Benzene Release - Status Report (U)

L. O. Dworjanyn

November 4, 1997

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Benzene Release - Status Report

by

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Keywords: In-Tank Precipitation, ITP
Tetraphenylborate, TPB
Benzene Retention in TPB
Benzene Release Rates
Slurry, Slurry Settling
Slurry Formulation

Retention Period: Lifetime

November 4, 1997

TO: W. L. Tamosaitis

FROM: L. O. Dworjany

Benzene Release Status Report (U)

INTRODUCTION

Scoping benzene release measurements were conducted on 4 wt % KTPB "DEMO" formulation slurry (Ref. 1) using a round, flat bottomed 100-mL flask containing 75 mL slurry (PNNL Report #11735, attached). The slurry was agitated with a magnetic stirrer bar to keep the surface refreshed without creating a vortex. Benzene release measurements were made by purging the vapor space at a constant rate and analyzing for benzene by gas chromatography with automatic data acquisition.

Release measurements were made on:

1. Freshly added liquid benzene, dispersed by magnetic stirrer agitation for about two hours prior to release measurements.
2. Liquid benzene homogenized with the slurry using a high speed, high shear stator/rotor device to make a smooth and uniform blend of benzene with KTPB.
3. Filtered slurry salt solution, saturated with benzene.
4. Sample of in-situ benzene slurry from DEMO Column #13.

Some of the data have been rounded or simplified in view of the scoping nature of this study. The PNNL Report (attached) includes the detailed results.

SUMMARY

1. Freshly dispersed benzene was readily released with gentle stirrer agitation at 100 to 300 $\mu\text{g}/\text{cm}^2\text{-min}$ (1 to 3 $\text{g}/\text{m}^2\text{-min}$), a rate approaching benzene release from a similarly agitated floating pool of liquid benzene, 400 $\mu\text{g}/\text{cm}^2\text{-min}$. Independent simulation of benzene dispersion using dyed benzene (Ref. 2) showed that the benzene was suspended in the form of discrete droplets, partially filled with KTPB (Ref. 3, Figure 1). This state of benzene is probably similar to the observed benzene drops or "fish eggs" formed during in-situ benzene generation in the DEMO tests. Independent simulation of benzene release using dyed benzene showed what looks like a "pool" of benzene in the center of the beaker (Figure 2). However photomicrographs of surface samples disclosed only an accumulation of darker dyed benzene droplets formed by dye concentration by benzene evaporation and dark brown solid dye residue which is insoluble in the salt solution (Figure 3), indicating benzene release is taking place.

During the simulated tests actual benzene release could not be captured photographically in the moving slurry (high intensity flash microscopy would be needed). However, a number of tests have demonstrated that "exposed" droplets of benzene evaporate in a fraction of a second, as captured by microscope video photography (Figures 5 to 9).

As the slurry agitation was turned off the release rate decreased by one hundred-fold to 4 $\mu\text{g}/\text{cm}^2\text{-min}$. Photomicrographs of similar slurry show that the benzene droplets submerged below the still liquid surface are quite stable below the interface, even under intense microscope lighting (Ref. 2). Benzene release to the vapor phase would require benzene dissolution to the liquid phase, followed by benzene release from the liquid to the vapor phase (Henry's law).

Significantly, the benzene release fell abruptly to zero as all benzene was released (PNNL Report, Figures 4b and 11), indicating little association of the dispersed benzene with KTPB.

2. The homogenized slurry released benzene at about 40 $\mu\text{g}/\text{cm}^2\text{-min}$. However the starting benzene concentration in the PNNL tests was probably under 3,000 $\mu\text{g}/\text{g}$ based on cumulative release (PNNL Report, Figure 13) vs. 11,800 $\mu\text{g}/\text{g}$ benzene added at SRTC, probably because of benzene losses during storage and shipment to PNNL. Benzene release simulation tests at SRTC showed similar initial release rates (3 hr. agitation) from dispersed and homogenized slurries, and negligible residual benzene (<10 $\mu\text{g}/\text{g}$) after 24 hr. agitation (Table 1). Photomicrographs of slurry homogenized with dyed benzene show that homogenization produces a fairly uniform distribution of benzene in KTPB (Figures 16 and 17). Magnetic stirrer agitation of the simulated homogenized slurry produced no visible accumulation of benzene color indication on the surface, however photomicrographs of surface samples showed fine

benzene droplets (Figures 18 and others) which evaporated rapidly when exposed to air (Figure 19).

3. Benzene release from an agitated saturated salt solution showed an initial rate of $11 \mu\text{g}/\text{cm}^2\text{-min}$ after equilibrating with vapor space and purging out the equilibrium vapor space (PNNL Report, Figure 7a). A log plot of benzene release rate showed that the release rate was proportional to solution concentration, indicating a well agitated liquid phase. By extrapolating to benzene solubility in salt solution, the release rate at saturation was estimated at $25 \mu\text{g}/\text{cm}^2\text{-min}$ (Figure 22), comparable to the release from homogenized slurry.

Release rate from stationary salt solution was also low, about $2 \mu\text{g}/\text{cm}^2\text{-min}$ at $170 \mu\text{g}/\text{g}$, equivalent to $3 \mu\text{g}/\text{cm}^2\text{-min}$ at $238 \mu\text{g}/\text{g}$ (Figure 23).

4. The available in-situ sample had very few solids (no method to measure % solids) and apparently little dissolved benzene, PNNL Report, Figure 9. However the small release seems real as indicated by the effect of daily temperature fluctuations, and the residual benzene shows strong retention by the KTPB.

CONCLUSIONS

- Benzene droplets dispersed in KTPB slurry or generated in-situ, as observed in the DEMO tests, are readily releasable with agitation, at a rate approaching "pools" of benzene on a liquid surface. There is no evidence or reason to suspect actual pools of benzene on a slurry surface since the benzene forms in solution, below the surface. Benzene release from droplets corresponds to the high initial releases observed in all tests, including DEMO, BOTTLE (Ref. 4) and Tank 48H.
- Homogenized slurry likely represents the state of benzene/KTPB association formed in-situ. This benzene may be highly bound at lower concentrations. Bound benzene is supported by lack of dyeability (Ref. 2) and lack of NMR signal at low concentrations (Ref. 6).
- Slurry agitation is essential to benzene release. Conversely, benzene release from unagitated slurry is negligible, even when liquid benzene droplets are present in the slurry. Effectiveness of Tank 48H slurry agitation has not been investigated, particularly with respect to release and homogenization which could reduce the release.
- It may be possible to avoid drop formation during in-situ benzene generation by controlling slurry agitation.

REMAINING TESTS IN PROGRESS

- Measure release rates from homogenized slurry containing 12,000 μg benzene per gram slurry. Verify residual concentration by chemical analyses.
- Determine release rates from dispersed benzene droplets in homogenized slurry.
- Quantify effect of temperature on release rate.
- Test in-situ DEMO sample, if available.
- Issue final report two (2) months after funds transferred to PNNL.

BENZENE RELEASE SIMULATIONS

Benzene release tests at PNNL were simulated at SRTC using dyed benzene to document the state of benzene in DEMO slurry and help explain the release measurements. The tests were conducted in open beakers, 5 cm diameter, to allow observation and sampling during magnetic stirrer agitation and benzene release.

KTPB Slurry with Dispersed Benzene.

This slurry was prepared to retain the benzene in droplet form to simulate benzene drops ("fish eggs") generated in-situ in the DEMO tests. Prior experience has shown that liquid benzene disperses easily in ITP slurry to form KTPB coated droplets 50 to 200 μm diameter (Ref. 2). The suspended droplets may be initially clear benzene, however with continuing agitation the interior fills rapidly with KTPB, particularly in DEMO slurry which contains insoluble metallic sludge. The drops observed in the DEMO tests were larger, up to 2,000 μm diameter since they were allowed to grow in absence of agitation. Lab tests have shown that minimal agitation would reduce the drop size to under 200 μm diameter. Hence benzene release rates from the simulated slurry should correspond to the rates from circulated DEMO slurry.

3 mL of dyed benzene (1% Sudan Red) was added to 200 mL of DEMO slurry and hand agitated to suspend the benzene. 75 mL of this slurry was placed in a covered 150-mL beaker and agitated with a magnetic stirrer to complete the dispersion. Photomicrographs showed that the benzene was suspended in the form of opaque droplets, partially filled with KTPB (Figure 1A), consistent with earlier observations (Ref. 2). The DEMO slurry has a characteristic light brown color as shown in Figure 1B, due to sludge and metal additives (Ref. 4).

Simulated benzene release test agitation in an open beaker showed good inner circle flow with little vortexing and slower movement near the beaker edge (Figure 2A). A flash photo showed what looks like a "pool" of benzene in the center of the beaker (Figure 2B). However photomicrographs of surface samples disclosed only an accumulation of darker dyed benzene formed by dye concentration by benzene evaporation and dark brown solid

dye residue which is insoluble in the salt solution (Figure 3), indicating benzene release had taken place. Fresh microscope slide samples showed distinct solid dye structure which often dissolved as the slide aged allowing the benzene to release from bulk slurry.

Initially, during agitation, the central rotating region was covered with a thin translucent layer (not analyzed), possibly suspended by benzene vapor (Figure 2B). Microscope videos showed the slurry flowing underneath the central covering. With continuing agitation and release a stationary ring of foam was formed around the beaker and a floating button of stiff foam accumulated in the center of the beaker (Figure 4).

Actual benzene release could not be captured photographically in the moving slurry (high intensity flash microscopy would be needed). However, a number of tests have demonstrated that "exposed" droplets of benzene can evaporate in a fraction of a second, as captured by microscope video photography.

Figure 5 shows a large drop of benzene spreading rapidly on the surface of deep slurry and evaporating, leaving the dye residue to mark where the benzene evaporated.

Figure 6 shows a smaller droplet (500 micron probe) on a thin slurry layer on a glass slide spreading within three video frames and evaporating in about 20 frames (< 1 sec).

Figure 7 shows benzene release from within KTPB slurry on an uncovered microscope slide. The excess slurry was moved aside with a probe, leaving two benzene droplets protected with a thin layer of salt solution. As the salt solution evaporated, sequential video frames show the larger drop spreading in a single frame and evaporation within three frames. The smaller drop disappeared between frames, in less than 1/30 sec.

Figure 8 demonstrates benzene release from slurry placed on blotting paper. The first three views, taken two frames apart, show benzene spreading over the slurry surface, and concentrating dye on the edges as the benzene evaporates. The fourth view shows the peripheral benzene fully evaporated. Figure 9A shows how the adjacent drop which was covered with more slurry on the top half, burst out in the lower half first exposed to air.

In the final state, Figure 9B, all submerged drops have lost the protective solution covering and all benzene has evaporated.

Homogenized Benzene/KTPB Slurry.

This slurry was prepared to simulate uniform in-situ benzene distribution to test benzene release in absence of free benzene droplets. Recently prepared samples of in-situ generated benzene for Vapor-Liquid Equilibria (VLE) measurements (Ref. 5) show uniform benzene distribution in the slurry as evidenced by addition of solid Sudan Red dye (Ref. 2). The benzene free 6.5 wt % VLE slurry shows no color development in the slurry, while specks of insoluble opaque dye can be clearly seen (Figure 10). After in-situ

benzene generation (approximately two weeks at 70 °C, Ref. 5) the slurry develops a deep red color in the presence of solid dye (Figure 11). Significantly, the KTPB particles become more cohesive forming large flakes, apparently "glued" together by the benzene (Ref. 6). This KTPB cohesiveness in the presence of benzene was evident in earlier in-situ samples (Ref. 2 and 8) and in samples from the DEMO columns (Ref. 1).

To break up the benzene structure formed by liquid benzene addition the slurry was homogenized using a high speed biological tissue homogenizing device. The homogenizer consists of toothed outer stator and closely fitting inner homogenizing blades (Figure 12). This device allows very efficient dispersion (1 min/ 100 mL), forming a slurry essentially free of liquid benzene (Figure 13). In contrast, an orbital shaker shows poorer dispersion after 24 hrs agitation (Figure 14) and the slurry contains many undispersed benzene areas (Figure 15).

To simulate PNNL release tests, DEMO slurry was homogenized with 15,000 ppm dyed benzene to yield a uniformly colored slurry free of benzene droplets or agglomerates (Figure 16). When the benzene color was developed fully with added solid dye (Figure 17) the slurry appearance resembled closely in-situ benzene slurry (Figure 11).

A 75 mL sample of the homogenized slurry was placed in a 150-mL open beaker and magnetic stirrer bar agitation was adjusted to provide steady flow as shown in Figure 2. The beaker head space was purged with air at about 1 L/min to assure benzene release.

Shortly after agitation was started a small stationary ring of foam formed at the outer edge of the slurry and foam started collecting in the center of the beaker. Initial surface samples from the central rotating region not covered by the foam showed numerous benzene droplets when viewed under a cover glass (Figure 18). Material exposed to the air outside the coverglass showed mostly dye residue from evaporated benzene (Figure 19). Bulk samples from the beaker were indistinguishable from the starting slurry.

After 1 hr agitation the moving surface slurry showed heavy benzene release from underlying KTPB flakes (Figure 20). After 4 hr agitation benzene release was still observable but at significantly reduced residual concentration (Figure 21).

After 23 hrs the remaining slurry was essentially color free, indicating complete benzene release.

Residual Benzene Concentrations

Small retain samples of starting slurry, after 3 hr. of agitated benzene release, and at the end of testing (24 hr.) were analyzed by gas chromatography for residual benzene in the slurry using the standard method of injecting a 0.25 mL sample into a 25 mL vial and measuring benzene in the vapor after equilibrium has been reached. To assure that any

potentially "bound" benzene is released two samples were analyzed by injecting slurry into a hot (boiling water) and evacuated 75 mL bulb. The results in Table 1 show a continuing discrepancy between benzene added and benzene analyzed (3,000 $\mu\text{g/g}$ loss). However, the residual benzene was comparable for both blended and homogenized slurries after 3 hr. agitated release. Also, there was no indication of any significant benzene retention after 24 hr. agitation.

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APPROVALS

12/1/97

J. T. Carter, Manager Date
ITP Flow Sheet Task Team

12-1-97

J. Barnes, Deputy Manager Date
Pretreatment Engineering

12/2/97

W. L. Tamosaitis, Manager Date
Waste Processing Technology

Table 1
Simulated Benzene Release Slurry
Residual Benzene Concentrations

DEMO Slurry		R2S	R2S	R2SG	Comments
Benzene blending method		Shake	Shake	Homog.	
Release purge flow		YES	NO	YES	
Goal benzene composition	ppm	15,000		15,000	
Slurry volume	mL	200		200	
Slurry weight	g	228.02		228.04	
Benzene weight	g	2.5625		2.5659	
Benzene added	$\mu\text{g/g}$	11,238		11,252	
Benzene analyzed					
Starting sample	$\mu\text{g/g}$	8,658		6,841	Cold vial
	$\mu\text{g/g}$			7,675	Hot evacuated bulb
3 hr. agitated	$\mu\text{g/g}$	4,832	4,867	4,906	Cold vial
24 hr. agitated	$\mu\text{g/g}$	4		2	Cold vial
	$\mu\text{g/g}$			9	Hot evacuated bulb

FIGURES

- Figure 1A. **Thin slide of DEMO slurry with dispersed dyed benzene, 155X.**
[Ref. 3, pp 58, 77; R2S + 15,000 ppm vol. dyed benzene]
- Figure 1B. **Thick slide of DEMO slurry with dispersed dyed benzene, 155X.**
[Ref. 3, pp 58, 77; R2S + 15,000 ppm vol. dyed benzene]
- Figure 2A, **Simulated agitation of dispersed benzene slurry, 1/30 sec exposure.**
[Ref. 3, p 78; R2S + 15,000 ppm vol. benzene; 5-cm beaker]
- Figure 2B, **Simulated agitation of dispersed benzene slurry, flash exposure.**
[Ref. 3, p 78; R2S + 15,000 ppm vol. benzene; 5-cm beaker]
- Figure 3, **Vortex surface sample showing benzene release (dark maroon) and submerged stable droplets (light red), 620X.**
[Ref. 3, p 78; dispersed R2S; 30 min agitation; covered slide]
- Figure 4, **Central foam accumulation - thin slide, 155X.**
[Ref. 3, p 78; dispersed R2SG; 5-cm beaker; 19 hr agitation]
- Figure 5, **Large benzene drop evaporation on bulk slurry surface.**
[PNNL S-VHS; Slurry #4; 2-cm beaker; 2 mm dropper]
- Figure 6, **Small benzene drop on a thin layer of slurry on slide.**
[S-VHS; Slurry #17K; 0.5 mm needle; successive frames]
- Figure 7, **Submerged benzene droplets in dispersed slurry on open slide, 122X**
[S-VHS; Slurry #4; 1/30 sec successive frames]
- Figure 8, **Submerged benzene droplets in dispersed slurry on paper, 122X**
[S-VHS; Slurry #4; 1/30 sec successive frames]
- Figure 9A, **Slurry on paper, near complete benzene evaporation, 122X**
[S-VHS; Slurry #4; approx. 10 frames]
- Figure 9B, **Slurry on paper, complete benzene evaporation, 132X**
[S-VHS; Slurry #4; approx. 1 min]
- Figure 10, **Fresh VLE Slurry with trace of solid Sudan Red dye, 155X**
[Ref. 5; Slurry IS-0, 6.5 wt %; covered glass slide]
- Figure 11, **VLE Slurry with in-situ generated benzene + solid dye, 155X**
[Ref. 5; Slurry IS-18, 6.5 wt %; covered glass slide]
- Figure 12, **Biological slurry homogenizer, 0.1 cm scale**
[Rotor pulled out from stator for clarity, flush during operation]
- Figure 13, **VLE Slurry homogenized with 15,000 ppm dyed benzene, 155X**
[Ref. 5; Slurry IS-0, 6.5 wt %; 1 min homogenization]
- Figure 14, **VLE Slurry agitated with 15,000 ppm dyed benzene, 155X**
[Ref. 5; Slurry IS-0, 6.5 wt %; 24 hr rotary agitation]

- Figure 15, **Residual undispersed benzene in agitated VLE Slurry, 155X**
[Ref. 5; Slurry IS-0, 6.5 wt %; 24 hr rotary agitation]
- Figure 16, **DEMO Slurry homogenized with 15,000 ppm dyed benzene, 155X**
[Ref. 1; DEMO formulation, 4.0 wt %; 1 min homogenization]
- Figure 17, **Homogenized DEMO Slurry enhanced with solid dye, 155X**
[Ref. 1; DEMO formulation, 4.0 wt %; 10 sec solid dye agitation]
- Figure 18, **Initial benzene release from agitated slurry - covered slide, 620X**
[Ref. 3; homogenized DEMO slurry; 10 min benzene release simulation]
- Figure 19, **Benzene released from agitated slurry - open surface, 310X**
[Ref. 3; homogenized DEMO slurry; 10 min benzene release simulation]
- Figure 20, **High benzene release from agitated slurry - covered slide, 620X**
[Ref. 3; homogenized DEMO slurry; 1 hr benzene release simulation]
- Figure 21, **Reduced benzene release after 4 hr agitation - covered slide, 310X**
[Ref. 3; homogenized DEMO slurry; 4 hr benzene release simulation]
- Figure 22, **Extrapolated estimate of benzene release from agitated salt solution.**
[PNNL Report, Figures 8a and 15]
- Figure 23, **Extrapolated estimate of benzene release from stationary salt solution.**
[PNNL Report, Figures 8b and 16]

MAGNIFICATION DETAILS

CalibMic SETTING	Scale mm	Micrographic Inches	Length MM	Calc Mag.	Label Mag X	6 in. Print mm Width	100 μ mm on Print
Low Mag							
.63X	25	4.67	118.6	5	5	32	0.5
1.0X	15	4.48	113.8	7.6	7.5	20	0.8
2.0X	5	2.95	74.9	15	15	10	1.5
4.0X	2.5	2.95	74.9	30	30	5	3.0
Stereo							
08x	10.0	4.79	121.7	12.2	12	12.5	1.2
20x	1.00	1.20	30.5	30	30	5.0	3.0
40x	1.00	2.41	61.2	61	61	2.5	6.1
60x	1.00	3.62	91.8	92	92	1.7	9.2
80x	1.00	4.82	122.4	122	122	1.2	12.2
Compound							
LO 10X					155	1.0	15.5
MD 20X	0.40	4.90	124.5	311	310	0.5	31.0
HI 40X	0.20	4.88	124.0	620	620	0.25	62.0

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Figure 1A. **Thin slide of DEMO slurry with dispersed dyed benzene, 155X.**
[Ref. 3, pp 58, 77; R2S + 15,000 ppm vol. dyed benzene]

Figure 1B. **Thick slide of DEMO slurry with dispersed dyed benzene, 155X.**
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[Ref. 3, p 78; dispersed R2S; 30 min agitation; covered slide]

Figure 4, **Central foam accumulation - thin slide, 155X.**
[Ref. 3, p 78; dispersed R2SG; 5-cm beaker; 19 hr agitation]

Figure 5, **Large benzene drop evaporation on bulk slurry surface.**
[PNNL S-VHS; Slurry #4; 2-cm beaker; 2 mm dropper]

PNNL

VIDEO

10-27-97

WSRC-NB-94-134 P82

Figure 6, **Small benzene drop on a thin layer of slurry on slide.**
[S-VHS; Slurry #17K; 0.5 mm needle; successive frames]

R2SM

DKC-5000

10-26-97

WSRC-NB-94-134 P82

Figure 7, Submerged benzene droplets in dispersed slurry on open slide, 122X
[S-VHS; Slurry #4; 1/30 sec successive frames]

Figure 8, **Submerged benzene droplets in dispersed slurry on paper, 122X**
[S-VHS; Slurry #4; 1/30 sec successive frames]

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[S-VHS; Slurry #4; approx. 10 frames]

Figure 9B, **Slurry on paper, complete benzene evaporation, 132X**
[S-VHS; Slurry #4; approx. 1 min]

Figure 10, **Fresh VLE Slurry with trace of solid Sudan Red dye, 155X**
[Ref. 5; Slurry IS-0, 6.5 wt %; covered glass slide]

ISO

VIDEO

10-29-97

WSRC-NB-94-134 PR2

Figure 11, **VLE Slurry with in-situ generated benzene + solid dye, 155X**
[Ref. 5; Slurry IS-18, 6.5 wt %; covered glass slide]

IS18

VIDEO

10-29-97

WSRC-NB-94-134 P82

Figure 12, **Biological slurry homogenizer, 0.1 cm scale**
[Rotor pulled out from stator for clarity, flush during operation]

Figure 13, **VLE Slurry homogenized with 15,000 ppm dyed benzene, 155X**
[Ref. 5; Slurry IS-0, 6.5 wt %; 1 min homogenization]

Figure 14, **VLE Slurry agitated with 15,000 ppm dyed benzene, 155X**
[Ref. 5; Slurry IS-0, 6.5 wt %; 24 hr rotary agitation]

Figure 15, **Residual benzene in agitated VLE Slurry, 155X**
[Ref. 5; Slurry IS-0, 6.5 wt %; 24 hr rotary agitation]

Figure 16, **DEMO Slurry homogenized with 15,000 ppm dyed benzene, 155X**
[Ref. 1; DEMO formulation, 4.0 wt %; 1 min homogenization]

R2S

DKC-5000

10-24-97

WSRC-NB-94-134 P78

Figure 17, **Homogenized DEMO Slurry enhanced with solid dye, 155X**
[Ref. 1; DEMO formulation, 4.0 wt %; 10 sec solid dye agitation]

ISO

VIDEO

10-29-97

WSRC-NB-94-134 P82

Figure 18, **Initial benzene release from agitated slurry - covered slide, 620X**
[Ref. 3; homogenized DEMO slurry; 10 min benzene release simulation]

R2SG

DKC-5000

10-25-97

WSRC-NB-94-134 P80

Figure 19, **Benzene released from agitated slurry - open surface, 310X**
[Ref. 3; homogenized DEMO slurry; 10 min benzene release simulation]

R2SG

DKC-5000

10-25-97

WSRC-NB-94-134 P80

Figure 20, **High benzene release from agitated slurry - covered slide, 620X**
[Ref. 3; homogenized DEMO slurry; 1 hr benzene release simulation]

Figure 21, **Reduced benzene release after 4 hr agitation - covered slide, 310X**
[Ref. 3; homogenized DEMO slurry; 4 hr benzene release simulation]

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[PNNL Report, Figures 8a and 15]

Figure 23, **Extrapolated benzene release from stationary salt solution.**
[PNNL Report, Figures 8b and 16]

Pacific Northwest National Laboratory

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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
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PNNL-11735

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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 $\mu\text{g benzene}/\text{cm}^2\text{-min}$ with gentle agitation, and about 4 to 6 $\mu\text{g benzene}/\text{cm}^2\text{-min}$ without agitation. For comparison, measurements showed that a floating layer of pure benzene gave about a 400 $\mu\text{g benzene}/\text{cm}^2\text{-min}$ release rate. Release rates for the KTPB slurry homogenized with 15,000 ppm benzene was ~ 30 $\mu\text{g benzene}/\text{cm}^2\text{-min}$ with gentle agitation, and about the same as above (4 to 6 $\mu\text{g benzene}/\text{cm}^2\text{-min}$) without agitation. And the release rate for KTPB slurry homogenized with 5,000 ppm benzene was ~ 2 $\mu\text{g benzene}/\text{cm}^2\text{-min}$ with gentle agitation. Benzene release rates for the DEMO column slurry sample were generally less than 0.1 $\mu\text{g benzene}/\text{cm}^2\text{-min}$, 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.

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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 toxicological 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 taken from a large demonstration (DEMO) column experiment performed in an attempt to recreate the phenomenon of benzene generation and release *in situ*. We will then 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- μ m 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 $\frac{1}{2}$ to 1-cm above the surface of 75-mL of sample (including stir bar) inside the flask. The internal diameter of the flask at this level is approximately 5.08-cm (2 in.), resulting in an exposed sample surface area of approximately 20-cm². 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 sight 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 ₂ SO ₄	142.05	30.85
Trisodium Phosphate 12-hydrate	Na ₃ PO ₄ X 12H ₂ O	380.16	99.10
Water	H ₂ O	18.016	6125.40
Sum			9687.48
NaTPB SOLUTION			
Sodium Tetraphenylborate	NaB(C ₆ H ₅) ₄	342.23	2684.96
Sodium Hydroxide	NaOH	40.0	75.75
Water	H ₂ O	18.016	11334.09
Total Solution			14094.79
SODIUM SALT SOLUTION			
Sodium Hydroxide	NaOH	40.0	5453.42
Sodium Carbonate	Na ₂ CO ₃	124.0	969.64
Aluminum Nitrate Nonahydrate	Al(NO ₃) ₃ X 9H ₂ O	375.14	2281.31
Water (subtracted mass of trim soln's)	H ₂ O	18.016	14867.74
Sum			23572.12
MONOSODIUM TITANATE SLURRY			
NaTi ₂ O ₅ H ₂ 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 ₂ O	232.62	1.81
Stannous Chloride 2-Hydrate	SnCl ₂ x 2H ₂ O	225.65	0.19
Zinc Nitrate 6-Hydrate	Zn(NO ₃) ₂ x 6H ₂ O	297.49	1.52
Ferric Nitrate 9-Hydrate	Fe(NO ₃) ₃ x 9H ₂ O	404.02	0.44
ACID SOLUTION			
Water	H ₂ O	18.016	20
Nitric Acid	HNO ₃	63.02	0.13
Sum Acid Solution			24.09
BASIC METAL TRIM SOLUTION			
Sodium Chromate	Na ₂ CrO ₄	162.0	9.88
Potassium Molybdate	K ₂ MoO ₄	238.13	1.29
NaOH	NaOH	40.0	0.4
Water	H ₂ O	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 ₆ H ₆	78.11	31.27
Phenol	C ₆ H ₅ OH	94.11	5.43
Phenylboric Acid	C ₆ H ₅ B(OH) ₂	121.9	5.43
Biphenyl	(C ₆ H ₅) ₂	154.2	6.52
Diphenylborinic Acid*	(C ₆ H ₅) ₂ BOH	182	6.72
Triphenylboron**	(C ₆ H ₅) ₃ B	242.1	70.29
Isopropyl Alcohol	(CH ₃) ₂ CHOH	60.09	2.17
Methanol	CH ₃ OH	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 ₂ O	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 CarbographTM capillary column with helium carrier gas flowing through the column. A sample is obtained by flowing the headspace vapor through a 100- μ L sample loop on a 10-port SupelcoTM 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 BasicTM 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 ExcelTM 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 $\{\mu\text{g of benzene}/(\text{cm}^2)(\text{min})\}$ from the surface between time 0 and time 1, expressed as a flux, can then be calculated as follows:

$$\text{ReleaseRate}_{\text{benzene}_{0,1}} = \frac{\text{average}[C_0, C_1] \times F_{\text{avg}} \times P_{\text{avg}} \times MW_{\text{benzene}}}{A_s \times R_G \times T}$$

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 cm², unless otherwise noted)

R_G = the ideal gas constant {82.06 (cm³)(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, $\mu\text{g benzene}/\text{cm}^2\text{-min}$. 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 homogenization). 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 $\sim 200 \mu\text{g benzene}/\text{cm}^2\text{-min}$. At approximately 2.5 hours, release rates drop quickly to $\sim 80 \mu\text{g benzene}/\text{cm}^2\text{-min}$. After about an hour of consistent release at $\sim 80 \mu\text{g benzene}/\text{cm}^2\text{-min}$, release rates began a slow descent to $\sim 30 \mu\text{g benzene}/\text{cm}^2\text{-min}$, 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 $\sim 300 \mu\text{g benzene}/\text{cm}^2\text{-min}$ to $\sim 100 \mu\text{g benzene}/\text{cm}^2\text{-min}$. And as expected, the release of benzene significantly fell upon halting agitation from $\sim 100 \mu\text{g benzene}/\text{cm}^2\text{-min}$ (with agitation) to $\sim 1 \mu\text{g benzene}/\text{cm}^2\text{-min}$, 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 $40 \mu\text{g benzene}/\text{cm}^2\text{-min}$, 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/ $\text{cm}^2\text{-min}$, then descended to ~140 μg benzene/ $\text{cm}^2\text{-min}$, 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/ $\text{cm}^2\text{-min}$ to ~100 μg benzene/ $\text{cm}^2\text{-min}$. 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/ $\text{cm}^2\text{-min}$, then steady out at between 1 and 0.5 μg benzene/ $\text{cm}^2\text{-min}$.

We now have quality average release rates of KTPB slurry with freshly added benzene: ~100 to 200 μg benzene/ $\text{cm}^2\text{-min}$ with agitation, and ~1 μg benzene/ $\text{cm}^2\text{-min}$ 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/ $\text{cm}^2\text{-min}$. 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 $\mu\text{g benzene}/\text{cm}^2\text{-min}$ and steadily declined to ~ 25 $\mu\text{g benzene}/\text{cm}^2\text{-min}$, at which point the agitation was shut off. When agitation was restarted, release rates resumed to ~ 30 $\mu\text{g benzene}/\text{cm}^2\text{-min}$, then reached a point (~ 5 hours) where they significantly and steadily dropped off. Release rates reached as low as ~ 0.2 $\mu\text{g benzene}/\text{cm}^2\text{-min}$ 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 $\mu\text{g benzene}/\text{cm}^2\text{-min}$) 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 $\sim 15,000$ -ppm from the slurry is on the order of 100 to 200 $\mu\text{g benzene}/\text{cm}^2\text{-min}$. Without agitation, though, both slurries with freshly added and homogenized benzene-slurry samples have approximately the same steady release rate of 1 to 2 $\mu\text{g benzene}/\text{cm}^2\text{-min}$. 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 $1 \mu\text{g benzene/cm}^2\text{-min}$, rapidly decreasing to $\sim 0.6 \mu\text{g benzene/cm}^2\text{-min}$, and then slowly and steadily declining to $< 0.1 \mu\text{g benzene/cm}^2\text{-min}$, 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 released. It is also hypothesized that this different benzene configuration resulting from homogenization 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/ $\text{cm}^2\text{-min}$ and quickly declined to ~ 0 μg benzene/ $\text{cm}^2\text{-min}$ in a span of about 3 hours. The benzene release rate for the unagitated solution began significantly lower at just over 2 μg benzene/ $\text{cm}^2\text{-min}$ and declined much slower, reaching ~ 0.1 μg benzene/ $\text{cm}^2\text{-min}$ 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 $0.17 \mu\text{g benzene/cm}^2\text{-min}$ and steadily declining to less than $0.04 \mu\text{g benzene/cm}^2\text{-min}$. 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 $\sim 0.04 \mu\text{g benzene/cm}^2\text{-min}$), release rate fluctuations took place over an extended period of time, which is believed to be caused from temperature fluctuations in the laboratory. It is important to note that there is a lasting residual release rate (0.03 to $0.02 \mu\text{g benzene/cm}^2\text{-min}$) 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 unforeseen 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, note 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 $\mu\text{g benzene}/\text{cm}^2\text{-min}$) comparable to that of pure benzene (~400 $\mu\text{g benzene}/\text{cm}^2\text{-min}$).
- KTPB slurry containing ~12,000-ppm benzene (by weight) and premixed by homogenization released benzene at a rate (~40 $\mu\text{g benzene}/\text{cm}^2\text{-min}$) 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 $\mu\text{g benzene}/\text{cm}^2\text{-min}$) 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 $\mu\text{g benzene}/\text{cm}^2\text{-min}$).

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