

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Direct Disposal of a Radioactive Organic Waste in a Cementitious Waste Form

John R. Zamecnik, Alex D. Cozzi, Russell E. Eibling,
Jon M. Duffey, Kimberly P. Crapse, and Timothy M. Jones.
Savannah River National Laboratory, Aiken, SC 29808
Andrew R. Marinik

formerly with Savannah River National Laboratory, Aiken, SC 29808

ABSTRACT

The disposition of ^{137}Cs -containing tetraphenylborate (TPB) waste at the Savannah River Site (SRS) by immobilization in the cementitious waste form, or grout called 'saltstone' was proposed as a straightforward, cost-effective method for disposal. Tests were performed to determine benzene release due to TPB decomposition in saltstone at several initial TPB concentrations and temperatures. The benzene release rates for simulants and radioactive samples were generally comparable at the same conditions. Saltstone monoliths with only the top surface exposed to air at 25 and 55°C at any tetraphenylborate concentration or at any temperature with 30 mg/L TPB gave insignificant releases of benzene. At higher TPB concentrations and 75 and 95°C, the benzene release could result in exceeding the Lower Flammable Limit in the saltstone vaults.

INTRODUCTION & BACKGROUND

The TPB waste exists in SRS Tank 48H from tests on a now abandoned process to immobilize ^{137}Cs from high molarity caustic salt waste. The activity of this waste is about $1.25 \times 10^7 \text{ MBq/m}^3$ (1.28 Ci/gal). The majority of the TPB in Tank 48H exists as the undissociated potassium salt (KTPB). The "saltstone" process takes low-level radioactive waste and mixes it with a cement-based "premix" consisting of coal power plant fly ash, slag from steelmaking, cement, and minor performance additives. These combine to form the durable waste form which is then stored in large concrete vaults. The saltstone vaults are rectangular cells approximately 30.5m x 30.5m x 7.6m high, for a total volume of about 7100 m³.

A major technical issue to be resolved was the generation of flammable gases from decomposition of the KTPB during processing steps and in the saltstone vaults. The release of benzene from decomposition of the KTPB was the major flammable gas concern, so tests examining the effects of KTPB concentration in the saltstone and temperature were conducted to determine a safe operating envelope for this process. Temperatures as high as 95°C can be reached during curing due to the heat of hydration of the cementitious reactions. Modeling of the pouring process has shown that a band of maximum temperature several meters below the surface of the saltstone will exist and its magnitude will depend on the pouring rate. The temperature at any elevation will remain elevated for up to 400 days. Example temperature profiles are shown in Figure 1; the location of the maximum temperature in the vault progresses upward, with this maximum being some distance below the surface of the grout.

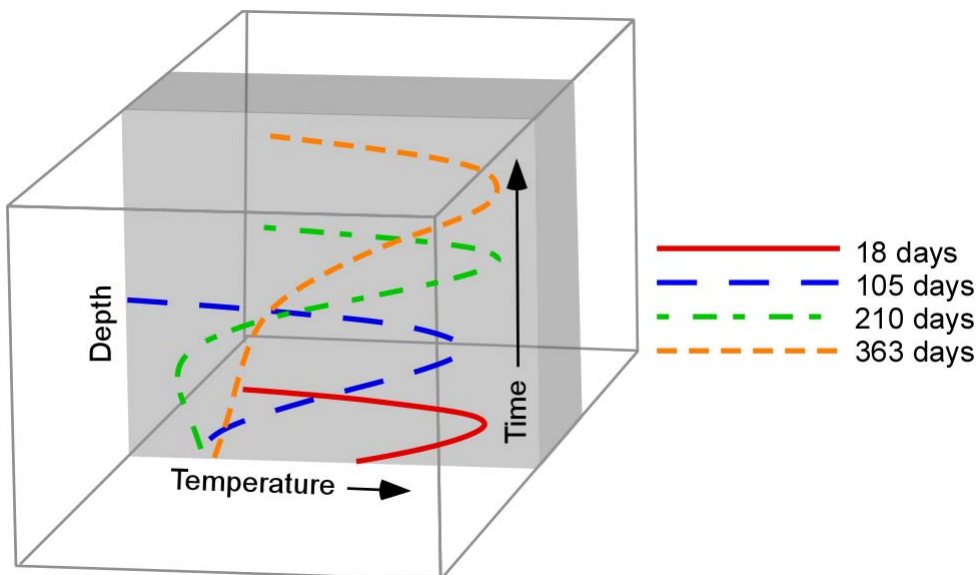


Figure 1 Example Temperature Profiles in Saltstone Vault

The decomposition of TPB anion has been studied in acidic and caustic solutions, but no work has been previously done with the saltstone matrix. TPB decomposition has been hypothesized to proceed down two pathways depending on the presence of catalysts, as shown in Figure 2. (1,2)

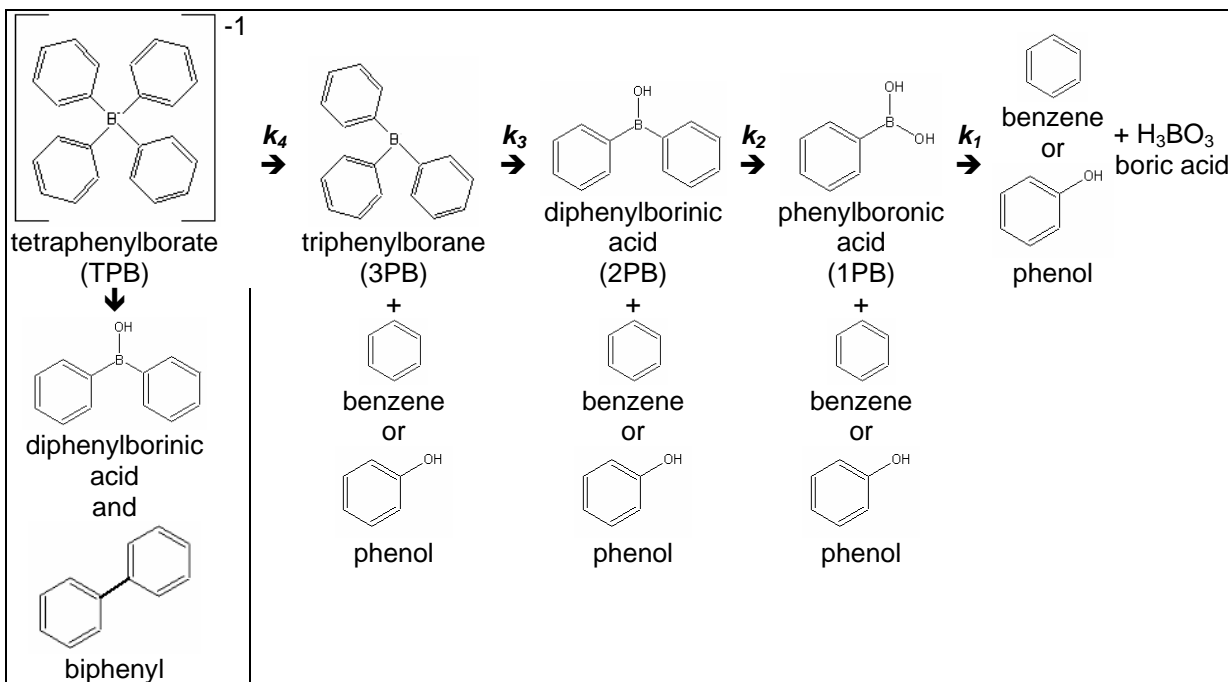


Figure 2 Possible Decomposition Pathways for Tetraphenylborate (1,2)

Inside saltstone, an aqueous alkaline solution exists in the pores that should be similar to that studied in this previous research. The top pathway has been proposed as the reactions occurring during the copper-catalyzed decomposition of soluble NaTPB in aqueous alkaline solutions. (2) The decomposition of the TPB was found to be slow,

followed by relatively fast decomposition of the 3PB, 2PB, and 1PB. Thermal decomposition rates were found to be similar, except that 3PB decomposed fastest versus 2PB in the copper catalyzed system. The reactions were not studied to long extents, so the ultimate distribution of products is not known.

For both the acid-catalyzed and thermal decompositions, the TPB decomposition was the rate limiting step. All of these reactions were reported to be first order in TPB concentration, with additional rate dependences on the Cu^+ or hydroxide concentrations. These rate equations were determined for the dissolved TPB anion in solution, whereas the reactant in saltstone is solid KTPB. Parallel reactions to form phenol and biphenyl rather than benzene have been identified.

The presence of oxygen was found to result in an induction period for the decomposition of TPB, followed by decomposition at a rate similar to a nitrogen-blanketed (anoxic) system that had no induction period. Also, under anoxic conditions, TPB decomposition formed only benzene, while the presence of oxygen gave about 1:10 phenol:benzene. The decomposition of 3PB, 2PB, and 1PB were all found to be faster in the presence of oxygen and 2PB and 1PB gave only phenol as the product.

Research on TPB decomposition on clay surfaces reported that TPB was decomposed to 2PB on minerals containing structural iron as Fe^{+3} and that the Fe^{+3} was reduced to Fe^{+2} as evidenced by a change of color to blue-green ($\text{Fe}^{+2}\text{-O-Fe}^{+3}$). (1) This reference does not mention what other products were formed from the TPB to 2PB decomposition. No formation of 3PB was found, but with Al^{+3} present, decomposition to 3PB was seen. The structure of the saltstone, meanwhile, is somewhat similar to the minerals studied, containing both Fe^{+2} and Fe^{+3} from slag and also Al^{+3} from slag and cement.

EXPERIMENTAL

A test program was designed to determine the benzene release rates from saltstone at several initial TPB concentrations and several temperatures. It is important to note that it is the rate at which benzene was released from the saltstone that was measured and not necessarily the generation rate. Accumulation of generated benzene could be possible and result in the generation and release rates being very different.

Most of the tests were conducted with the saltstone as a right cylindrical cylinder (monolith) with only the top exposed to the vapor phase, as shown in Figure 3. Although there will be temperature gradients in the vault, the release of benzene was studied at constant temperatures to simplify the experiments. As shown in Figure 1, the maximum temperature will be below the grout surface. Tests conducted at constant temperature at the maximum are therefore conservative because the benzene generation from the cooler region above this maximum temperature is expected to be lower than in the region of the maximum temperature. All tests were done in temperature-controlled ovens. As the program evolved, several additional test temperatures and geometries were added. Due to the long duration of the tests, the short timeline for the needed results, and the cost, follow-up experiments to improve understanding of this problem were not possible. Tests with actual radioactive waste and with simulants were performed.

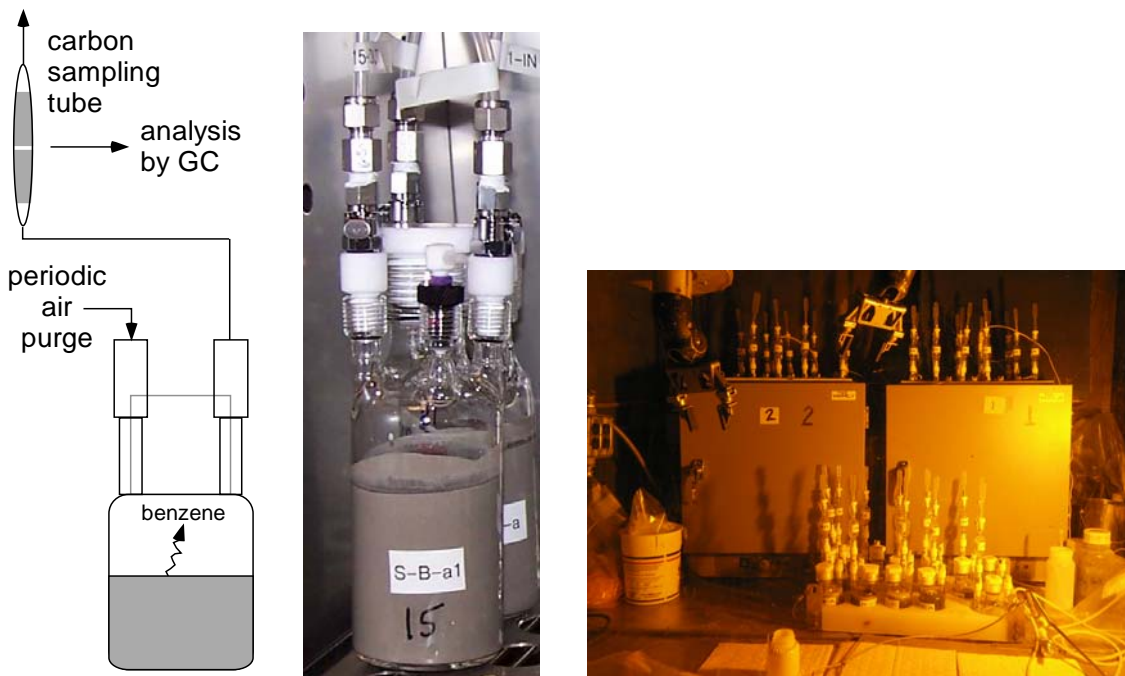


Figure 3 Test Vessel and Sampling Method; Test Equipment in Radiological Containment

The benzene collection method was based on National Institute for Occupational Safety and Health (NIOSH) Method 1501.3. In addition to benzene, toluene and xylenes were also collected from some samples. The saltstone samples were vented through a carbon bed sampling tube (SKC Anasorb[®] CSC Catalog #226-01) fitted with a Viton[®] O-ring seal; the sampling tubes were located outside the ovens. This configuration kept the vessels from pressurizing and ensured that any benzene released prior to active sampling would collect on the carbon bed. The vessels were sampled by purging with organic-free air at about 100 mL/min for several minutes. The sampling frequencies were adjusted so that the sample concentrations would be above the detection limit of the analytical method and below the capacity of the carbon tubes.

Benzene was recovered from the sample tubes by desorption with carbon disulfide. The mean recovery of benzene standards on the sample tubes was 98% for the simulant tests and 103% for the radioactive tests. Benzene recovery from the test vessels was about 60%, so all results were divided by 60%. The low recovery has been attributed to benzene loss through the Teflon[™] tubes used for the air purge line and the outlet line to the sample tube.

Quantitation of the organic compounds recovered from the carbon tubes was performed using an SRI Series 8610C gas chromatograph equipped with a stainless steel capillary column and a flame ionization detector. The capillary column had a polydimethylsiloxane stationary phase (Restek MXT[®]-1, 30 meters, 0.53 mm ID, 3.0 micron film thickness). Primary identification was based on retention time. Some samples were analyzed by gas chromatography-mass spectrometry (GC-MS) on an HP 5890C with a DB-5MS, 30 meter, 0.25 mm ID, 0.25 micron film thickness capillary column.

Benzene contained within saltstone was measured by solvent extraction followed by analysis of the extract. This measurement was difficult due to the potential loss of volatile benzene during processing and to the possibility that the extraction technique

would cause additional TPB decomposition to form benzene. All monolith samples had to be crushed and size-reduced prior to extraction. Crushing at both room temperature and with prior freezing in liquid nitrogen showed minimal differences. Additional size reduction and extraction were done in sealed containers. Extractions were done using water, dichloromethane, and the Toxicity Characteristic Leaching Procedure (TCLP) solvent.⁴ For the water and dichloromethane extraction methods the solvent added was at approximately twice the mass of saltstone. Although the TCLP solvent is acidic, which could result in acid-catalyzed decomposition of the KTPB, no detectable decomposition was found; the TCLP solvent was quickly neutralized by the caustic saltstone. The mass of extraction fluid for the TCLP was 20 times the saltstone mass. The extractions using dichloromethane did not provide quantitative benzene results because the dichloromethane and benzene could not be resolved on the GC-MS while the HPLC benzene detection limit was near 5 mg /L. The water and TCLP extractions were analyzed using GC-MS with a benzene detection limit of 0.025 mg /L.

The saltstone mixture was prepared from a Defense Waste Processing Facility (DWPF, treats high-level radioactive waste) recycle simulant and either Tank 48H actual waste or a simulant containing KTPB. Table I lists the nominal composition of the Tank 48H waste. The organics tetraphenylborate, triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB) are the potential sources of benzene from the saltstone. The DWPF recycle simulant composition used is also shown in Table I. The waste and the recycle simulant were blended in different proportions to give the target KTPB concentrations in the saltstone.

Table I Nominal Composition of Tank 48H Waste and Recycle Simulant
Tank 48H Waste - Organics **DWPF Recycle Simulant**

Component (mg/L)						Component (mg/L)		
Tetraphenylborate (TPB): $(C_6H_5)_4B^-$						18000-21000	Na	17940
Triphenylborane (3PB): $B(C_6H_5)_3$						<50-160	Hg	14.5
Diphenylborinic Acid (2PB): $(C_6H_5)_2BOH$						<50-150	Pd	1.3
Phenylboronic Acid (1PB): $C_6H_5B(OH)_2$						<50-150	nitrite	14720
Phenol: C_6H_5OH						700-1000	nitrate	3720
Biphenyl: $(C_6H_5)_2$						380-630	hydroxide	7480
Benzene: C_6H_6						55	carbonate	4200
Inorganics & Properties						Properties		
Al	2240	Mo	13	nitrite	30400	total solids (wt%)		5.2
B	1030	Na	74900	nitrate	18750			
Ba	3	P	207	hydroxide	19600			
Ca	21	S	245	carbonate	56000			
Ce	7	Sb	12	sulfate	528			
Cr	51	Si	106	chloride	370			
Cu	3	Sn	22	oxalate	1613			
Fe	43	Sr	5	formate	680			
K	2380	Ti	840	density (kg/L)	1.165			
Mg	19	U	18	total solids (wt%)	20.2			
Mn	6	Zn	12					

Saltstone grout was prepared using these salt solutions and the premix materials. The premix used was about 45 wt% class F fly ash, 45 wt% ground granulated blast furnace slag, and 10 wt% cement. Approximately 1.6 g of premix was used per gram of waste. A set retarder (Daratard[®]17, W.R. Grace) and an antifoam (Q2-3183A, Dow-Corning) were also added.

For all tests, the target concentrations of TPB anion in the liquid portion were 30, 1000, and 3000 mg/L (33.7, 1122, and 3367 mg/L KTPB). The initial tests were performed at ambient (~25), 55 (simulant only), 75, and 95°C with the cylindrical saltstone forms, as shown in Figure 3. Ambient temperature varied ±4°C, while the higher temperatures varied ±1°C for the simulant tests and up to ±8°C for the radioactive tests. Tests at 84°C with monolithic shapes and at 75°C with wide, flat monoliths and with randomly crushed saltstone were added later when the effect of surface area-to-volume ratio (A/V) was found to be potentially important. Most tests were done with triplicate saltstone samples; results are generally the mean of the triplicate tests.

Upon completion of the first phase of tests, various shapes were tested at 55°C with 3000 mg/L TPB to determine the effect of A/V on the release of benzene. The shapes tested were crushed saltstone of two diameters, spheres of two diameters, cylinders, and monoliths. All but the monoliths were open to the air on all sides. The crushed samples were made by casting saltstone into sealed plastic bags, the spherical forms were made using glass molds, and the cylindrical samples were made by casting into plastic molds. All samples were allowed to cure for two weeks in a humidified (saturated) chamber at room temperature. The sheets of saltstone for crushing were crushed in a sealed bag with a hammer and then sized using sieves. The crushed samples were not spherical.

Radioactive tests with crushed saltstone were also performed. Temperatures of 55 and 65°C were used. The results of these tests were inconclusive due to poor temperature control and failures of the ovens used to heat these samples. The overall test matrix is shown in Table II.

Table II Test Matrix

TPB Conc. (mg/L in salt)	Simulant						Radioactive					
	Temperature (°C)						Temperature (°C)					
	25	55	65	75	84	95	25	55	65	75	84	95
30	M	M		M		M	M			M		M
1000	M	M		M		M	M			M		M
3000	M	M		M	M	M	M			M		M
				W ^a			W ^b					W ^b
		AV		C			AV	AV				

M: monoliths C: crushed with distribution of sizes
W: 'wide' monoliths (^a 19.5 x 0.55 cm; ^b 10.5 x 5 cm)

AV: various A/V ratios

Various dimensions for the crushed, spherical, and cylindrical forms and the A/V ratios for the AV tests from Table II are shown in Table III.

Table III Dimensions and Area / Volume Ratios for AV Tests at 55°C

Form	Nominal Diameter Range (cm)	Mean Diameter (for spheres) (cm)	Area / Volume (cm ⁻¹)	Characteristic Length (Volume / Area) (cm)
Crushed	0.05 - 0.1	0.075	80	0.0125
Crushed	0.40 - 0.63	0.515	11.7	0.0858
Spherical	1.44 ± 0.05	1.44	4.17	0.240
Spherical	2.39 ± 0.05	2.39	2.51	0.398
Cylindrical (open all sides)	1.95 dia. x 2.8 to 4.3 high	NA	2.62	0.382
Cylindrical (open one end only)	3.9 dia.	NA	0.149	6.70
Randomly Crushed (75°C)	0.02 – 1.92	0.267	22.4	0.0446

RESULTS

The most illustrative way to examine the data collected is in plots of the benzene generation rates at different conditions on the same graph. The benzene generation rates are expressed as µg/kg saltstone/h, mg/kg TPB/h, or cumulative benzene generated as percent of theoretical benzene from TPB (4 benzenes per TPB). Figure 4 compares benzene evolution rates at 95°C for simulant monoliths on a per kg saltstone and also a per kg TPB basis. When expressed on a per kg TPB basis, the rates at each TPB concentration were found to be similar. The rates at 75°C were also found to be approximately equal on a per kg TPB basis.

Figure 5 shows that the benzene evolution rate at 95°C from the radioactive tests was of comparable magnitude to the simulant tests. All of the data shown are for 6 cm diameter monoliths, except for one set for a 10.5 cm diameter monolith (W). However, beyond about 75 days, the radioactive rates had declined to be significantly less than the simulant rates. Initially, the temperature in the radioactive test may have exceeded 95°C for several days, which would account for the initially higher rates and for the earlier decline in release, possibly due to depletion of the reactants.

The release rates at 75°C are given in Figure 6. For all sizes, the rates range within 0.5-4 mg/kg TPB/h. The 75°C rates are significantly lower and show the effect of temperature on the release rate. The release rates at 25 and 55°C in Figure 7 are about an order of magnitude lower than for 30 mg/L TPB at 75°C (for reference, symbol ◇ same as in Figure 6). The rates for blank tests with no TPB added at 25 and 95°C are also shown (which is why these rates are shown per kg saltstone rather than per kg TPB). Both blanks had higher release rates than the 25 and 55°C samples with 30-3000 mg/L TPB, so the rates at these lower temperatures could not be distinguished from the background benzene release. The benzene release from the blanks was found to be due to the fly ash. The fly ash contained varying amounts of benzene, toluene, and m-xylenes. Release rates at 84°C were between those at 75 and 95°C, as expected and shown in Figure 8.

The effect of surface area to volume was initially tested with randomly crushed saltstone and a wide (19.5 cm diameter) monolith. The surface area to volume ratio (A/V) was found to have a significant effect on the benzene release rate, as shown in Figure 9. The rate for crushed saltstone at 75°C was almost as high as for the monolith at 95°C.

The cumulative release of benzene shows the effect of surface area even more dramatically. Figure 10 shows that the cumulative release of benzene was an order of magnitude higher for the crushed saltstone. The cumulative percent released of benzene for the 75°C crushed saltstone is shown to be about equal to that evolved at 95°C with 30 and 1000 mg/L TPB in Figure 11. Note that the cumulative benzene release may be a function of the initial concentration; the total benzene released was higher at higher initial TPB concentration.

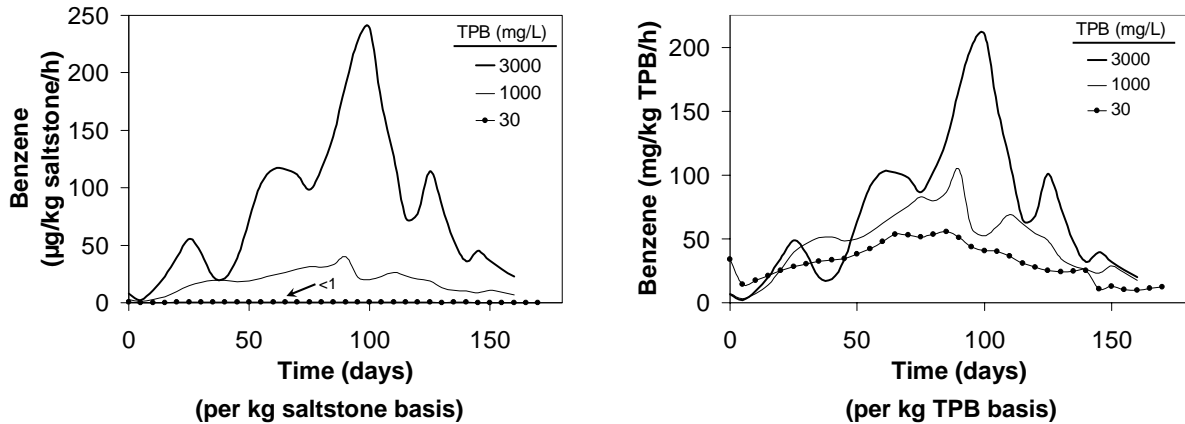


Figure 4 Benzene Release Rates from Simulant Monoliths at 95°C

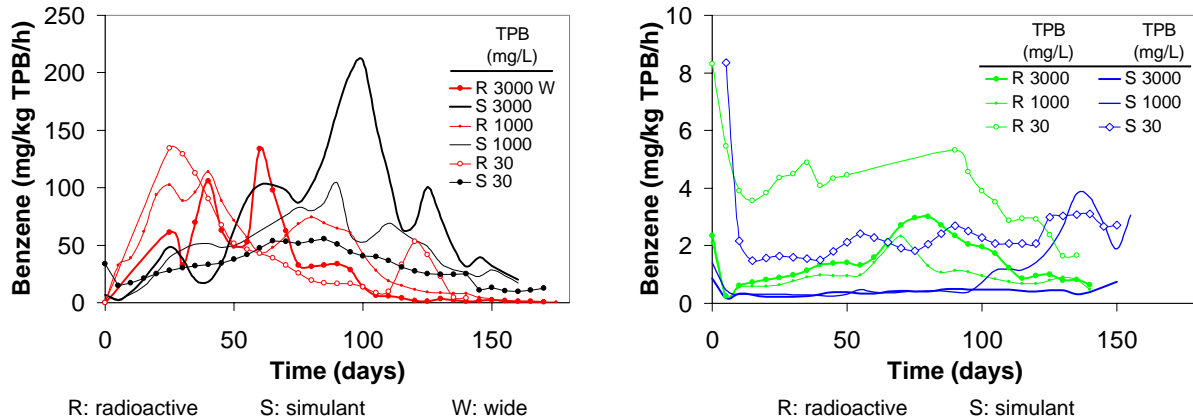


Figure 5 Benzene Release Rates per kg TPB at 95°C from Simulant & Radioactive Monoliths

Figure 6 Benzene Release Rate per kg TPB at 75°C from Simulant & Radioactive Monoliths

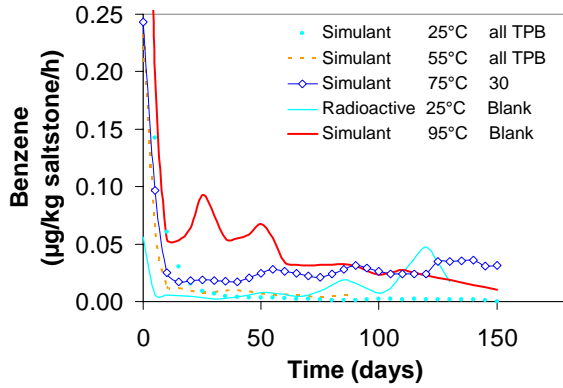


Figure 7 Benzene Release Rates from Blank Monoliths

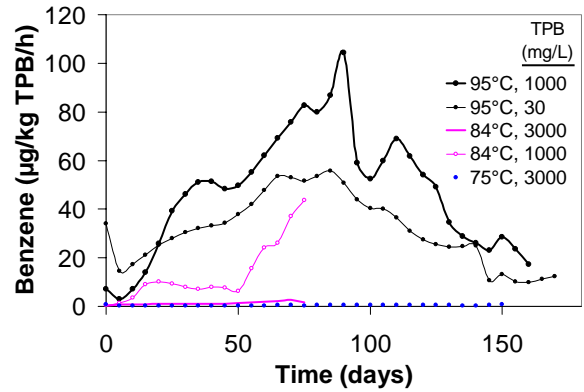


Figure 8 Benzene Release Rates from Simulant Monoliths at 75, 84, & 95°C

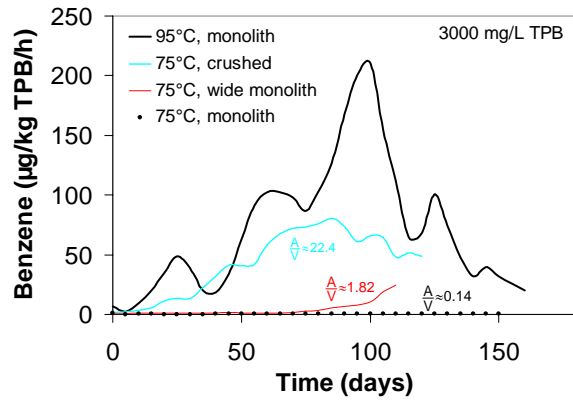


Figure 9 Benzene Release Rates from Simulant Monoliths at 75 & 95°C and Crushed Simulant at 75°C

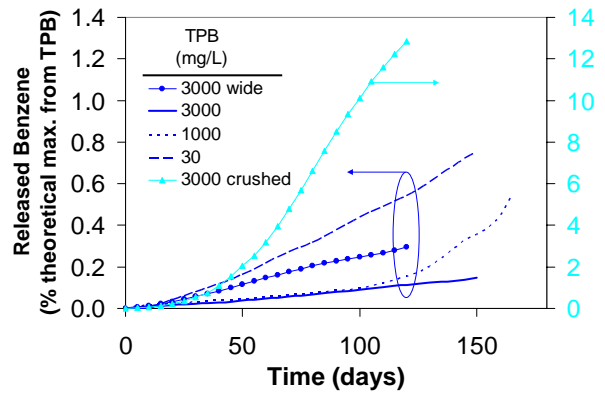


Figure 10 Cumulative Benzene Release from Simulant Saltstone at 75°C

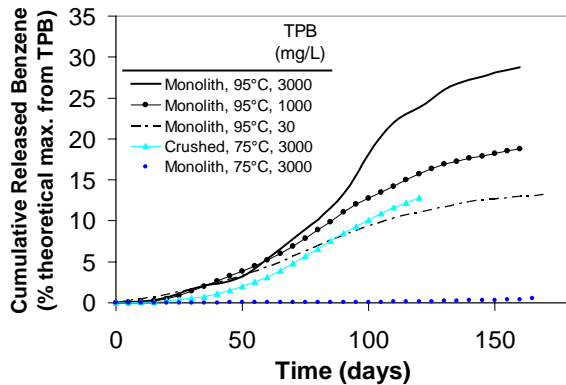


Figure 11 Cumulative Benzene Release from Simulant Saltstone at 75 & 95°C

Accumulation of Benzene in Saltstone Monoliths

Initially, the relatively high benzene release rate from crushed saltstone data at 75 °C suggested that a substantial amount of benzene could be accumulating within the saltstone monoliths. Figure 12 and Figure 13 show that the potential buildup of benzene within the monoliths is 130 mg/kg at 75°C and 13 mg/kg at 55°C. The difference between the amount of benzene released from the higher A/V forms and the standard monoliths was assumed to be the potential accumulation in the standard monoliths. The generation of benzene inside the saltstone was assumed to be homogeneous throughout. The higher release rates seen for the small crushed particles were assumed to be due to the shorter path length for diffusion to the surface. Therefore, significant benzene accumulation in the saltstone monoliths was expected.

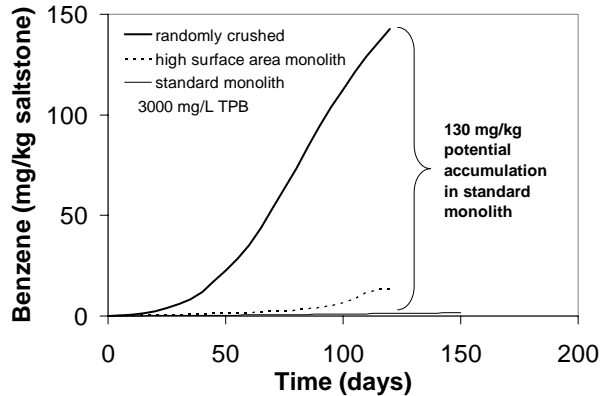


Figure 12 Potential Accumulation of Benzene in Saltstone Monoliths at 75°C

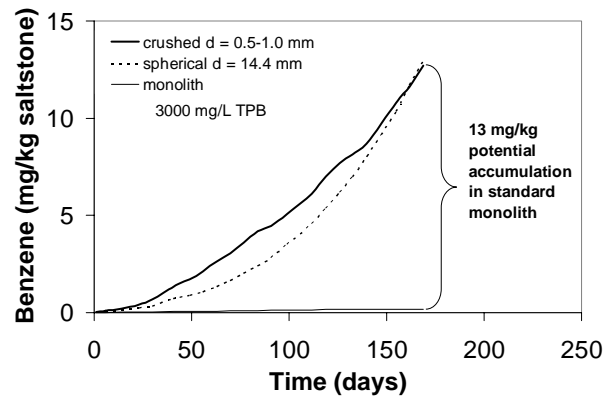


Figure 13 Potential Accumulation of Benzene in Saltstone Monoliths at 55°C

Measurement of residual benzene in several samples was performed to test this hypothesis and to determine if the saltstone would become hazardous waste due to the formation of benzene. The amounts of benzene actually found in several of the samples are summarized in Table IV.

The highest amounts of retained benzene were around 6 mg/kg, which was much lower than expected based on the accumulation hypothesis. The sample analyzed by both the water solvent extraction and the TCLP showed good agreement for the calculated amount of residual benzene in the saltstone. The total benzene release was 2 to 50 times higher than the amount retained. The benzene retained at 95°C was about the same for each sample, even though the benzene released was much higher in the simulant test. Similarly, the benzene retained in the 65°C samples was about the same, but the amount released from the crushed sample (#8) was 22 times higher. Therefore, a model was needed for the formation and release of benzene from saltstone that accounted for both the low accumulation and the dependence of the release rates on the surface area to volume ratio.

Table IV Benzene Contained Within Saltstone

	Temperature (°C)	(R)adioactive or (S)imulant	Water Extraction (mg/kg saltstone)	TCLP Extraction (mg/kg saltstone)	Cumulative Benzene Released (mg/kg saltstone)
1	95	S	—	6.3	320
2	95	R	—	4.0	55
3	95	R	—	6.6	69
4	84	S	0.22	0.26	2.6
5	75	S	0.19	—	1.6
6	75	R	—	2.9	5.6
7	65	R	—	1.1	7.4
8	65	R	—	1.7	161

All samples at 3000 mg/L TPB except 3: 1000 mg/L and standard monoliths except 8: 4.0-6.3 mm diameter crushed

Models for TPB Decomposition and Benzene Formation in Saltstone

Decomposition of TPB in Liquid Solution

To gain insight into the thermal decomposition of TPB, benzene generation at 55°C in a liquid solution was studied. Figure 14 shows the cumulative release of benzene from a liquid sample maintained at 55°C. These data were fit to a model with the decomposition of TPB as a first-order decay. (A fit to 1.25 order is also shown and will be discussed later.) Because a significant amount of phenol was detected in the product liquid, a parallel decomposition pathway was assumed as shown in Eq. (1). The actual pathway to benzene probably involves intermediate reactions, but the apparent reaction the first order appearance of benzene. The first order disappearance of TPB or appearance of benzene is given by Eq. (2), which can be manipulated to give Eq. (3), and solved to give Eq. (4). These equations describe a first order (or apparent first order) decomposition of TPB to form benzene, with the factor n_B being the mass of benzene produced per mass of TPB and k_B being the rate constant. In this model, the decomposition of the TPB is the rate limiting step, which agrees with past research. (2) Because TPB contains four benzene rings, the maximum possible value for n_B would be $4 \times MW_{\text{benzene}}/MW_{\text{TPB}}$, or 0.979 where MW is molecular weight. This value would be less if the decomposition of TPB to benzene were not complete or if the extent of the alternate pathway were significant.

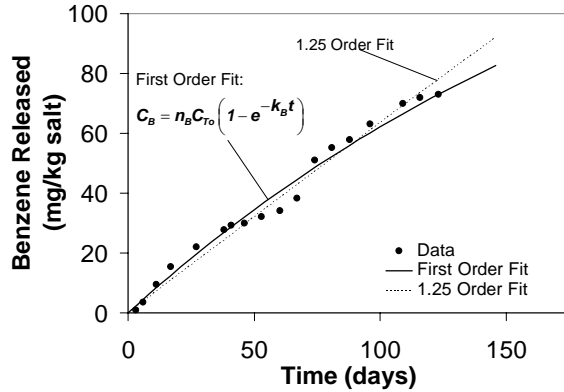
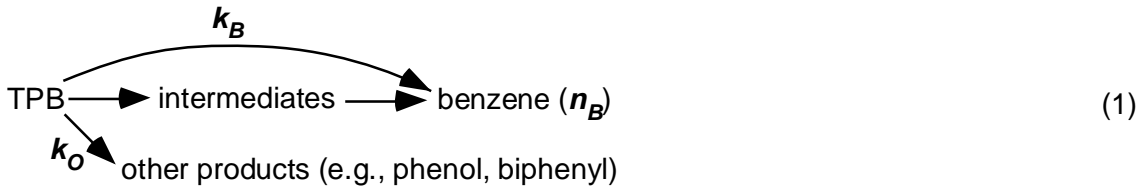


Figure 14 Cumulative Benzene Release from Liquid at 55°C



$$-\frac{dC_T}{dt} = \frac{1}{n_B} \frac{dC_B}{dt} = k_B C_T \quad (2)$$

$$\frac{dC_B}{dt} = n_B k_B C_{T0} e^{-k_B t} \quad (3)$$

$$C_B = n_B C_{T0} (1 - e^{-k_B t}) \quad (4)$$

where C_{T0} = initial concentration of TPB (mg/kg salt) = 2841
 C_B = concentration (total released) of benzene (mg/kg salt)
 k_B = apparent first order rate constant (h^{-1}) = 1.86×10^{-4}
 n_B = mass benzene produced per mass TPB = 0.061

The apparent rate constant k_B was found to be $1.86 \times 10^{-4} \text{ h}^{-1}$ and is consistent with previous work on decomposition of TPB.(2) The measured ratio of benzene produced to TPB initially present was $0.82/30.91 = 0.027 \text{ g/g}$, which is similar to the best fit value found for n_B (0.061). These results suggested that similar equations might be used to describe the formation of benzene in saltstone.

Figure 15 and Figure 16 show for the 95°C tests that the measured percentage release of benzene was higher at higher initial TPB concentrations. The total released benzene also appears to reach or be reaching an asymptotic value, with this asymptote being different for each initial TPB concentration. Similar behavior was seen for the 75°C simulant data. The 3000 mg/L data show that about 25-29% of the TPB decomposed to form benzene that was released, while the 1000 and 30 mg/L tests gave 18-19% and 10-13%, respectively. For a first order decomposition, the percent released is not a function of the initial TPB concentration and the all the data would fall on the same curve rather than three separate curves.

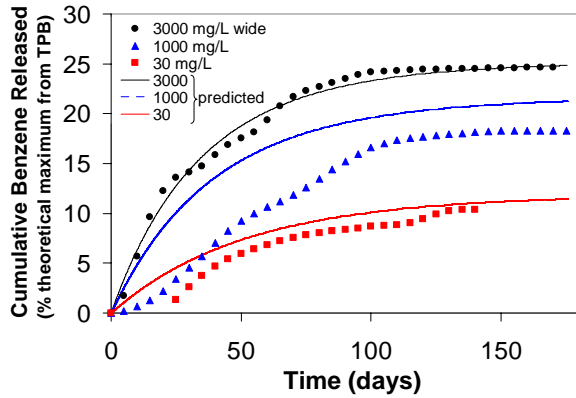


Figure 15 Cumulative Benzene Released at 95°C from Radioactive Tests

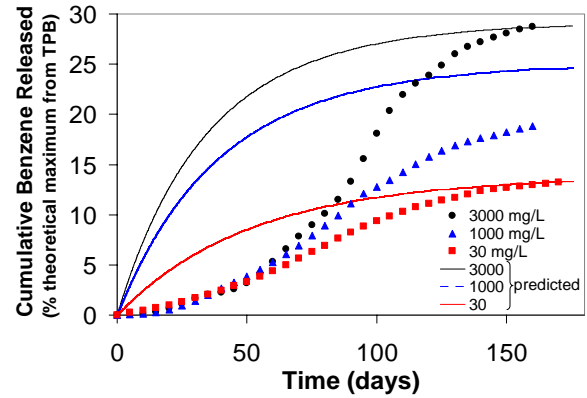


Figure 16 Cumulative Benzene Released at 95°C from Simulant Tests

If phenol were the major “other product” in Eq. (1) and the reaction order for its generation were lower than the order for benzene, then higher initial concentration would favor formation of benzene. The order with respect to benzene has been assumed to be unity, but with the limited range and accuracy of the data and the probable complexity of the actual reaction mechanism, the apparent reaction order to form benzene could easily be 1.25 or higher. The predicted curves shown in Figure 15 and Figure 16 are for 1.25 order to benzene and first order to the other products.

Therefore, at least qualitatively, the formation of benzene from TPB in both saltstone and a liquid solution is described by an apparent first-order, or close to first order, decomposition of TPB. A lower order reaction to form alternate products also seems likely. As shown in Figure 16 for the simulant tests, the initial benzene release rates were much lower than in the radioactive tests, resulting in s-shaped curvature. Ultimately, the amounts of benzene released became similar to the radioactive tests. These differences show that there are additional effects occurring beyond the reaction kinetics.

Initially, the s-shaped curvature was hypothesized to be due to either the rate-determining step being the formation of benzene from 1PB only or to delayed release due to diffusion of benzene within the saltstone to the surface. In the reaction sequence given in Figure 2, if benzene were formed only from 1PB, the benzene versus time curve could be s-shaped as shown in Figure 17.

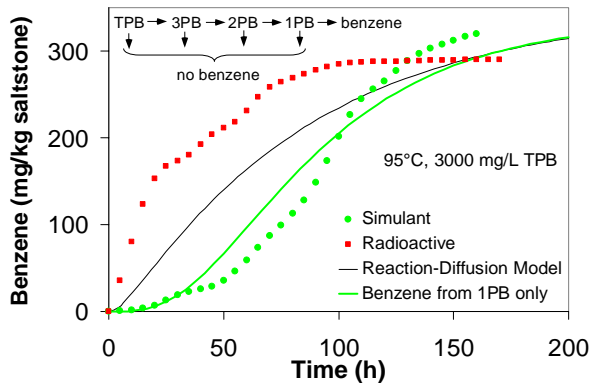


Figure 17 Reaction-Diffusion and Benzene from 1PB Models for Benzene Generation

However, the radioactive 95°C data, some of the 75°C data, and the previous work on TPB decomposition made this mechanism doubtful. Another factor that could not be accounted for is the possibility that different reactions could occur at different temperatures or that the rates of competing reactions could have significantly different dependencies on temperature.

A model with homogeneous first-order formation of benzene from TPB with diffusion of the benzene through the saltstone to the surface would result in a delay in the release of benzene such that the release curve would be slightly s-shaped as shown in Figure 17, but this delay would not be significant.

The 55°C simulant and 55 and 65°C radioactive tests with crushed, spherical, and cylindrical saltstone forms were begun to better understand the effect of the surface area to volume ratio. Figure 18 shows the ratio of benzene released from these various forms to the benzene released from the monolith; this ratio is referred to as the release ratio. This same ratio for biphenyl is given in Figure 19. This ratio for biphenyl for all sizes is relatively constant, indicating that relative to the monolith, the release behavior of biphenyl from all sizes was the same. Approximately constant release is consistent with depletion of the biphenyl by diffusion where the depletion rate is roughly dependent on the area to volume ratio. The data in Table V show that, within measurement uncertainty ($\pm 20\%$), the total amount of biphenyl released was not greater than the initial amount present for the crushed and spherical forms, and was less than the amount initially present for the cylinders and the monolith. These results suggest that little or no biphenyl was formed from TPB decomposition. However, measurements of residual biphenyl in the saltstone were not performed because the amount present would be below the analytical detection limit. The amount of benzene released for each size relative to the potential amount available from TPB is also shown in Table V.

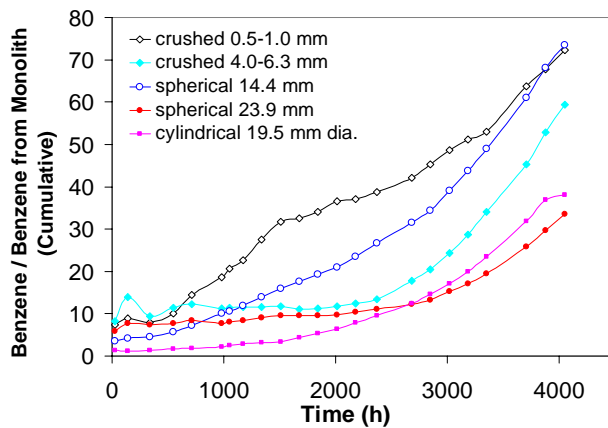


Figure 18 Benzene Release Relative to Monolith

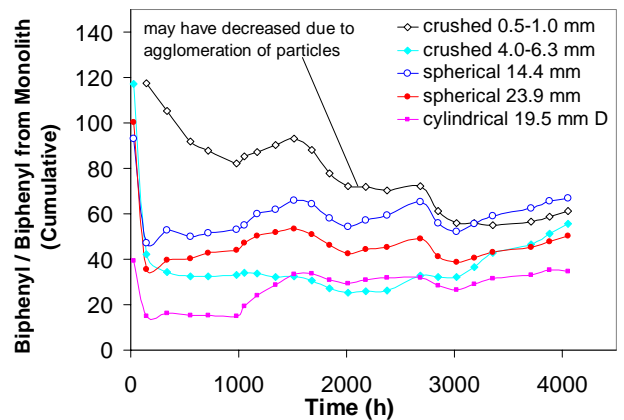


Figure 19 Biphenyl Release Relative to Monolith

Table V Biphenyl and Benzene Release Ratios for 55°C Simulant Samples

	Biphenyl: Offgas/Initial (%)	Benzene: Offgas/(4X Initial TPB) (%)	Area to Volume Ratio (cm⁻¹)
Crushed 0.5-1.0 mm	108	1.14	80
Crushed 4.0-6.3 mm	98	0.94	11.7
Spherical 14.4 mm	117	1.16	4.17
Spherical 23.9 mm	88	0.53	2.51
Cylindrical 19.5 mm D	61	0.60	2.62
Monolith 39 mm D x 67 mm H	1.8	0.016	0.149

(data at 170 days duration)

The release ratios for each size for benzene in Table V all increase with time, with the smaller sizes increasing more quickly. This behavior is not consistent with the simple diffusion mechanism that adequately describes the biphenyl data. If benzene were generated homogeneously throughout the saltstone, its release ratio would remain constant like that of biphenyl even though benzene is being generated rather than just depleted. That is, the concentration of benzene in the saltstone will be increasing, but the ratio to the concentration in the monolith should be independent of the shape.

In the diffusion mechanism, the release ratios are roughly directly proportional to the A/V ratios and remain constant in time (biphenyl), but this is not true for benzene. The A/V ratio would have to change in time for the release ratio to also change, but this is not true because A/V is a constant value for each shape.

Reaction Zone Model

A hypothesis that is consistent with increasing release ratio is that the effective volume in which the decomposition reactions are occurring increases with time. In this hypothesis, the underlying assumption is that to become reactive, the saltstone must undergo a change that is dependent on the surface area to volume ratio. If the TPB decomposition reaction only occurs in an increasing volume reaction zone as shown Figure 20, then although the A/V ratio of the saltstone does not change, the A/V_{rxn} ratio does, where V_{rxn} is the “reactive” volume where the decomposition reaction occurs. This mechanism of increasing reaction volume also supports finding very low residual amounts of benzene in the saltstone. In a large fraction of the saltstone, little or no decomposition may have occurred.

In Figure 20, this model is shown for a sphere and for a cylinder with one end open to the atmosphere (monolith). There is negligible benzene formed in the unreacted volume, while the amount of benzene in the reaction zone is higher and depends on the relative rates of the chemical reaction(s) producing benzene and the diffusion of the benzene out of the saltstone. For modeling purposes, the rate of diffusion out of the reaction zone into the vapor was assumed to be fast compared to the actual benzene generation rate. These assumptions result in models that predict no accumulation of benzene within the saltstone, which is approximately correct.

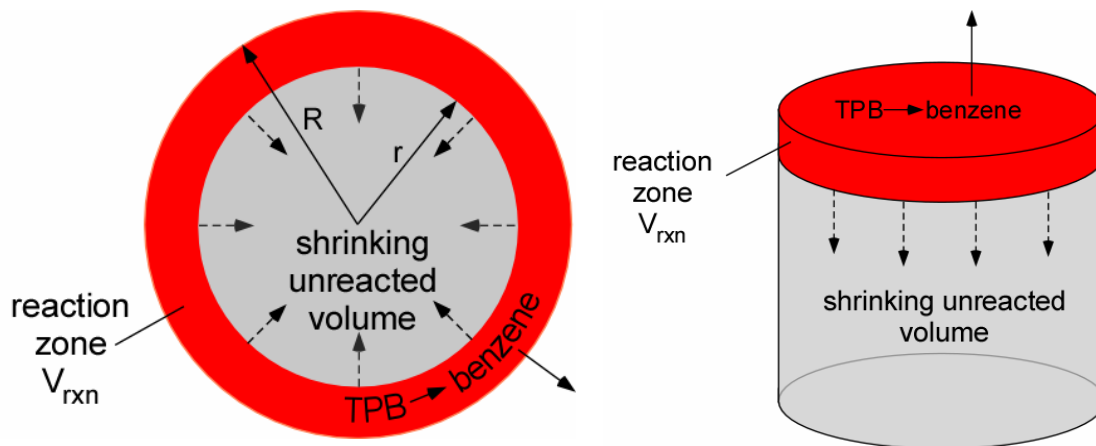


Figure 20 Increasing Reaction Zone Model for TPB Decomposition

The reaction zone model can be described by the combination of the reaction kinetics equation (apparent first order reaction) and a model for the increase in reaction zone volume as a function of time. The increase in volume was considered to be a linear function of the radius for spherical particles. For the single-ended monoliths, a functionality versus depth was assumed. The details of the development of these models are not discussed here and will be the subject of a future publication. The general dependence of the benzene released is:

$$\langle C_B \rangle = f(r, R, k, \omega)$$

where $\langle C_B \rangle$ = mean concentration of benzene in reaction zone* (g/cm³)

r = radius at reaction zone boundary (cm)

R = radius of particle (cm)

k = apparent first order rate constant (h⁻¹)

ω = rate of increase of reaction zone (cm/h)

* concentration that would exist in reaction volume if benzene had not diffused out

The reaction zone models were applied to the simulant 55°C data. The results of fitting each individual set to the models are shown in Figure 21. The fit of each data set is qualitatively good, but most of the data sets show sharper curvature than accounted for by the model. This deviation may be due to ignoring a finite rate of diffusion through the saltstone and the small accumulation of benzene within the saltstone that actually occurs.

The simulant and radioactive data at 95°C and the crushed simulant at 75°C are shown fit by these models in Figure 22. Each data set is fit reasonably well by the models. For the 95°C data, a maximum fraction converted to benzene had to be assumed so that the models would predict the asymptotic approach to a constant amount of benzene produced. The models were able to fit both the radioactive and simulant data by having different reaction zone increase rates (ω). A much higher ω results in virtually no s-shape for the radioactive data.

The higher ω value for the radioactive results would make sense if the reaction zone increase rate were the rate of drying of the saltstone samples. The degree of saturation

in the pores is a function of time due to both the rate of incorporation of pore water into the cement matrix and to evaporation of water at the elevated temperatures. Higher temperatures should result in higher drying rates. For the radioactive samples, the drying rate was probably higher because the radioactive samples were subjected to ~105°C for several days at the beginning of the tests due to oven temperature control problems. Figure 23 shows what is believed to have occurred for samples that were initially subjected to higher than the nominal temperatures. For some initial period, the benzene release rate is significantly higher than at the lower temperature because the higher drying rate increases the reaction zone volume much more quickly. When the temperature is dropped back to the nominal level, the benzene release rate returns to the rate corresponding to the rate that would have occurred later.

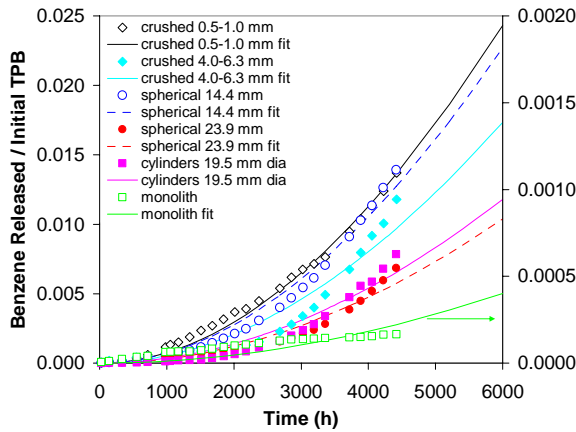


Figure 21 Simulant Data at 55°C Fit by Reaction Zone Models

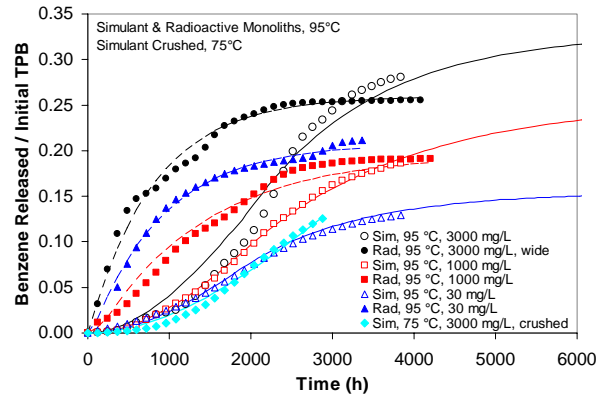


Figure 22 Simulant and Radioactive Data at 95 & 75°C Fit by Reaction Zone Models

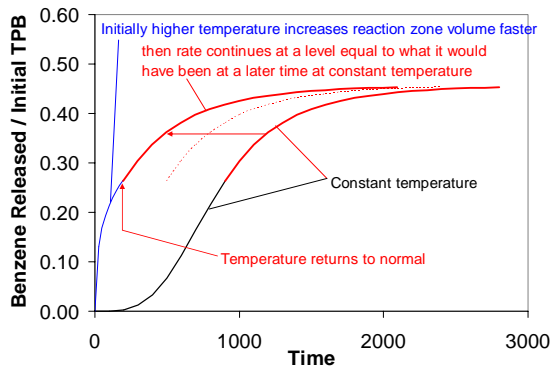


Figure 23 Higher Initial Benzene Release Due to Higher Temperature

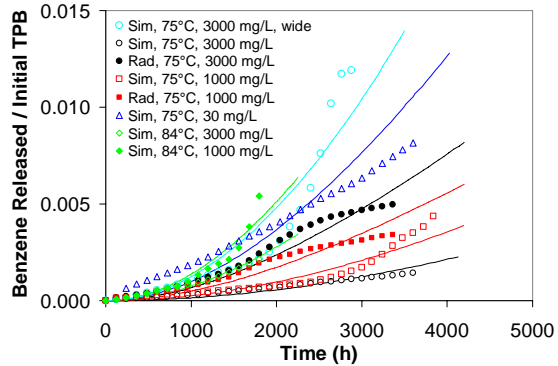


Figure 24 Simulant and Radioactive Data at 75 & 84°C Fit by Reaction Zone Models

The model fits of the 75 and 84°C data are shown in Figure 24. The remaining data at 25 and 55 °C was fit to the models, but the amounts of benzene measured for these data sets were so small that it is difficult to determine if the models actually fit.

Figure 25 and Figure 26 show the apparent first order rate constant k (h^{-1}) and the drying rate ω (cm/h), respectively, as functions of temperature. The drying rate is plotted versus temperature and is fit by a curve with a form similar to the typical Antoine equation fit

applied to vapor pressure data. This curve fits all of the predicted drying rates reasonably well except for the 25°C values, which were comparable or higher than the values at 55°C. Therefore the data at 25°C was not used to generate the curve fit. The drying rate for the radioactive 95°C samples was plotted at 105°C because of the initial temperature excursions that probably increased the drying rate of these samples. The reaction rate constants were fit reasonably well by the typical activation energy Arrhenius plot in Figure 25. As with the drying rates, the 25°C rate constants did not fit the Arrhenius temperature dependence. In general, the rate constants at 25°C were about equal to those at 55°C, whereas they were expected to be about an order of magnitude lower.

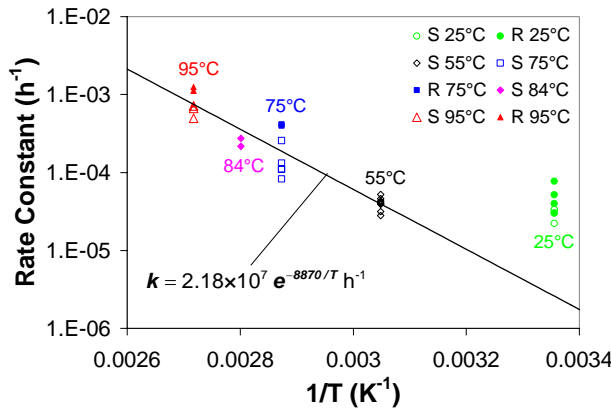


Figure 25 Apparent First Order Rate Constant for Formation of Benzene from TPB

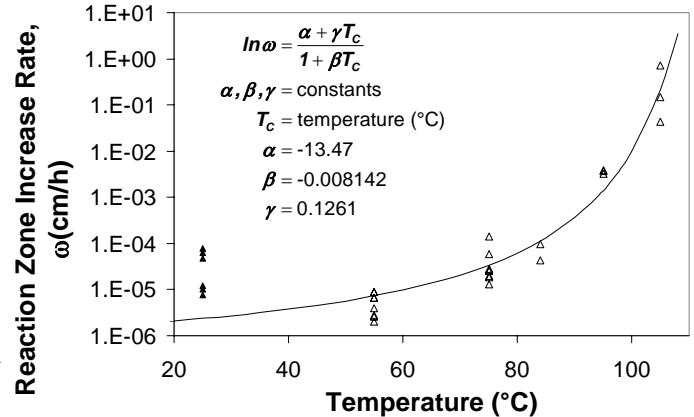


Figure 26 Drying Rate as a Function of Temperature

CONCLUSIONS

The benzene release rates for simulants and radioactive samples were generally comparable at the same conditions. Saltstone monoliths with only the top surface exposed to air at 25 and 55°C at any tetraphenylborate concentration or at any temperature with 30 mg/L TPB gave insignificant releases of benzene. At higher TPB concentrations and 75 and 95°C, the benzene release could result in exceeding the Lower Flammable Limit in the saltstone vaults.

Overall, the use of an apparent first order rate constant for the decomposition of TPB and a drying factor that describes the portion of the saltstone sample that that is reactive (reaction zone) provides a reasonable representation of the observed data. The apparent first order rate constant has a typical Arrhenius temperature dependence and the drying rate is also dependent on temperature, but in a more complicated way.

Phenol was found to be another product of the TPB decomposition, but there was no conclusive evidence for biphenyl formation. The release rate of benzene was proportional to the surface area to volume ratio. The accumulation of benzene within the saltstone was negligible such that the saltstone would not become a hazardous waste based on benzene content.

REFERENCES

- 1 D.B. Hunter, P.M. Bertsch, *In Situ Measurements of Tetraphenylboron Degradation Kinetics on Clay Mineral Surfaces by IR*, **Environ. Sci. Technol.**, **28**, 686-691 (1994).
- 2 C.L. Crawford, M.J. Barnes, R.A. Peterson, W.R. Wilmarth, M.L. Hyder, *Copper-catalyzed sodium tetraphenylborate, triphenylborane, diphenylborinic acid and phenylboronic acid decomposition kinetic studies in aqueous alkaline solutions*, **J. Organomet. Chem**, **581**, 194-196 (1999).
- 3 *NIOSH method 1501, Issue 3, Hydrocarbons, Aromatic*, March 2003.
- 4 Office of Solid Waste, U.S. EPA, *Method 1311 Toxicity Characteristic Leaching Procedure*, in **Test Methods for Evaluating Solid Waste; Physical/Chemical Methods, Third Edition; EPA 530/SW-846**, National Technical Information Service, Washington, DC, 1986.