - 155 days).
- The quiescent time had no significant effect on the average quiescent benzene flux in this test.
- Increasing temperature increased the average quiescent flux and integrated quiescent benzene release with a 3.5 M sodium slurry. Because of the limited quiescent release data collected, an effect was not measured with 4.7 M sodium slurries.
- Salt solution type had no effect on benzene retention and release, as expected. Since changing anion concentrations should have no effect on the benzene generation rate, the benzene vapor pressure, or the mass transfer coefficient, it will have minimal effect on the benzene flux.
- Sludge concentration had no effect on the amount of benzene released during the quiescent and agitation phases. The maximum flux during agitation increased with decreasing sludge concentration. This effect could be caused by differences in mixing effectiveness, or an effect of sludge concentration on slurry yield stress.
- Good mixing is imperative for removing benzene from KTPB slurries, especially at high KTPB concentrations.
- In this test, when the slurry benzene level exceeded a threshold concentration, it became "readily releasable". The threshold concentration increases with KTPB concentration.

Introduction

Sodium tetraphenylborate used to precipitate cesium from salt solution decomposes with time to generate benzene. The benzene is retained in solution until energy, such as from mixing, is introduced to release benzene from the slurry to the vapor phase.

SRTC conducted a program to develop a more thorough understanding of benzene release and to determine the effects of variables on benzene retention and release in the process. SRTC performed tests in 2-Liter glass kettles.

The purpose of the tests was to investigate the effects of operating parameters, such as KTPB concentration, time, sodium molarity, temperature, salt composition, sludge concentration, and radiation dose, on benzene retention and release. This paper describes the results of the tests.

Mass Transfer

Figure 1 describes mass transfer between a liquid with no insoluble solids and a gas. In Figure 1, C_l is the bulk liquid phase benzene concentration, C_{l-int} is the liquid phase benzene concentration at the interface, C_{g-int} is the vapor phase benzene concentration at the interface, and C_g is the bulk vapor phase benzene concentration.

Diffusion Controlled Mass Transfer

A boundary layer is a region close to the interface where both phases influence the mass transfer process. Benzene is transported from the bulk liquid phase to the liquid boundary layer. (The edge of the boundary layer is generally defined as the point at which the concentration is within 1% of the bulk phase concentration.) Within the liquid phase boundary layer, mass transfer occurs from the edge of the boundary layer to the vapor-liquid interface by diffusion and the flux is described by equation [1]

$$J = \alpha A \Delta C / \Delta y \quad [1]$$

where J is the benzene flux, α is the molecular diffusivity, A is the surface area, C is the benzene concentration, and y is distance. At the vapor-liquid interface, the vapor and liquid are in equilibrium. The benzene is also transported from the vapor-liquid interface to the edge of the vapor boundary layer by diffusion, and then transported from the vapor boundary layer to the bulk vapor.

Interphase Mass Transfer

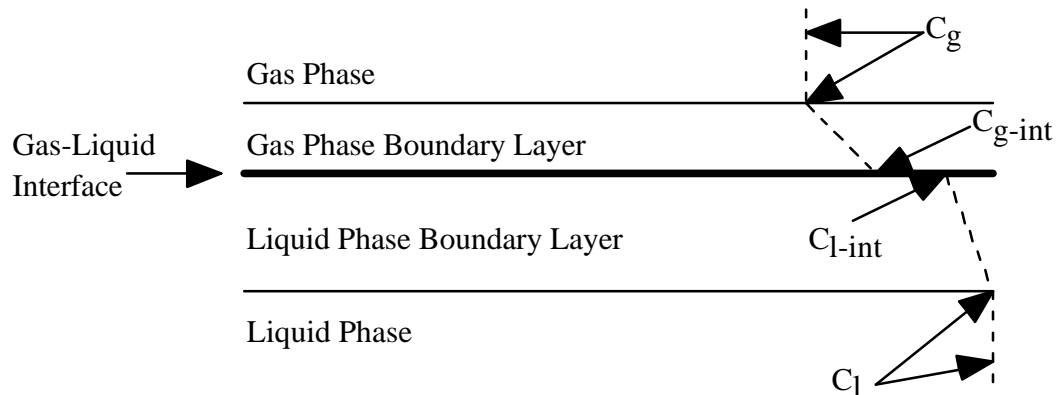


Figure 1. Interphase Mass Transfer

The flux across either the liquid or vapor phase boundary layer can be changed by changing the molecular diffusivity, the surface area, the concentration difference across the boundary layer (ΔC), or the boundary layer thickness.

The term $\alpha/\Delta y$ can be replaced by a constant, k , which is called the mass transfer coefficient. The mass transfer coefficient can be changed by changing the boundary layer thickness or the molecular diffusivity.

As the benzene is transported from the liquid phase to the vapor phase, the liquid phase boundary layer is replenished from the bulk liquid. If the bulk liquid does not replenish the benzene lost from the liquid phase boundary layer, the liquid phase boundary layer thickness will increase and the mass transfer coefficient will

decrease. If the bulk liquid transports benzene to the liquid boundary layer faster than it is removed, the liquid boundary layer thickness decreases and the mass transfer coefficient increases.

Convective Mass Transfer

Convective mass transfer from the liquid phase to the vapor phase can be described with a mass transfer coefficient. The flux is equal to the product of the mass transfer coefficient, the surface area, and the concentration difference (Flux = $k A \Delta C$). The concentration difference can be the concentration difference across the gas phase boundary layer, the concentration difference across the liquid phase boundary layer, the concentration difference between the bulk vapor and the vapor which would be in equilibrium with the bulk liquid, or the concentration difference between the bulk liquid and the liquid which would be in equilibrium with the bulk vapor. If the concentration difference across the gas phase boundary layer is used, the mass transfer coefficient is called a gas phase mass transfer coefficient. If the concentration difference across the liquid phase boundary layer is used, the mass transfer coefficient is called a liquid phase mass transfer coefficient. If the concentration difference between the bulk vapor and the vapor which would be in equilibrium with the bulk liquid is used, the mass transfer coefficient is called an overall mass transfer coefficient. If the concentration difference between the bulk liquid and the liquid which would be in equilibrium with the bulk vapor is used, the mass transfer coefficient is also called an overall mass transfer coefficient.

The vapor phase mass transfer coefficient is described by equation [2], and the liquid phase mass transfer coefficient is described by [3].

$$J = k_g A (C_{g-int} - C_g) \quad [2]$$

$$J = k_l A (C_l - C_{l-int}) \quad [3]$$

In equations [2] and [3], J is the flux, A is the interfacial area, k_g is the vapor phase mass transfer coefficient, and k_l is the liquid phase mass transfer coefficient.

Since C_{g-int} and C_{l-int} are difficult to determine, while C_g and C_l can usually be measured or calculated, the overall mass transfer coefficient can be described by equations [4] and [5]

$$J = K_g A (C_g^* - C_g) = K_g A (H C_l - C_g) \quad [4]$$

$$J = K_l A (C_l - C_l^*) = K_l A (C_l - C_g/H) \quad [5]$$

In equations [4] and [5], K_g is the overall mass transfer coefficient based on vapor phase driving force, K_l is the overall mass transfer coefficient based on liquid phase driving force, C_g^* is the concentration of benzene in the vapor phase which is in equilibrium with the bulk liquid, C_l^* is the liquid phase benzene concentration which is in equilibrium with the bulk vapor, and H is the Henry's law constant.

Since at steady state, the fluxes calculated with equations [2] - [5] are equal, relationships between the mass transfer coefficients described in the equations are derived in the literature¹ and shown in equations [6] - [8].

$$1/K_g = 1/k_g + H/k_l \quad [6]$$

$$1/K_l = 1/k_l + 1/H k_g \quad [7]$$

$$K_l = H K_g \quad [8]$$

The overall mass transfer coefficient is a function of the liquid phase and vapor phase mass transfer coefficients; that is, the combined resistance to mass transfer across both the liquid and vapor boundary layers. If the vapor

phase mass transfer coefficient (k_g) is much larger than the liquid phase mass transfer coefficient (k_l), the overall mass transfer coefficient (K_l) is approximately equal to the liquid phase mass transfer coefficient: in other words, because the resistance to mass transfer in the vapor phase is low, the liquid phase resistance controls the mass transfer process. Previous research investigating the removal of organic species from water under quiescent and agitated conditions found the vapor phase mass transfer coefficient to be more than 20 times the liquid phase mass transfer coefficient.^{2,3}

Therefore, in a system containing a benzene at low concentration, the benzene will be transferred from the liquid phase boundary layer to the vapor phase faster than it can be transferred from the bulk liquid to the liquid phase boundary layer. The liquid phase boundary layer will become depleted in benzene, and increase in thickness. The thicker boundary layer will lead to a smaller mass transfer coefficient and a lower mass transfer rate.

Equations [9] and [10] describe the relationship between overall mass transfer coefficients and individual phase mass transfer coefficients in this work.

$$K_g \cong k_l/H \quad [9]$$

$$K_l \cong k_l \quad [10]$$

The reciprocal of the product of the mass transfer coefficient and area is often referred to as the resistance to mass transfer. The overall resistance to mass transfer through both the liquid and vapor boundary layers is reflected in the overall mass transfer coefficient, either K_g or K_l .

Application to Benzene Release from KTPB Slurries

This mass transfer theory can be applied to following situations expected with TPB slurries:

- Aqueous solutions without KTPB solids
 - Quiescent solution with no insoluble solids and benzene at or below the solubility limit
 - Quiescent solution with no insoluble solids and benzene above the solubility limit
- Slurries with KTPB solids
 - Non-isothermal, quiescent, sunk KTPB slurry
 - Quiescent, floating KTPB slurry
 - Mixed or agitated KTPB slurry

All of the cases discussed below assume a flowing vapor phase.

Aqueous Solutions Without KTPB Solids

In a vessel containing a quiescent aqueous solution with no insoluble solids and benzene at or below its solubility, the following outcome is expected: The benzene release is liquid phase diffusion controlled. The liquid boundary layer thickness increases until steady-state (constant flux) is reached (the liquid concentration will decrease with time assuming the generation rate is zero or less than the flux established). If temperature is increased, the diffusivity increases as well as the equilibrium vapor concentration. Benzene flux increases until a new steady-state is reached.

If the generation rate is higher than the established flux, the benzene concentration will increase above the solubility limit. The following outcome is expected: A second liquid phase which is almost pure benzene is formed and accumulates at the liquid-vapor interface. No liquid boundary layer exists in the salt solution. Mass transfer is by direct evaporation from the floating benzene phase. Since no liquid phase mass transfer resistance exists, mass transfer is controlled by the vapor phase resistance. Benzene flux and vapor phase benzene concentration are higher than when the liquid benzene level is below the solubility limit. That is, in equation [6] k_l becomes very large and $K_g \cong k_g$.

Slurries with KTPB Solids

With a non-isothermal, quiescent, sunk KTPB slurry, the following outcome is expected: The temperature gradient between the slurry-liquid interface and the liquid-vapor interface creates convective mixing in the liquid layer. The mixing replenishes the liquid boundary layer causing it to become thin. As the liquid boundary layer becomes thin, the mass transfer coefficient increases, flux increases, and the vapor benzene concentration increases. As the temperature gradient within the slurry increases, the convective mixing increases, the liquid boundary layer thickness decreases, and the mass transfer rate increases.

With a quiescent, floating slurry, the following outcome is expected: The slurry is stagnant and consolidated. The slurry contains KTPB and interstitial liquid. Boundary layers exist at slurry-liquid and liquid-vapor interfaces. The benzene is soluble, adsorbed to the KTPB solids, small free benzene droplets, or large globules coated with KTPB, biphenyl, or other organic by-products. The mass transfer of benzene through the liquid takes place in a two step process: (1) soluble benzene evaporates from the salt solution into the vapor, and (2) benzene dissolves from the droplets/globules into unsaturated salt solution. The solids in the slurry reduce the effective mass transfer surface area which lowers the benzene flux and the vapor benzene concentration.

With a mixed or agitated slurry, the following outcome is expected: The slurry becomes homogeneous regardless of whether it was sunk or floating at the start. Two cases are considered, globules and droplets.

Globules are defined as coated benzene droplets which are large enough that if sufficient energy is provided when they reach the surface they break open and form a small benzene pool. The mixing brings the globules to the surface or allows them to reach the surface (due to buoyancy forces). If the globules are present, the release rate is similar to free benzene. The approach of the release rate to free benzene evaporation is determined by the total effective surface area of the open globules.

Droplets are defined as free benzene droplets which are small enough that the mixing energy is insufficient to overcome surface tension and they do not break open. Soluble benzene is transferred to the vapor phase by the two step process described previously. The mixing reduces the liquid boundary layer thickness which increases the benzene flux and the benzene vapor concentration as compared to a quiescent, floating slurry. The droplets replenish the soluble benzene which is transferred to the vapor. When mixing stops, the liquid boundary layer thickness increases, and the flux and vapor benzene concentration decrease.

Temperature, viscosity, mixing effectiveness, KTPB concentration, and ventilation rate will affect the boundary layer thickness and mass transfer process. For an aqueous salt solution with no insoluble solids, temperature affects the mass transfer process in the following manner: Increasing the temperature increases the molecular diffusivity, decreases solution viscosity, and increases the equilibrium vapor pressure. Increasing the molecular diffusivity increases benzene flux as seen in equation [1]. Since the boundary layer thickness decreases with decreasing viscosity, increasing temperature will decrease the boundary layer thickness and increase mass transfer. Increasing the equilibrium vapor pressure will increase the concentration difference ($C_g^* - C_g$) which will increase mass transfer.

For an aqueous salt solution with no insoluble solids, mixing effectiveness has the following effect on the mass transfer process: Vigorous mixing will cause the liquid phase boundary layer to become smaller and increase the mass transfer coefficient.

When the salt solution contains KTPB precipitate, the KTPB concentration has the following effect on mass transfer. Increasing the KTPB concentration increases the slurry yield stress and consistency. The increase in yield stress and consistency increases the boundary layer thickness, which decreases the flux and the vapor benzene concentration.

Ventilation rate changes will affect the vapor phase boundary layer and mass transfer process in the following manner: If the ventilation rate increases, the vapor phase is diluted, the concentration difference across the vapor phase boundary layer increases, the vapor phase boundary layer thickness decreases, and the vapor phase mass transfer coefficient increases. Since in this test and the precipitation process, the vapor phase mass transfer

coefficient is typically much larger than the liquid phase mass transfer coefficient, increasing the ventilation rate will have a small effect on the overall mass transfer coefficient. If the ventilation rate is decreased, the flux will decrease while the bulk vapor concentration increases, approaching the equilibrium vapor pressure as the ventilation rate approaches zero. The vapor phase mass transfer coefficient will decrease and eventually approach the magnitude of the liquid phase mass transfer coefficient and have a significant effect on the overall mass transfer coefficient.

Experiments

The parameter tests are divided into two sets, a factorial matrix and single parameter effect tests. Table 1 shows the factorial test matrix which examined the influence of insoluble solids (KTPB, sludge, and titanate) and quiescent time on benzene release and retention.

Table 1. Factorial Test Matrix

Test	NaTPB (M)	KTPB (wt. %)	Cu (mg/L)	Sludge (mg/L)	Titanate (mg/L)	Na (M)	Salt	Temp (°C)	Quiescent Time (Days)
1	0.03	1	10	600	200	4.7	Avg.	50	33
2	0.03	10	10	6000	2000	4.7	Avg.	50	65
3	0.03	1	10	600	200	4.7	Avg.	50	64
4	0.03	10	10	6000	2000	4.7	Avg.	50	34
5	0.03	5.5	10	3300	1100	4.7	Avg.	50	44
6	0.03	5.5	10	3300	1100	4.7	Avg.	50	45

Table 2 shows the test matrix for the single parameter effect tests. Tests 7 and 8 were performed at 40° C and will be compared with Tests 3, 21 and 22 to determine the effect of temperature. Test 9 examined the effect of an intermediate radiation dose on a 1 wt. % KTPB, 4.7 M sodium slurry, and will be compared with Test 1. Tests 10 and 21 examined the effect of an intermediate sodium concentration which would occur during washing. Tests 11 and 12 examined the effect of other salt solution components as reflected in the high and low hydroxide salt solution types. Tests 13 and 14 examined the effect of sludge and titanate concentration. Tests 15 and 16 examined the effect of intermediate sodium molarities expected during washing in the precipitation process. Tests 17 and 18 simulate KTPB concentration, Na concentration, and radiation dose expected in Tank 49H and Late Wash. Tests 19 and 20 simulate freshly washed precipitate in Tank 48H. Tests 22 and 23 provide additional data on the impact of quiescent time on benzene retention and release with a 1 wt. % KTPB slurry.

Table 2. Single Parameter Effect Test Matrix

Test	NaTPB (M)	KTPB (wt.%)	Cu (mg/L)	Sludge (mg/L)	Titanate (mg/L)	Rad Dose (Mrad)	Na (M)	Salt	Temp (°C)	Quiescent Time (Days)
7	0.03	1	10	600	200	0	3.5	Avg.	40	75
8	0.03	1	10	600	200	0	4.7	Avg.	40	76
9	0.03	1	10	600	200	50	4.7	Avg.	50	30
10	0.03	1	10	600	200	0	2.0	Avg.	50	99
11	0.03	1	10	600	200	0	4.7	High	50	102
12	0.03	1	10	600	200	0	4.7	Low	50	103
13	0.03	1	10	300	100	0	4.7	Avg.	50	90
14	0.03	1	10	1200	400	0	4.7	Avg.	50	90
15	0.03	10	10	6000	2000	0	3.5	Avg.	50	33
16	0.03	10	10	6000	2000	0	2.0	Avg.	50	100
17	0.03	10	10	6000	2000	95	0.4	Avg.	50	32
18	0.03	10	10	6000	2000	95	0.4	Avg.	50	59
19	0.03	10	10	6000	2000	0	0.4	Avg.	50	65
20	0.03	10	10	6000	2000	0	0.4	Avg.	50	32
21	0.03	1	10	600	200	0	3.5	Avg.	50	76

22	0.03	1	10	600	200	0	4.7	Avg.	50	69
23	0.03	1	10	600	200	0	4.7	Avg.	50	155

In all of the tests, the NaTPB concentration was 0.03M, the copper concentration was 10 mg/L, and the palladium concentration was 2.6 mg/L. The approximate species concentrations in the slurry are shown in Table 3. It was prepared according to the following method: The solutions specified in Table 3 were prepared. The potassium salt solution was added to a container. The container was agitated and purged with nitrogen. The NaTPB solution was added to the container. The sludge, titanate, acid metal trim chemicals, basic metal trim chemicals, and noble metals were added to the container. The organic species, except for benzene and biphenyl, were added to the container. The benzene and biphenyl were added later, after the retention vessel was sealed. The slurry was sampled and qualitatively tested to confirm all of the potassium has precipitated. The sample was filtered and divided into two portions. One filtered sample was mixed with KNO₃ and the other was mixed with NaTPB. If all of the potassium has precipitated and an excess of dissolved NaTPB is present, the filtered sample mixed with KNO₃ should form a precipitate and the filtered sample mixed with NaTPB should not. After complete potassium precipitation was verified, the sodium salt solutions were added to the container, and the slurry was ready for benzene retention and release tests.

SRTC constructed a laboratory-scale apparatus to perform the benzene retention and release tests. Figure 2a is a picture of the apparatus, and Figure 2b is a schematic drawing. The apparatus contains twenty, 2-Liter glass kettles with five ports located on the top. The center port is for the agitator which mixes the vessel. The other ports are for an Omega RTD temperature probe, slurry sampling, nitrogen inlet tubing, and vapor outlet tubing. The inlet tubing is connected via a manifold to a high pressure nitrogen cylinder. The nitrogen flow rate through the vessels is controlled with a needle valve on the rotameters. The outlet tubing is connected to a tee. One side of the tee is connected to a manifold which is vented to a hood. The other side of the tee is connected to a manifold which is connected to an MTI online Gas Chromatograph (GC) for vapor benzene sampling. The kettles are placed in a water bath and controlled to the desired temperature with a Cole-Parmer digital immersion circulator.

The benzene retention and release tests were performed in the following manner: The KTPB slurries were prepared to yield the initial compositions shown in Tables 1 and 2 using the appropriate quantities of chemicals shown in Table 3. All of the constituents except for benzene and biphenyl were added to the kettle. The kettle was sealed and placed in the apparatus. The nitrogen purge was set to 10 ml/min, and the kettle was mixed for 15 minutes. After 15 minutes, the benzene and biphenyl were injected subsurface through a septum into the slurry. The slurry was mixed for another 45 minutes, and the agitation stopped. The sample valve was opened and the vapor sampled for approximately two hours. The agitator was turned off and the kettle remained quiescent for the time specified in Tables 1 and 2. During quiescent phases, the kettles were purged with nitrogen at 10 ml/min and the vapor benzene concentration was measured periodically with the GC. Slurry samples were collected weekly and analyzed for TPB, triphenylboron (3PB), and diphenylborinic acid (2PB) analyses.

The release tests were performed in the following manner: The vapor was sampled with no agitation at a purge rate of 10 ml/min. The purge rate was increased to 1 L/min, to minimize vapor phase mass transfer resistance, and the vapor sampled until the concentration reached steady-state. The agitator was turned on and the vapor benzene concentration measured for approximately 2 - 5 hours. The agitator was turned off and the vessel remained quiescent for seven days. After seven days, the agitation test was repeated for approximately 2 - 5 hours, or until the measured benzene concentration was less than 10 ppm. Following the release tests, the slurries were sampled and analyzed for TPB, 3PB, 2PB, phenylboric acid (1PB), phenol, biphenyl, boron, and potassium analyses. In some instances when the vapor benzene concentration was greater than 100 ppm at the end of the second release test, additional release tests were performed until the vapor benzene concentration was less than 100 ppm.

In addition to the benzene retention and release tests, baseline benzene release tests were performed. One of the glass kettles was filled with approximately 800 ml of deionized water and heated to 50° C. The kettle was purged with 1 L/min of nitrogen. Approximately 10 ml of benzene was added to the kettle, the kettle was agitated, and the vapor benzene concentration was measured as a function of time.

When performing the agitation tests, good mixing is imperative if the benzene is to be released. With Bingham plastic fluids, such as KTPB slurries, a mixing cavern could form. Inside the cavern, vigorous fluid motion would occur and the fluid would be well mixed. Outside the cavern, the fluid would be stagnant, and mixing would occur by natural convection and molecular diffusion only.^{4,5} If the mixing cavern does not reach the wall, the fluid at the wall will be stagnant. Mixing effectiveness in these tests was determined qualitatively by observing the fluid motion at the wall. If good fluid motion occurred at the wall, the vessel was considered well mixed. If the fluid was stagnant at the wall, the fluid was not considered well mixed.

Table 3. KTPB Slurry Recipe

<u>Component</u>	<u>Concentration (g/kg slurry)</u>
<u>Potassium Salt Solution</u>	
NaOH	1.25 - 10.9
KNO ₃	0.33 - 11.3
KNO ₂	0 - 14.3
CsNO ₃	0.01 - 0.025
NaNO ₃	0.06 - 146.76
NaNO ₂	18.28 - 43.86
NaCl	0.01 - 0.694
NaF	0.008 - 0.284
Na ₂ SO ₄	0.055 - 4.2
Na ₃ PO ₄ ·12H ₂ O	0.32 - 1.93
<u>NaTPB Solution</u>	
NaTPB	16.93 - 106.3
NaOH	0.2 - 3.0
<u>Sodium Salt Solution</u>	
NaOH	44.3 - 147
Na ₂ CO ₃ ·H ₂ O	2.63 - 18.92
Al(NO ₃) ₃ ·9H ₂ O	1.27 - 158.9
<u>Sludge/Titanate Solutions</u>	
Sludge	300 - 6000
NaTi ₂ O ₅ H	100 - 2000
<u>Acid Metal Trim Solution</u>	
Cu(NO ₃) ₂ ·2.5H ₂ O	36.6
SnCl ₂ ·2H ₂ O	4.4
Zn(NO ₃) ₂ ·6H ₂ O	35
Fe(NO ₃) ₃ ·9H ₂ O	10.1
AgNO ₃	0.79
RuCl ₃	9.44
Pd(NO ₃) ₂	4.76
Rh(NO ₃) ₃	3.37
HNO ₃	2.84 - 55.0
<u>Basic Metal Trim Solution</u>	
Na ₂ CrO ₄	95 - 227
K ₂ MoO ₄	12 - 30
NaOH	4 - 12.5
<u>Noble Metal Solutions</u>	
RuCl ₃	1.64
Pd(NO ₃) ₂	0.87
Rh(NO ₃) ₃	0.56
<u>Organic Trim Chemicals</u>	
	<u>Concentration (mg/L Slurry)</u>
Benzene	720
Phenol	125
Phenylboric Acid	125

Biphenyl	150
Diphenylborinic Acid	125
Triphenylboron	125
Isopropyl Alcohol	50
Methanol	5

Results

Factorial Test Matrix

Table 4 shows the results of the Factorial Matrix tests. Figure 3 show an example of the quiescent and agitated benzene release rates. The top plot shows quiescent benzene flux and the bottom plot shows the agitated benzene flux. Table 4 also shows the maximum flux from the baseline test in which 10 ml of benzene was injected into 800 ml of deionized water at 50° C, purged with nitrogen at 1 L/min, and agitated at 159 rpm. Figure 4 shows the benzene release flux from the baseline test as a function of time.

Table 4. Factorial Matrix Test Results

Test	KTPB (wt. %)	Quiescent Time (days)	Maximum Flux During Agitation (g/m ² min)	Average Quiescent Flux (g/m ² hr)	Quiescent Release (grams)	Agitated Release (grams)	Total Release (grams)
1	1.0	33	2.86	0.27	1.60	1.62	3.47
2	10.0	65	1.24	0.56	6.55	0.95	8.44
3	1.0	64	5.62	0.35	4.00	1.92	6.20
4	10.0	34	0.02	0.25	1.53	0.03	1.56
5*	5.5	44	3.08	0.33	2.58	4.50	7.09
6*	5.5	45	1.19	0.16	1.26	4.62	6.43
Average			2.34	0.32	2.92	2.27	5.53
σ_{total}			1.97	0.14	2.04	1.89	2.53
σ_r			1.66	0.09	0.67	0.45	0.59
σ_{ho}			0.77	0.12	1.31	0.32	2.08
Baseline			30	N/A	N/A	N/A	N/A

* More than two agitation tests performed

In Tests 1, 2, 3, and 6, the quiescent benzene release showed a large peak of approximately 0.1 g/m²min on the first day which decreased to an approximately steady value of 0.005 g/m²min. The probable cause of the large peak is the free benzene which was added to the slurry, subsurface. This large peak was not observed in Tests 4 and 5. The reason the large peak was not observed is probably the high KTPB concentration, yield stress, and consistency of the slurry. Tests 4 and 5 had KTPB concentrations of 10 wt. % and 5.5 wt. %, respectively. Previous SRTC work predicts a yield stress of < 10 dynes/cm² for a 1 wt. % KTPB slurry, 98 dynes/cm² for a 5.5 wt. % KTPB slurry, and 267 dynes/cm² for a 10 wt. % KTPB slurry. The predicted consistencies are < 10 cp. for a 1 wt. % KTPB slurry, 18 cp. for a 5.5 wt. % KTPB slurry, and 46 cp. for a 10 wt. % KTPB slurry. A high yield stress and consistency would reduce fluid motion and benzene transport to the slurry-vapor interface. This result will be discussed in the next section.

In general, the agitated benzene release plots showed a rapid benzene peak and a gradual decrease in benzene flux as the slurry became depleted of benzene. Tests 1, 3, and 5 showed a peak flux of 3 - 6 g/m²min. Test 2 showed a very quick, narrow peak, followed by a decrease in benzene flux, and an increase in benzene flux as agitation speed was increased. Tests 4 and 6 showed no initial benzene flux peak. Tests 4 and 6 had KTPB concentrations of 10 wt. % and 5.5 wt. %, respectively. The probable cause of this observation is the high KTPB concentration, yield stress, and consistency of the slurry. The high yield stress and consistency reduce fluid motion and benzene

transport to the surface. Mixing difficulties were observed in tests 4 and 6. In test 6, the fluid motion at the very wall was very slow. In test 4, no fluid motion was observed at the wall. Tests 5 and 6 showed a long steady release of approximately $1 \text{ g/m}^2\text{min}$.

The average quiescent flux, the quiescent release, and total release in test 2 may be biased high by a single point collected on day 65. This point is higher than the other pre-agitation quiescent data and contributed approximately 1.5 grams to the quiescent release and $0.13 \text{ g/m}^2\text{hr}$ to the average quiescent flux.

The maximum flux during agitation and the agitated release are dependent on the quiescent release. If a large quiescent benzene release occurred, insufficient benzene remained to obtain good characterization of the agitated release.

The baseline tests with benzene and water showed a rapid increase in flux to approximately $30 \text{ g/m}^2\text{min}$ which is much higher than in any of the KTPB slurries.

Five results were examined to determine the impact of KTPB concentration and time: (1) maximum benzene flux during agitation, (2) average quiescent flux, (3) integrated quiescent benzene release, (4) integrated agitated benzene release, and (5) integrated total benzene release. The integrated quiescent release is the benzene released prior to the start of the first agitation test. The integrated total release includes the quiescent release prior to the start of agitation, quiescent releases after the first agitation test, and agitated benzene releases. One must exercise caution in interpreting the maximum flux during agitation and the integrated agitated release data. If a large integrated quiescent release occurred, very little benzene remained in the slurry to be released during agitation. The effect of interactions between quiescent time and KTPB concentration was not measured in this study. Table 5 shows the average of these results as a function of KTPB concentration and time.

Table 5. Average Response by Variable

Variable	Maximum Flux During Agitation ($\text{g/m}^2\text{min}$)	Average Quiescent Flux ($\text{g/m}^2\text{hr}$)	Quiescent Release (grams)	Agitated Release (grams)	Total Release (grams)
1 wt. %	4.24	0.31	2.80	1.77	4.83
5.5 wt. %	2.14	0.24	1.92	4.56	6.76
10.0 wt. %	0.63	0.40	4.04	0.49	5.00
Effect	-3.61	0.09	1.24	-1.28	0.17
33 - 34 days	1.44	0.26	1.57	0.83	2.52
44 - 45 days	2.14	0.24	1.92	4.56	6.76
64 - 65 days	3.43	0.46	5.28	1.44	7.32
Effect	1.99	0.20	3.71	0.61	4.80
σ_{total}	1.97	0.14	2.04	1.89	2.53
$2\sigma_r$	3.33	0.18	1.35	0.90	1.17
$2\sigma_{\text{ho}}$	1.55	0.23	2.62	0.63	4.16

The table shows the maximum flux during agitation decreases with KTPB concentration. The integrated agitated benzene release increases, and then decreases with KTPB concentration. The average quiescent flux, integrated quiescent release, and integrated total release show slight variations with KTPB concentration. The probable reason for the large total release with the 5.5 wt. % slurries is more than two release tests were performed with each of these slurries. The additional release tests occurred approximately 30 days after the second release test. The additional time would allow more TPB decomposition and benzene formation.

The maximum flux during agitation, average quiescent flux, integrated quiescent benzene release, and integrated total benzene release increase with quiescent time. The agitated release increases, and then decreases with time.

To determine whether the variations in responses are significant, the effect of a variable is calculated by taking the difference between the average response at the highest KTPB concentration or time and the average response at the lowest KTPB concentration or time (see equation [11]).⁶

$$\text{Effect} = (y_{+\text{avg}} - y_{-\text{avg}}) \quad [11]$$

In equation [11], $y_{+\text{avg}}$ is the average response at the highest value of the variable of interest and $y_{-\text{avg}}$ is the average response at the lowest value of the variable of interest. The effect is compared with the experimental uncertainty of the response calculated from the tests. If the absolute value of the effect is greater than the experimental uncertainty, the effect is significant. If it is less than the experimental uncertainty, it is not significant.

Table 4 contains three estimates of the standard deviation: an overall standard deviation based on all six tests, a standard deviation calculated from replicated tests, and a standard deviation calculated from higher order interactions.

The factorial matrix was designed with Tests 5 and 6 being replicates. Test 22 in the single parameter effect tests is a replicate of Test 3. A standard deviation (σ_r) can be calculated from these four tests using equation [12].⁶

$$\sigma_r^2 = (s_1^2 + s_2^2)/2 = (d_1^2/2 + d_2^2/2)/2 \quad [12]$$

In equation [12], s_1^2 is the variance of measurements in Tests 3 and 22, s_2^2 is the variance of measurements in Tests 5 and 6, d_1 is the difference between measurements in Tests 3 and 22, and d_2 is the difference between measurements in Tests 5 and 6. Caution must be exercised when calculating the experimental uncertainty by this method, because it is based on tests with 1 wt. % and 5.5 wt. % KTPB slurries. The uncertainty with 10 wt. % slurries may be larger. Test results with 10 wt. % slurries show they are very sensitive to mixing effectiveness.

Another method for estimating the experimental uncertainty is to assume the higher order effects are insignificant and calculate the standard deviation from the higher order effects.⁶ In this test, the only higher order effect which can be measured is the interaction of KTPB concentration and quiescent time. The effect is calculated from equation [13]

$$E = Y(10\%, 60 \text{ days}) + Y(1\%, 30 \text{ days}) - Y(10\%, 30 \text{ days}) - Y(1\%, 60 \text{ days}) \quad [13]$$

where Y is the measured response.⁶ Since only one higher order effect can be measured, the standard deviation is equal to that effect ($\sigma_{ho} = E$). Caution must be exercised in applying this method since the insignificance of the KTPB - time interaction has not been proven, and this method is normally applied to effects 3rd order and higher, and to factorial matrices which are 2³ and higher.

A final method for calculating the experimental uncertainty is to calculate the standard deviation from all six tests. This estimate will be biased by KTPB concentration and quiescent time effects, but it does allow a comparison of those effects with the variations throughout the test. The standard deviation can be calculated with equation [14]

$$\sigma_{\text{total}} = [\sum (y_i - y_{\text{avg}})^2 / (n-1)]^{1/2} \quad [14]$$

where y_i is the measured response, y_{avg} is the average response, and n is the number of data points.⁷

If the data follow a normal distribution, 95% of the data will be within two standard deviations of the mean.^{6,8} To determine if the effects are significant, they should be compared with the standard deviation calculated from all six tests (σ_{total}), two times the standard deviation calculated from the replicates ($2\sigma_r$), and two times the standard deviation calculated from the higher order interactions ($2\sigma_{ho}$). Because of the bias due to KTPB and time effects, the standard deviation calculated from all six tests was not multiplied by two. To determine if the effects are important, they were compared with all three estimates of the experimental uncertainty. Table 5 shows the results.

From Table 5, one can see that KTPB concentration has a significant effect on the maximum benzene flux during agitation. KTPB concentration does not have a significant effect on the average quiescent flux, the integrated quiescent benzene release, or the integrated total benzene release. It has a nonlinear effect on the benzene release during agitation, with the maximum integrated benzene release occurring with the 5.5 wt. % KTPB slurries rather than the 1 wt. % or 10 wt. % slurries. The probable explanation for this result will be discussed in the next section.

Time has a significant effect on the integrated quiescent benzene release, the integrated total benzene release, and the maximum benzene flux during agitation. It does not have a significant effect on the agitated benzene release. The large integrated agitated release observed at 45 days is more likely due to a concentration effect rather than a time effect. There appears to be an effect of time on the average quiescent flux, but only one of the 64-65 day tests shows the effect. The effect in that test may be due to a single high data point. This point is higher than the other pre-agitation quiescent data and contributed approximately $0.13 \text{ g/m}^2\text{hr}$ to the average quiescent flux.

Single Parameter Tests

Table 6 and shows the single parameter test results. Figure 5 shows a sample plot of benzene release flux versus time. The top plot is the quiescent benzene flux, and the bottom plot is the agitated benzene flux. Table 6 includes the benzene baseline test results. The average and total standard deviations shown in Table 6 are for all 23 tests. The experimental uncertainties calculated from higher order interactions and replicates are the same as in Table 5.

In Tests 7, 8, 10, 11, 12, 13, 14, 16, 19, 21, and 22, the quiescent benzene release showed a large peak of $0.08 - 0.2 \text{ g/m}^2\text{min}$ on the first day which decreased to an approximately steady value ($\sim 0.006 \text{ g/m}^2\text{min}$). The probable cause of the large peak is the free benzene which was added to the slurry, subsurface. This large peak was not observed in Tests 9, 15, 18, 20, and 23. In Test 23, the vapor benzene concentration was not measured on the first day. The slurries in Tests 15, 18, and 20 were 10 wt. % KTPB. The 10 wt. % slurries would have a higher yield stress and consistency which would decrease benzene transport to the vapor phase. Tests 9 and 18 were performed with irradiated slurries. Much of the benzene formed may have been released prior to the start of the test.

In general, the agitated benzene release plots showed a rapid benzene peak and a gradual decrease in flux as the slurry became depleted of benzene. Some of the plots do not show a large benzene flux peak. With the 10.0 wt. % slurries, the probable cause of the lack of a peak is the high KTPB concentration, yield stress, and consistency of the slurry which reduces benzene transport. With the 1.0 wt.% slurries, the probable cause of this observation is the long quiescent time which allowed the slurry to deplete much of its benzene before the release test started. Within about one hour, the benzene release flux started to decline in the 1 wt. % slurries. With the 10 wt. % slurries, a steady flux occurred for several hours, and increased as agitator speed increased.

To determine if parameters have a significant effect, the differences in test results are compared with the experimental uncertainties in Table 6.

To determine the effect of temperature on benzene retention and release, Test 7 can be compared to Test 21, and Test 8 can be compared with Tests 3 and 22. Table 7 shows the comparison. With the 3.5 M slurries, increasing temperature caused an increase in the average quiescent flux and the integrated quiescent benzene release. The integrated agitated release is higher for the 40°C slurry, because most of the benzene had been released prior to agitation with the 50°C slurry. Because of the differences in test time and the limited quiescent data collected, no temperature effects could be measured with 4.7 M sodium slurries. Test 22 was performed with an agitator speed of 60 - 80 rpm rather than 120 - 150 rpm which explains the lower maximum flux during agitation.

Table 8 shows the effects of sodium concentration on benzene retention and release. Tests 7 and 8 were performed with 1 wt. % slurries at 40°C . The sodium concentration ranged from 3.5 - 4.7 M. Tests 1, 3, 10, 21, 22, and 23 were performed with 1 wt. % slurries at 50°C . The sodium concentration ranged from 2.0 - 4.7 M. Tests 2, 15, 16, 19, and 20 were performed with 10 wt. % slurries at 50°C . The sodium concentration ranged from 0.4 - 4.7 M. No effect of sodium concentration was measured between 2.0 M and 4.7 M sodium. The integrated quiescent releases and integrated total releases for Tests 1 and 15 are significantly lower than in the other tests. The likely

cause of this observation is the short quiescent time (33 days versus 64 - 155 days). With the 0.4 M sodium and 10 wt. % KTPB slurries, large increases were observed in the maximum flux during agitation, average quiescent flux, integrated agitated benzene release, and integrated total benzene release. Several possible explanations exist for this observation. The slurries were 10 wt. % KTPB and 0.4 M sodium. The low sodium concentration would lead to a higher KTPB solubility, but SRTC testing has shown reducing the sodium concentration reduces the decomposition reaction rate constant. Another explanation is the better slurry mixing observed in Tests 19 and 20 than in the other tests with 10 wt. % slurries. The reason for this result will be discussed in the next section.

Table 6. Single Parameter Test Results

Test	Maximum Flux During Agitation (g/m ² min)	Average Quiescent Flux (g/m ² hr)	Quiescent Release (grams)	Agitated Release (grams)	Total Release (grams)
7	5.03	0.27	3.64	1.76	5.69
8	4.24	0.32	4.39	1.29	5.94
9	3.09	0.26	1.40	2.86	4.85
10*	0.61	0.31	5.55	0.04	5.71
11	0.53	0.27	5.04	0.15	7.26
12	0.02	0.30	5.57	0.01	5.60
13	10.40	0.47	7.67	2.44	10.87
14	4.06	0.52	8.35	2.46	11.09
15*	0.99	0.15	0.90	2.64	4.35
16	0.80	0.34	6.03	0.37	7.00
17	0.52	0.29	1.65	0.75	2.61
18	1.01	0.27	2.85	0.85	3.70
19	12.10	0.62	7.28	6.40	14.05
20*	9.52	1.32	7.60	9.18	16.78
21	0.27	0.51	6.98	0.16	7.39
22	2.88	0.30	3.74	1.03	5.23
23	0.48	0.25	7.04	0.15	7.19
Avg.	2.57	0.38	4.49	2.01	6.89
σ_{total}	3.20	0.24	2.43	2.29	3.53
$2\sigma_r$	3.33	0.18	1.35	0.90	1.77
$2\sigma_{\text{ho}}$	1.55	0.23	2.62	0.63	4.16
Baseline	30	N/A	N/A	N/A	N/A

* More than two agitation tests performed

Table 7. Temperature Effects On Benzene Release And Retention

Test	Temp- erature (° C)	Na (M)	Time (Days)	Maximum Flux During Agitation (g/m ² min)	Average Quiescent Flux (g/m ² hr)	Quiescent Release (grams)	Agitated Release (grams)	Total Release (grams)
7	40	3.5	75	5.03	0.27	3.64	1.76	5.69
21	50	3.5	76	0.27	0.51	6.98	0.16	7.39
8	40	4.7	76	4.24	0.32	4.39	1.29	5.94
3	50	4.7	64	5.62	0.35	4.00	1.92	6.20
22	50	4.7	69	2.88	0.30	3.74	1.03	5.23

Table 9 shows the effect of salt composition on benzene retention and release. The results show salt solution type has no significant effect on quiescent benzene release and retention. The differences observed are less than the experimental uncertainty. Because most of the benzene release occurred during the quiescent phase, caution must be exercised in interpreting the agitation release data.

Table 10 shows the effect of sludge concentration on benzene release and retention. The difference between the average quiescent flux, integrated quiescent release, integrated agitated release and integrated total release for tests 14 and 13 is less than the experimental uncertainty. The differences in the maximum flux during agitation are probably due to differences in mixing effectiveness or an effect of the additional sludge on the slurry yield stress and consistency. Both Tests 13 and 14 had higher benzene releases than the slurries with average sludge.

Table 11 shows the effect of irradiation on benzene retention and release. The 50 Mrad slurry showed no significant difference in benzene release from the unirradiated 1 wt % KTPB slurry. The 95 Mrad slurries showed a decrease in the maximum benzene flux during agitation, the average quiescent flux, the integrated quiescent release, the integrated agitated benzene release, and the integrated total benzene release. These results will be discussed later.

Table 8. Sodium Molarity Effects on Benzene Release and Retention

Test	Temperature (°C)	Na (M)	KTPB (wt. %)	Time (Days)	Maximum Flux During Agitation (g/m ² min)	Average Quiescent Flux (g/m ² hr)	Quiescent Release (g)	Agitated Release (g)	Total Release (g)
8	40	4.7	1.0	76	4.24	0.32	4.39	1.29	5.94
7	40	3.5	1.0	75	5.03	0.27	3.64	1.76	5.69
1	50	4.7	1.0	33	2.86	0.27	1.60	1.62	3.47
3	50	4.7	1.0	64	5.62	0.35	4.00	1.92	6.20
22	50	4.7	1.0	69	2.88	0.30	3.74	1.03	5.23
23	50	4.7	1.0	155	0.48	0.25	7.04	0.15	7.19
21	50	3.5	1.0	76	0.27	0.51	6.98	0.16	7.39
10	50	2.0	1.0	99	0.61	0.31	5.55	0.04	5.71
2	50	4.7	10.0	65	1.24	0.56	6.55	0.95	8.44
15	50	3.5	10.0	33	0.99	0.15	0.90	2.64	4.35
16	50	2.0	10.0	100	0.80	0.34	6.03	0.37	7.00
19	50	0.4	10.0	65	12.1	0.62	7.28	6.40	14.05
20	50	0.4	10.0	32	9.52	1.32	7.60	9.18	16.78

Table 9. Effect of Salt Composition on Benzene Retention and Release

Test	Salt Solution	Time (Days)	Maximum Flux During Agitation (g/m ² min)	Average Quiescent Flux (g/m ² hr)	Quiescent Release (g)	Agitated Release (g)	Total Release (g)
11	High OH	102	0.53	0.27	5.04	0.15	7.26
12	Low OH	103	0.02	0.30	5.57	0.01	5.60
3	Average OH	64	5.62	0.35	4.00	1.92	6.20
23	Average OH	155	0.48	0.25	7.04	0.15	7.19
22	Average OH	69	2.88	0.30	3.74	1.03	5.23

Table 10. Effect of Sludge Concentration on Benzene Retention and Release

Test	Sludge Concentration	Time (Days)	Maximum Flux During Agitation (g/m ² min)	Average Quiescent Flux (g/m ² hr)	Quiescent Release (g)	Agitated Release (g)	Total Release (g)
14	High Sludge	90	4.06	0.52	8.35	2.46	11.09
13	Low Sludge	90	10.40	0.47	7.67	2.44	10.87
3	Average Sludge	64	5.62	0.35	4.00	1.92	6.20
23	Average Sludge	155	0.48	0.25	7.04	0.14	7.28
22	Average Sludge	69	2.88	0.30	3.74	1.03	5.23

Table 11. Irradiation Effects on Benzene Retention and Release

Rad	Maximum Flux	Average	Quiescent	Agitated	Total
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Tes t	KTPB (wt. %)	Dose (Mrad)	Time (Days)	During Agitation (g/m2min)	Quiescent Flux (g/m2hr)	Release (g)	Release (g)	Release (g)
1	1.0	0	33	2.86	0.27	1.60	1.63	3.65
9	1.0	50	30	3.09	0.26	1.40	2.76	4.70
17	10.0	95	32	0.52	0.29	1.65	0.75	2.61
18	10.0	95	59	1.01	0.27	2.85	0.85	3.70
19	10.0	0	65	12.1	0.62	7.28	6.40	14.05
20	10.0	0	32	9.52	1.32	7.60	9.18	16.78

Discussion

This test program evaluated the impact of the variables KTPB concentration, sodium concentration, sludge concentration, salt solution type, radiation dose, and time on benzene retention and release in simulated KTPB slurries.

The benzene flux can be described by equation [17].

$$J = K_g A (C_g^* - C_g) = K_g A (P_{\text{vap}} - P_b) \quad [17]$$

In equation [17], J is the benzene flux, K_g is the overall mass transfer coefficient, A is the surface area, C_g^* is the vapor concentration of benzene which is in equilibrium with the slurry, C_g is the bulk vapor benzene concentration, P_{vap} is the vapor pressure of the benzene in the salt solution, and P_b is the partial pressure of benzene. To change the benzene flux, one must change the mass transfer coefficient (K_g), the surface area (A), or the concentration difference ($C_g^* - C_g$).

KTPB Concentration Effects

The KTPB concentration was observed to have an impact on the maximum benzene release flux during agitation, with increasing KTPB concentration causing a decrease in the maximum benzene release flux during agitation. The cause of this decrease is the increasing yield stress and consistency of the slurry which increases resistance to benzene transport. A 1 wt. % slurry would have a yield stress of less than 10 dynes/cm² and a consistency of less than 10 cp., and a 10 wt. % slurry would have a yield stress of 267 dynes/cm² and a consistency of 46 cp. The higher yield stress and consistency will cause less vigorous agitation to occur which will reduce the transport of benzene to the vapor phase.

KTPB concentration also had an effect on the amount of benzene released during agitation. The effect appears to be nonlinear with the maximum agitated release occurring with a 5.5 wt. % KTPB slurry. Even though no effect was measured, one would expect a higher KTPB concentration to lead to less quiescent release and more benzene retention. Since the slurry temperature is 40° - 50° C, and the purge gas is at ambient temperature, a heat loss will occur from the slurry to the gas. Since the vessels were contained in a water bath with the water level exceeding the slurry height, no thermal convection will occur through the bottom or side of the vessel. Thermal convection will only occur through the top of the slurry into the purge gas. The thermal gradient will cause convective mass transfer. The slurry yield stress and consistency would reduce fluid motion and convective mass transfer. The 5.5 wt. % and 10 wt. % slurries would have more retained benzene when agitation started. The 5.5 wt. % slurry has a low enough yield stress and consistency (~ 98 dynes/cm² and ~ 18 cp.), the agitation releases most of the retained benzene. Because the 10 wt. % slurry has a very high yield stress and consistency (~ 267 dynes/cm² and ~ 46 cp.), fluid motion within the slurry is less, and less of the retained benzene is released. No significant difference was observed in the agitated benzene release between the 1 wt. % slurries and the 10 wt. % slurries.

No effect from KTPB concentration was measured on the average quiescent flux, the integrated quiescent benzene release, or the integrated total benzene release. One would expect the 10 wt. % slurry to release less benzene during its quiescent phase. In these tests, some of the 10 wt. % slurries dried out and/or foamed. This drying out or foaming created more surface area at the slurry-vapor interface which would increase benzene transport to the vapor phase. Additionally, a couple of data points with high benzene concentrations in the vapor phase may have skewed these results.

Quiescent Time Effects

The quiescent time had a significant effect on the integrated quiescent benzene release and the integrated total benzene release, with increasing quiescent times leading to increasing benzene releases over the time studied (30 - 155 days). The quiescent time had no effect on the integrated agitated benzene release. The large value for integrated agitated release at 45 days is more likely due to the KTPB concentration effect rather than quiescent time effect.

Table 5 shows quiescent time may have an effect on average quiescent flux. The trend is only observed with the 10 wt. %, 65 day slurry, and is due to a single data point. This point is higher than the other pre-agitation quiescent data and contributed approximately 0.13 g/m²hr to the average quiescent flux. By reviewing Tables 4 and 6, one can see all of the average quiescent fluxes are within the experimental uncertainty, except for three tests (numbers 15, 19, and 20). The average quiescent flux in Test 15 is just outside the experimental uncertainty. Tests 19 and 20 showed significantly increased benzene releases and will be discussed later. As the quiescent time becomes very long and the slurry becomes depleted of benzene, the average quiescent flux will decrease.

Quiescent time appears to have an effect on the maximum benzene release flux during agitation. The reason for the effect is the longer the slurry remains quiescent, the more time the phenylborates have to decompose and form benzene. The reason for the effect on maximum benzene release flux is the long quiescent time allows the benzene to be generated and build up in the slurry.

Temperature Effects

Temperature was observed to have an effect on benzene retention and release with the 3.5 M sodium slurries at 40° and 50° C. The 50° C slurry had a higher average quiescent flux and quiescent release than the 40° C slurry. The reasons for this result are at higher temperatures, the TPB decomposition reaction is faster, fluid viscosity decreases⁹, yield stress decreases¹⁰, consistency decreases¹⁰, diffusivity increases¹¹ and benzene vapor pressure increases¹¹. The increased generation rate provides more benzene for release. The lower viscosity, yield stress, and consistency, and the higher diffusivity increase the rate of transport of the benzene to the vapor phase. As the temperature of a 4.7 M sodium slurry increases from 40° C to 50° C, the benzene vapor pressure increases by 45%. The reason for the higher maximum agitated flux and the higher agitated release at 40° C rather than at 50° C is more of the benzene had been removed from the 50° C slurry prior to the release test. Because of differences in test time and the limited quiescent data collected, no temperature effects were observed with the 4.7 M slurries.

Sodium Concentration Effects

With the exception of a 10 wt. % KTPB, 0.4 M sodium slurry, sodium molarity did not have a significant effect on benzene release. The differences observed in the quiescent release and total release in Table 8 for 2.0 - 4.7 M sodium slurries are due to differences in quiescent time and/or experimental uncertainties. The differences in the maximum flux during agitation are due to differences in quiescent release. This result is expected.

At constant temperature, the benzene vapor saturation concentration is independent of salt solution sodium concentration. With a saturated salt solution, the sodium concentration has no effect on the equilibrium vapor benzene concentration, C_g^* . Changing the sodium concentration will have no effect on the concentration gradient until the slurry benzene concentration is less than the solubility limit.

The liquid phase mass transfer coefficient in agitated vessels can be described by equation [18].¹²

$$k_1 = 0.138 (4 N_p N^3 D_I^5 / 3.14 D_T^2 H)^{1/4} (\alpha^{2/3} / \nu^{5/12}) \quad [18]$$

In equation [18], N_p is the power number, N is the agitator speed, D_I is the impeller diameter, D_T is the vessel diameter, H is the fluid height, α is the molecular diffusivity, and ν is the kinematic viscosity. Only the molecular diffusivity and kinematic viscosity will be affected by changes in sodium concentration. Previous work investigating the effect of conductivity on diffusion in electrolyte solutions shows changes of less than 20 % in molecular diffusivity as the conductivity increases.¹¹ With salt solutions such as NaNO_3 , the kinematic viscosity changes by less than 45% as the concentration increases from 0.36 - 5.0M.¹³ According to equation [18], decreasing the molecular diffusivity by 20% and increasing the kinematic viscosity by 45%, will decrease the mass transfer coefficient by less than 30%. Since $K_g \equiv k_1/H$ and changes in the sodium concentration change the liquid phase mass transfer coefficient by less than 30%, changes in sodium concentration will change the overall mass transfer coefficient by less than 30%. Since the change in sodium concentration will have minimal effect on the mass transfer coefficient, reducing the sodium concentration should have a small effect on the benzene release flux.

The 0.4 M sodium, 10 wt. % KTPB unirradiated slurries had a higher maximum flux during agitation, average quiescent flux, integrated quiescent release, integrated agitated release, and integrated total release. From measuring the boron production data, one can see that more TPB decomposition occurred than in the other tests (2 - 4X). Even though the TPB decomposition reaction is slower at 0.4 M than at 4.7 M, the higher NaTPB and KTPB solubility provides more material for benzene generation and benzene release. No significant differences in mixing effectiveness were observed. The high benzene releases observed are more likely due to benzene generation rather than a mixing effect.

Salt Solution Type and Sludge Concentration Effects

Salt solution type had no significant effect on benzene retention and release, as expected. Changing the concentrations of NO_3^- , NO_2^- , OH^- , SO_4^- , CO_3^- , and AlO_2^- should have no effect on benzene generation. None of these species has been identified as a catalyst in TPB decomposition. Changing their concentrations should have no effect on the mass transfer coefficient. Previous SRTC work investigating the vapor pressure of benzene over salt solutions shows for a constant sodium molarity, changing the anion concentrations will change benzene solubility and Henry's law constant, but will not significantly affect the benzene vapor pressure over a solution saturated with benzene.

Sludge concentration had no significant effect on benzene retention and release, as expected. It did have an effect on the maximum flux during agitation. The effect may be due to differences in mixing effectiveness or to an effect of sludge concentration on the slurry yield stress.

Radiation Dose Effects

The 50 Mrad, 1 wt. % KTPB slurry showed no significant difference in benzene release from the unirradiated 1 wt. % KTPB slurry. It did show higher measurable soluble boron and potassium than the unirradiated 1 wt. % KTPB, 4.7 M sodium slurries which would indicate more TPB decomposition occurred with the irradiated slurry than with the unirradiated slurry. Possible reasons for the lack of difference in quiescent and agitated release data are the additional benzene formed was released prior to the start of the test, or the TPB decomposed to products other than benzene. The increased TPB decomposition may be due to the additional quiescent time which occurred during the transportation of the slurries to the Co-60 source, the irradiation time, and the transport of the slurries to the test apparatus (approximately 2 - 4 weeks).

The 95 Mrad, 10 wt. % KTPB slurries showed a decrease in the maximum flux during agitation, the average quiescent flux, the integrated quiescent release, the integrated agitated benzene release, and the integrated total benzene release. One explanation for this phenomenon is the irradiation increases TPB decomposition, and much of the benzene release occurs prior to the start of the test. Since irradiation decreases the slurry yield stress and consistency, it should allow generated benzene to be transported to the vapor phase faster. Another explanation is

the irradiation leads to the formation of other aromatic compounds. The chemist who performed the HPLC analysis of the slurries noticed very distinct peaks with the non-irradiated slurries. With the irradiated slurries, he noticed interferences on the chromatograms, which would indicate the presence of other organic species. Previous SRTC investigations of the effect of radiation on TPB has shown it decomposes to a variety of organic species. A radiation dose of 95 Mrad would decompose approximately 10 % of the TPB, with a 50% benzene yield. The formation of radiolysis products other than benzene would account for only part of the difference observed. The soluble boron production in the 95 Mrad slurries was the same as in the unirradiated slurries, indicating approximately the same TPB decomposition. Other SRTC work has shown radiation reduces the vapor pressure of benzene over a KTPB slurry. Since the vapor benzene concentration at the end of the release tests was less than 10 ppm, the slurries appear to be depleted of benzene. The most likely explanation for the results observed with irradiated slurries is much of the benzene formed prior to the start of the test was lost prior to placing slurries in experimental apparatus.

Additional Observations

During the tests, good mixing was imperative for removing benzene from the slurries. Benzene release rate was found to vary with agitator speed for a given slurry. In tests with low agitator speeds (40 - 80 rpm), controlling the speed was very difficult. The agitated release fluxes varied as the speed varied. The 10 wt. % slurries were extremely difficult to mix. As the agitation tests started, the vessels were examined to determine whether good fluid motion existed at the walls. If the fluid at the walls was stagnant, the agitator speed was increased. In some instances agitator speeds of 210 rpm were needed (typical agitator speeds during release tests were 120 - 150 rpm). When agitation stopped, the benzene flux decreased rapidly.

Globules were observed in the 1 wt. % slurries at the liquid-slurry interface (see Figure 6). They were not observed in the 5.5 and 10 wt. % slurries. This observation would suggest the concentration of benzene needed to form the globules is a function of KTPB concentration. In one release test, the agitator was stopped after 10 min-utes. The globules were observed at the slurry-vapor interface. Since the agitation stopped for only 1 - 2 minutes, no change in flux was observed.

After the 1 wt. % slurry release tests, a white film was observed at the liquid-vapor interface (see Figure 7). The film disappeared after several days. A sample of the film was collected, filtered, and analyzed by HPLC. The results were 974 mg/L TPB, 37 mg/L 3PB, < 10 mg/L 2PB, 46 mg/L 1PB, 543 mg/L phenol, and 15 mg/L biphenyl.

The 1 wt. % and 5.5 wt. % slurries floated at the start of the test. During the quiescent phase, pieces of slurry would sink. Generally, the 1 wt. % slurries would sink after the release test. In some cases when a slurry was not depleted of benzene, it would float after the release test. In some tests, because of the long quiescent time, the slurry was almost completely sunk at the start of the release test. A plausible explanation for this phenomenon is the benzene and KTPB form a benzene-KTPB matrix. The matrix has a lower density than KTPB, and the matrix floats. As benzene is released, its concentration in the matrix is reduced increasing the density. After the slurry is depleted of benzene, its density is large enough the slurry sinks. The 5.5 wt. % slurries floated at the end of those release tests.

Mechanism for Benzene Release

This section describes a hypothesis for benzene release from KTPB slurries. Benzene release from KTPB slurries occurs by two mechanisms: convective mass transfer and "readily releasable" benzene. Figure 8 describes the mechanisms.

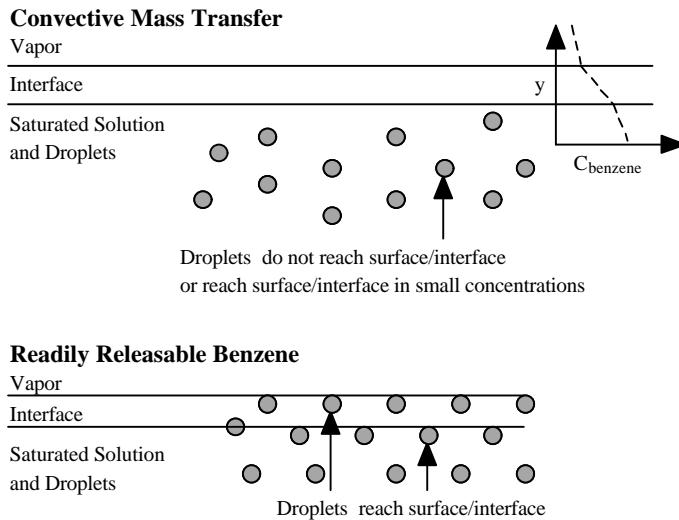


Figure 8. Mechanisms for Benzene Release

In convective mass transfer, the slurry contains benzene at or below its solubility and droplets (if above the solubility limit) containing benzene, biphenyl, and TPB. The droplets vary in size and are much smaller in a system which has been mixed. The large droplets observed are referred to as globules. The droplets exist in the slurry and supernate, but do not penetrate the vapor-slurry interface. As the droplets form, the KTPB slurry prevents them from reaching the surface in significant concentration where they can be readily released. The benzene release is driven by the benzene concentration gradient across the liquid and vapor boundary layers.

In the “readily releasable” benzene mechanism, slurry agitation allows the droplets to reach the interface. If the droplets reach the surface in significant concentration and have sufficient energy, the benzene is released at a rate approaching evaporation from a free benzene layer. Convective mass transfer will still occur, but the “readily releasable” mechanism will dominate. Typical agitated fluxes in this test program reached 1 - 10 $\text{g/m}^2\text{min}$ versus 30 $\text{g/m}^2\text{min}$ for immiscible benzene with deionized water. The reason for the lower fluxes with KTPB slurries than with water could be the presence of biphenyl in the droplets, which reduces the vapor pressure, as well as the lack of complete coverage of the slurry-vapor interface with the droplets. In the baseline tests with benzene and water, a layer of liquid benzene was observed at the vapor-liquid interface.

Tests 1, 3, 5, 7, 8, 9, 13, 14, and 22 showed “readily releasable” benzene. “Readily releasable” benzene can be distinguished from convective mass transfer by examining the plots of flux versus time and mass transfer coefficient versus time. Figure 9 shows a sample plot. In the plot, after an initial large release, a distinct change in flux and mass transfer coefficient is observed. Toward the end of the test, a dramatic increase is observed in the mass transfer coefficient. The reason for this increase is the vessels are assumed to be depleted of benzene at the end of the test. They probably contained a few milligrams of benzene. The mass transfer coefficient is calculated by dividing the flux by the concentration gradient. As the concentration approaches zero, the difference between the assumed concentration at the end of the test and the actual concentration becomes important and causes the increases observed.

After determining the transition from “readily releasable” benzene to convective mass transfer and assuming the slurry becomes depleted of benzene at the end of the test, one can numerically integrate the flux versus time plot and calculate the amount of benzene released by each mechanism. Table 12 shows the results. Two theories were evaluated to explain the “readily releasable” benzene: (1) the “readily releasable” benzene is a fraction of the total benzene retained by the slurry, or (2) all benzene above a threshold concentration retained by the slurry is “readily releasable”. The fraction of “readily releasable” benzene varied between 6% and 67%. This variation is too large to conclude the amount of “readily releasable” benzene is a consistent fraction of the total generated benzene.

Table 12. Fraction of “Readily Releasable” Benzene

Tes t	KTPB (wt. %)	Agitated Benzene Release (g)	“Readily Releasable” (%)	Threshold Slurry Benzene Concentration (g/L)	Threshold Slurry Benzene Conc. (g/L wt.% KTPB)
1	1.0	1.63	29	1.5	1.5
3	1.0	1.92	66	0.9	0.9
5	5.5	4.51	3	7.4	1.3
7	1.0	1.79	29	1.5	1.5
8	1.0	1.29	32	1.5	1.5
9	1.0	2.87	17	3.6	3.6
13	1.0	2.45	67	2.1	2.1
14	1.0	2.52	6	4.5	4.5
22	1.0	1.03	13	1.2	1.2

Table 12 also shows the estimated slurry benzene concentration at the transition from “readily releasable” benzene to convective mass transfer, termed the threshold concentration. With the 1 wt. % KTPB slurries, the threshold concentration ranged from 0.9 - 4.5 g/L. The median concentration was 1.5 g/L and the average was 2.1 g/L. In the tests with 1 wt. % KTPB which did not show “readily releasable” benzene, the slurry benzene concentration at the start of the agitation was much less than 0.9 g/L. With the 5.5 wt. % KTPB slurry, the threshold concentration was 7.4 g/L. This result suggests the threshold concentration increases with increasing KTPB, or more mixing energy is needed to remove “readily releasable” benzene as the KTPB concentration increases.

“Readily releasable” benzene was not observed with the 10 wt. % KTPB slurries. Two plausible explanations exist for “readily releasable” benzene not occurring with the 10 wt. % slurries: inadequate mixing and insufficient benzene. Mixing effectiveness in these tests was evaluated qualitatively by examining the fluid motion at the vessel wall. Fluid motion at the wall was less vigorous with the 10 wt. % slurries than with the 1 wt. % slurries. A threshold benzene concentration for 10 wt. % KTPB slurries can be estimated by multiplying the threshold concentrations in the 1 and 5.5 wt. % slurries by 10 and 1.82, respectively. Using this method, a threshold concentration of 13 - 21 g/L is calculated for 10 wt. % slurries. The slurry benzene concentration at the start of agitation with the 10 wt. % KTPB slurries was less than 8.5 g/L in all of the tests. The very high fluxes observed in tests 19 and 20 are due to the high agitator speeds.

Other SRTC testing has shown a change in the benzene release rate at a slurry benzene concentration of 4 - 8 g/L. Since those slurries contained 4 wt. % KTPB, the estimated threshold concentration would be 1 - 2 g/L wt. % KTPB. This number agrees well with the 2.1 g/L wt. % KTPB observed in this test.

An SRTC review of the precipitation process operation showed a rapid benzene release occurred when the tank liquid benzene concentration was approximately 8 g/L. Since the tank contained 3 wt. % KTPB, an estimated concentration at the start of that incident would be 2.67 g/L wt. % KTPB. This number also agrees reasonable well with the 2.1 g/L wt. % KTPB observed in this test.

The threshold concentration for “readily releasable” benzene is influenced by a number of variables which may include the benzene generation rate, the quiescent time, mixing effectiveness, surface area of the slurry-liquid interface, temperature, sodium concentration, KTPB concentration, and local benzene concentrations. The generation of “readily releasable” benzene will depend on the path, or operating history, of the tank.

The following mechanism is proposed for the generation and release of “readily releasable” benzene: Soluble TPB, 3PB, 2PB, and 1PB decompose to form benzene. The benzene accumulates in the slurry, and eventually exceeds the solubility limit. After the solubility limit is exceeded, the benzene coats the KTPB solids. The exact nature of the coating or adsorption is not known. There is an association with the solids which has little, if any, effect on the benzene vapor pressure. After the solids are coated, globules of free benzene and other organic species are formed. When the slurry benzene concentration exceeds a threshold value of 0.9 - 4.5 g/L for 1 wt. % KTPB, the benzene release rate for agitated slurry increases significantly until the slurry benzene concentration becomes less than 0.9 -

4.5 g/L. A minimum energy is required to release the benzene droplets, and the minimum energy increases with increasing KTPB concentration.

Conclusions

The conclusions of the work are:

- Increasing the KTPB concentration decreases the maximum benzene release flux during agitation. As KTPB concentration increases, slurry yield stress and consistency increase and the mixing effectiveness decreases if agitation speed is constant.
- Increasing the quiescent time increases the integrated quiescent benzene release, the integrated total benzene release, and the maximum benzene flux during agitation over the range of quiescent times investigated (30 - 155 days).
- The quiescent time had no significant effect on the average quiescent benzene flux in this test.
- Increasing temperature increased the average quiescent flux and integrated quiescent benzene release with a 3.5 M sodium slurry. Because of the limited quiescent release data collected, an effect was not measured with 4.7 M sodium slurries.
- Salt solution type had no effect on benzene retention and release, as expected. Since changing anion concentrations should have no effect on the benzene generation rate, the benzene vapor pressure, or the mass transfer coefficient, it will have minimal effect on the benzene flux.
- Sludge concentration had no effect on the amount of benzene released during the quiescent and agitation phases. The maximum flux during agitation increased with decreasing sludge concentration. This effect could be caused by differences in mixing effectiveness, or an effect of sludge concentration on slurry yield stress.
- Good mixing is imperative for removing benzene from KTPB slurries, especially at high KTPB concentrations.
- In this test, when the slurry benzene level exceeded a threshold concentration, it became “readily releasable”. The threshold concentration increases with KTPB concentration.

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Figure 2a. Laboratory-Scale Benzene Retention Apparatus Picture

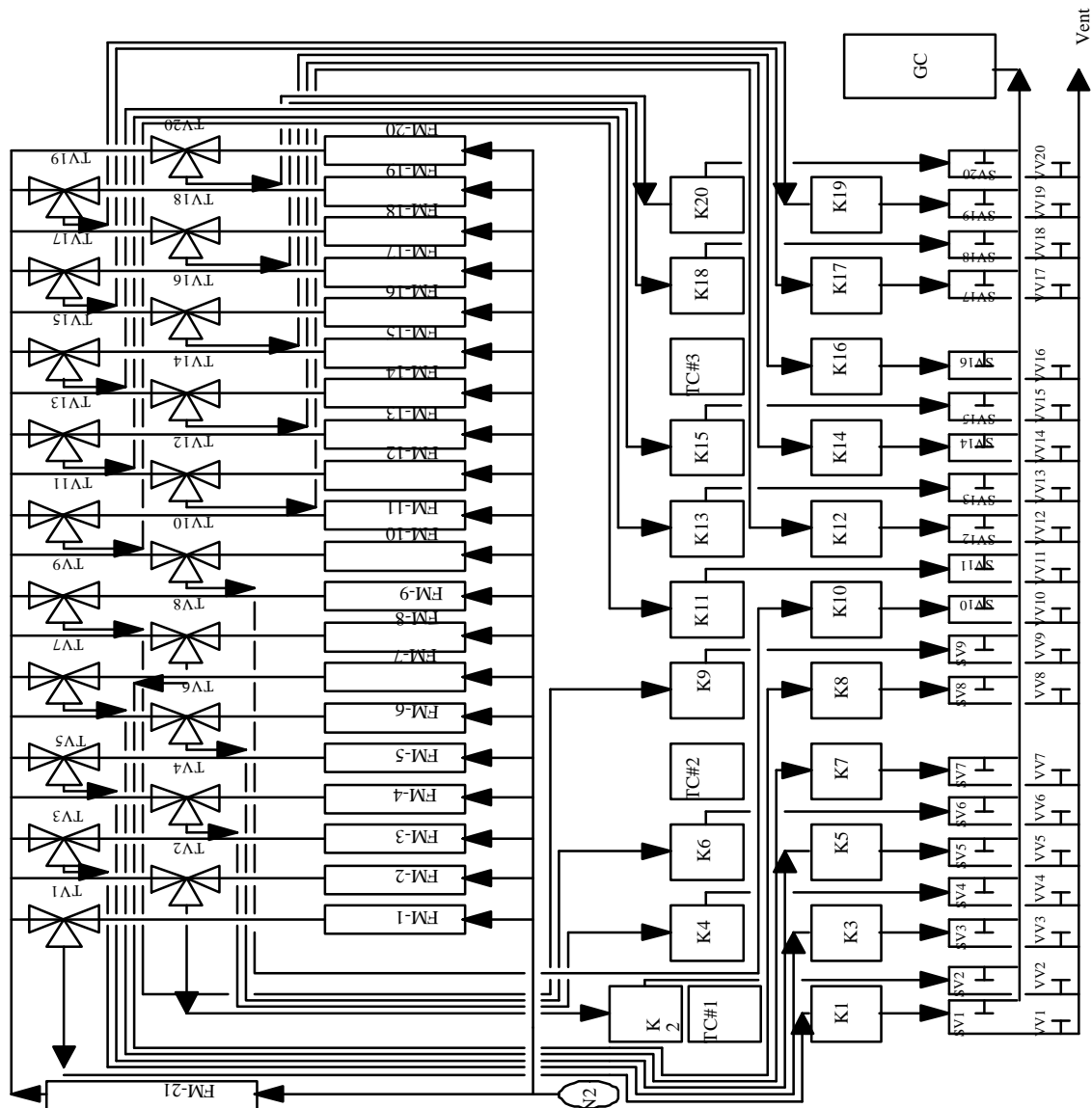
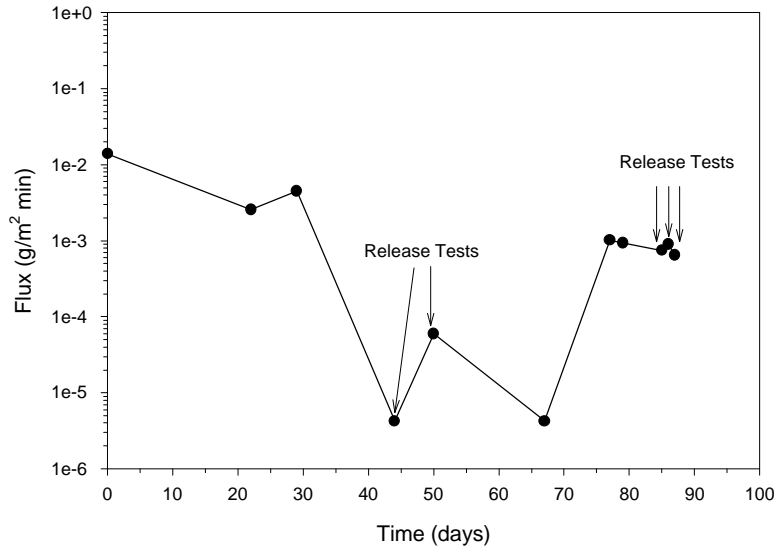


Figure 2b. Laboratory-Scale Benzene Retention Apparatus Sketch

Quiescent Benzene Release Test #5
 Matrix Test, 5.5 Wt%, 4.7M Na, Avg. Salt, 50°C, 44 Days
 Total Benzene Loss: 2.74 g



Benzene Release Test #5
 Agitation Speed: 133-159 rpm
 Matrix Test, 5.5 Wt%, 4.7M Na, Avg. Salt, 50°C, 44 Days
 Total Benzene Released: 4.50 g

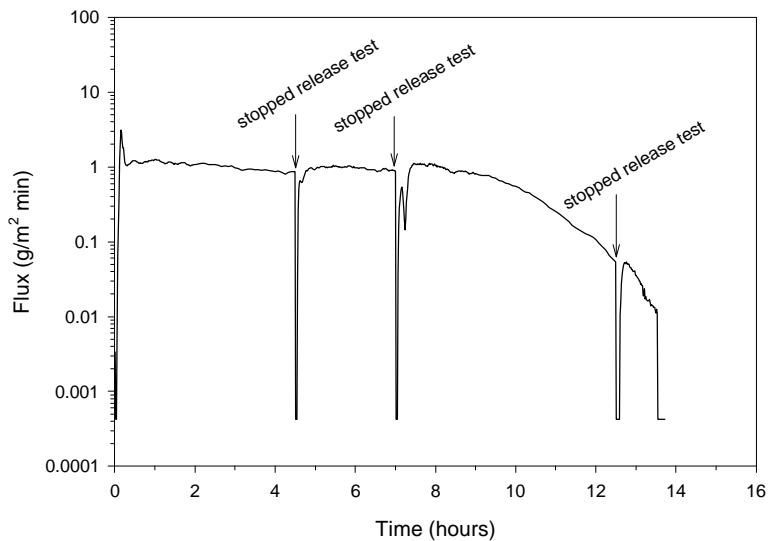


Figure 3. Test 5 Benzene Flux

Baseline Test
Total Benzene Released: 6.68 g

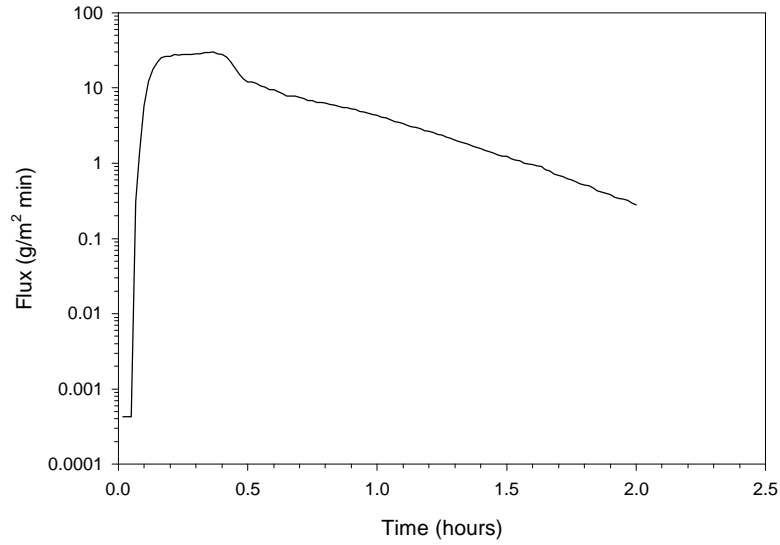
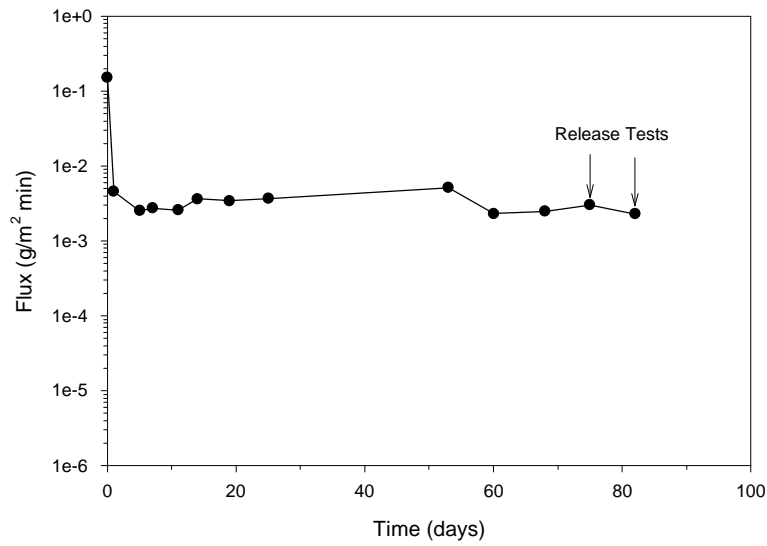


Figure 4. Baseline Benzene Release Test

Quiescent Benzene Release Test #7

1 Wt%, 3.5M Na, Avg. Salt, 40°C, 75 Days
Total Benzene Loss: 3.93 g



Benzene Release Test #7

Agitation Speed: 127-164 rpm
1 Wt%, 3.5M Na, Avg. Salt, 40°C, 75 Days
Total Benzene Released: 1.76 g

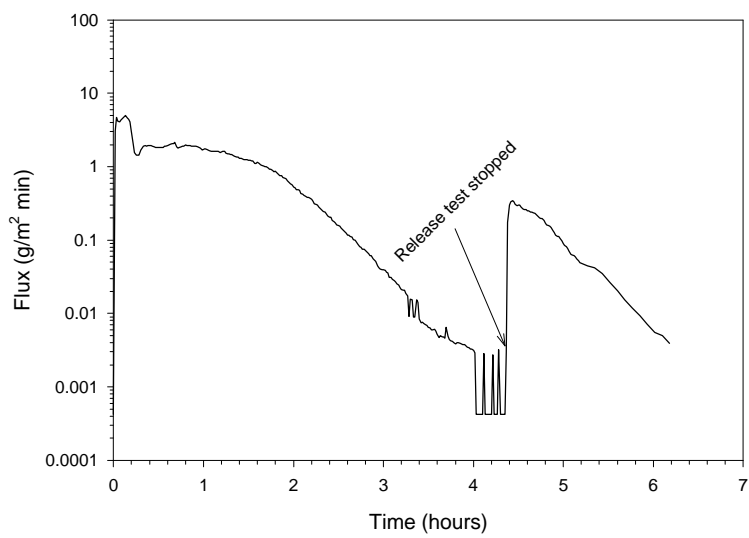


Figure 5. Test 7 Benzene Flux

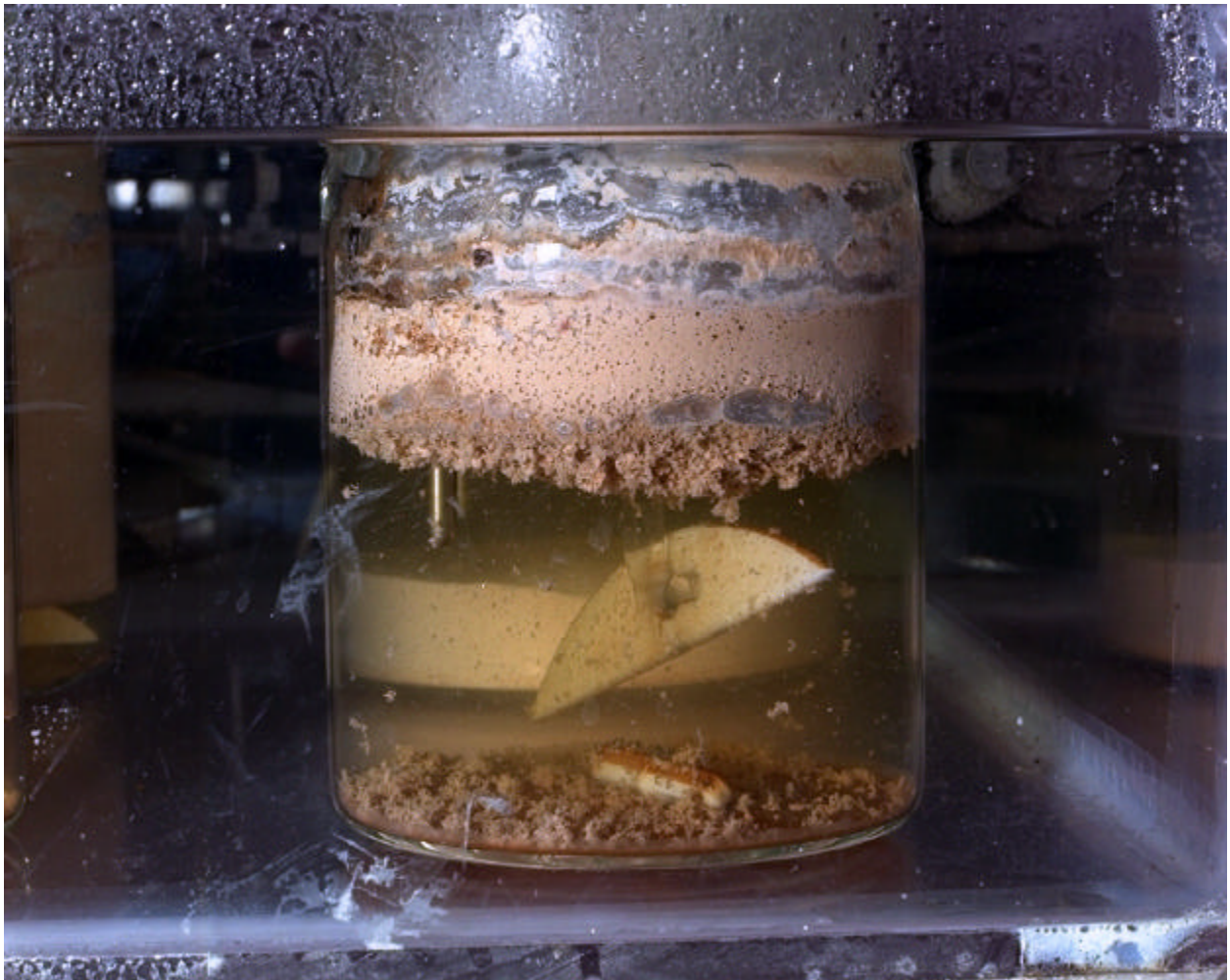


Figure 6. Globules in 1.0 wt. % KTPB Slurry

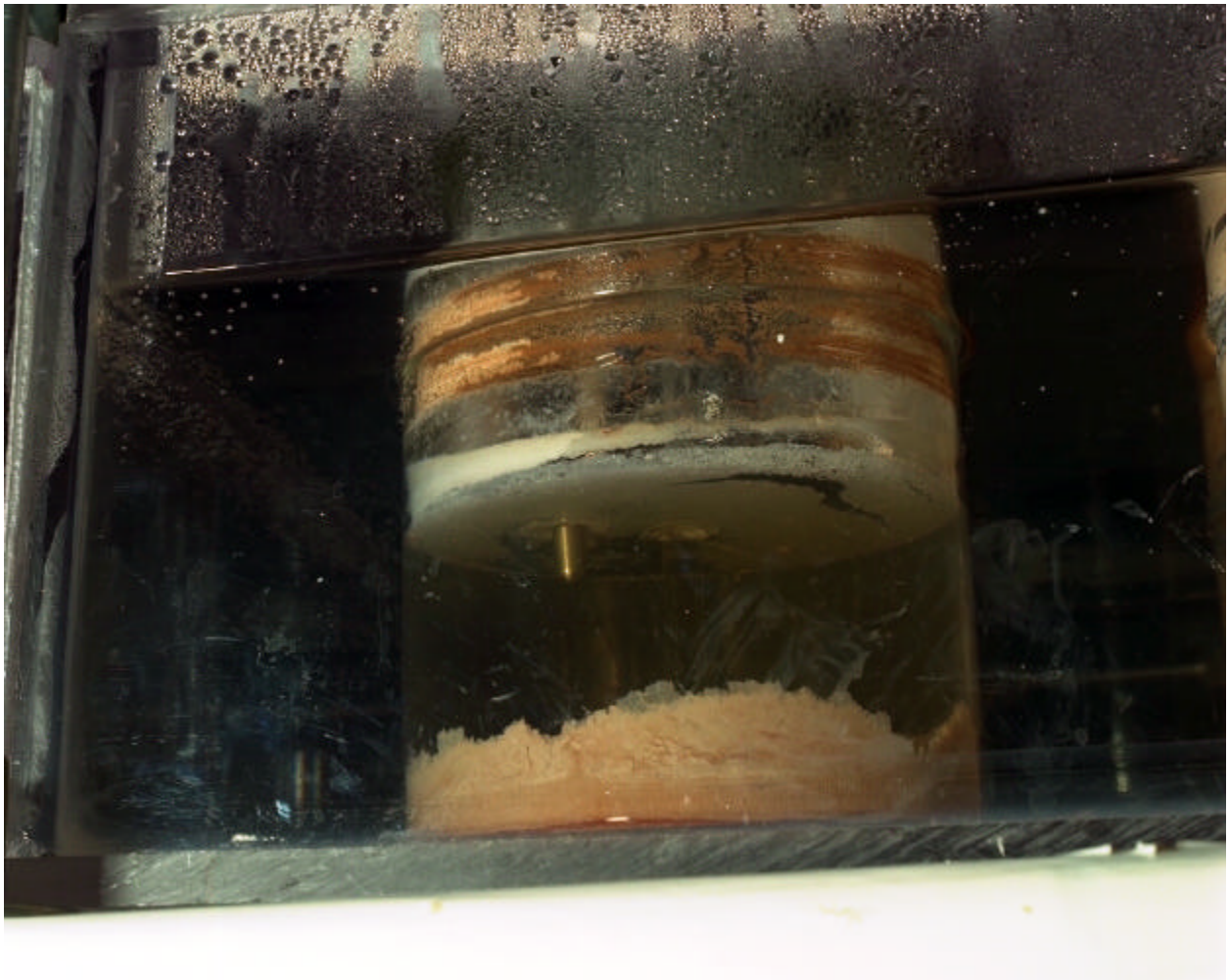


Figure 7. White Film observed in 1.0 wt. % KTPB Slurry

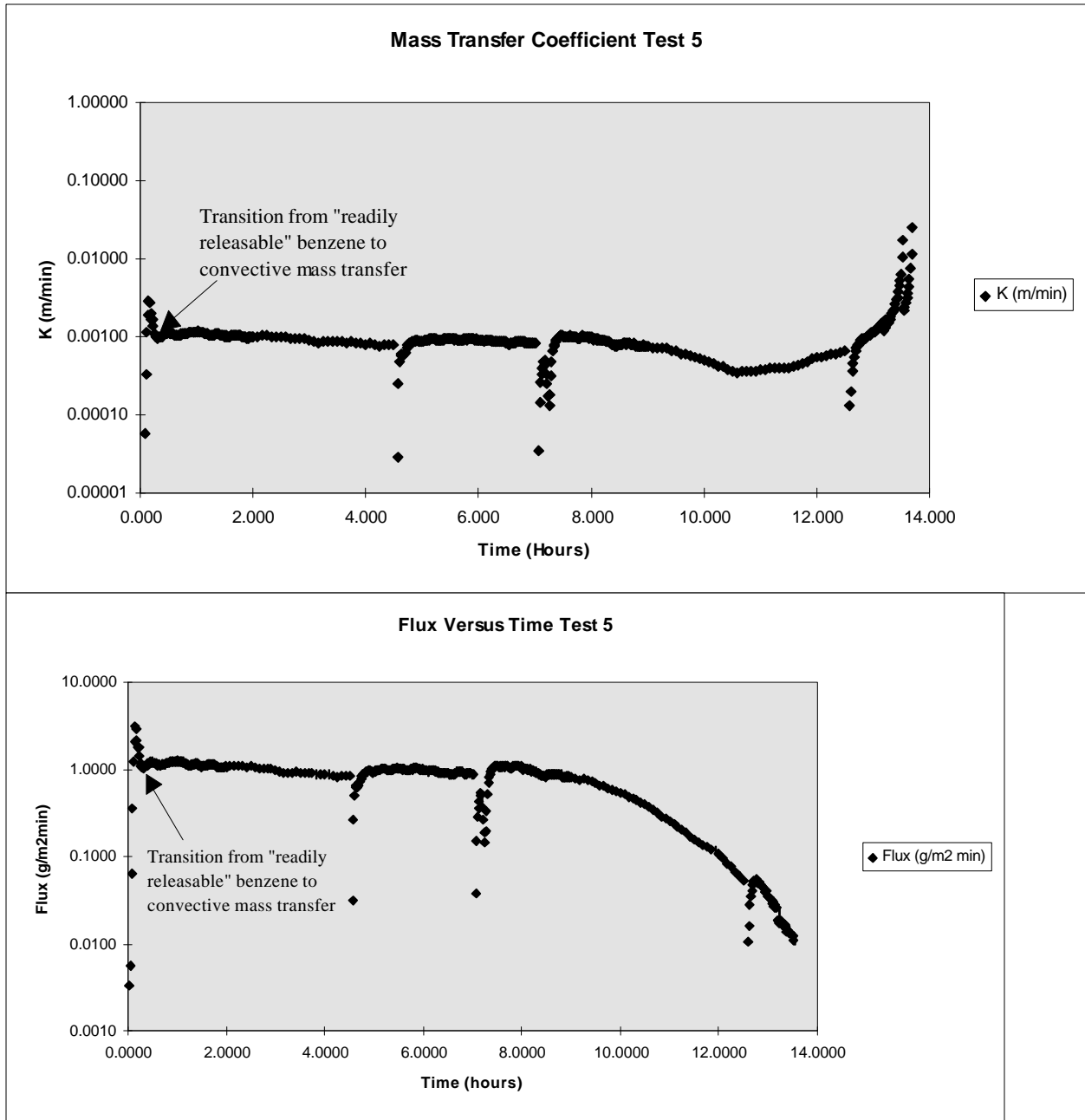


Figure 9. Mass Transfer Coefficient and Flux Test 5