Evaluation of Organic Vapor Release from Cement-based Waste Forms

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Abstract

A cement based waste form was evaluated to determine the rates at which various organics were released during heating caused by the cementitious heat-of-hydration reaction. Saltstone is a cement-based waste form for the disposal of low-level salt solution. Samples were prepared with either Isopar® L, a long straight chained hydrocarbon, or (Cs,K) tetraphenylborate, a solid that, upon heating, decomposes to benzene and other aromatic compounds. The saltstone samples were heated over a range of temperatures. Periodically, sample headspaces were purged and the organic constituents were captured on carbon beds and analyzed.

Isopar® L was released from the saltstone in a direct relationship to temperature. An equation was developed to correlate the release rate of Isopar® L from the saltstone to the temperature at which the samples were cured. The release of benzene was more complex and relied on both the decomposition of the tetraphenylborate as well as the transport of the manufactured benzene through the curing saltstone. Additional testing with saltstone prepared with different surface area/volume also was performed.

Introduction

Tank 48H contains approximately 250,000 gallons of salt waste. The waste contains approximately 19,000 kg of organic material, primarily as potassium tetraphenylborate (KTPB). The tetraphenylborate, along with approximately 1450 kg monosodium titanate, was added to Tank 48H during the demonstration and startup of the In-Tank Precipitation Facility (ITP). After the shutdown of the ITP process, no process existed for the destruction of the organic material in Tank 48H.

The operating strategy for processing at the Savannah River Site Saltstone facility is projected to result in elevated temperatures in the waste vaults over a period of months. A review of documentation for the production of benzene via the decomposition of potassium tetraphenylborate (KTPB) solids at elevated temperatures indicated that benzene and other flammable gases could accumulate in the vault vapor space.

The Decontaminated Salt Solution (DSS) waste stream from the Modular Caustic Side Solvent Extraction (CSSX) Unit (MCU) and the Salt Waste Processing Facility (SWPF) is anticipated to contain entrained extraction solvent, primarily Isopar® L. The decontaminated salt solution is scheduled to be processed through the Saltstone facility and may occur concurrently with the KTPB solids. The solvent concentration in the MCU DSS exit stream has also raised flammability concerns in the Saltstone vault. Because of these concerns, the release of benzene (due to the decomposition of KTPB) and the volatile

MCU solvent component Isopar® L from saltstone have been studied independently to assess possible flammability issues in the saltstone vault.

Approach

Preparation

Saltstone grout was prepared using the salt solutions representing either the salt waste containing KTPB (mixed with some amount of recycled salt solution from the Defense Waste Processing Facility to obtain the desired TPB concentration) or the DSS waste simulant, Table I . The salt waste is mixed with the dry premix materials obtained from the Saltstone Processing Facility. Table II lists the premix composition and the water to premix ratios. The water to premix ratio is defined as the ratio of the mass of evaporable water from the waste (at ~110 °C) to the combined mass of cement, slag, and fly ash. For the purposes of processing, fixed concentrations (0.25 wt% of salt solution) of set retarder [*] and antifoam[†] were added to the TPB salt solutions. No admixtures were required to prepare the saltstone with the DSS.

Table I. Salt Solution Waste used Prepare Saltstone.				
	3000 mg/L TPB	1000 mg/L TPB	30 mg/L TPB	DSS
Component	(mg/L)	(mg/L)	(mg/L)	(mg/L)
tetraphenylborate	2962	984	28.4	—
triphenylborane (3PB)	10	3.5	0.1	—
diphenylborinic acid (2PB)	20	6.7	0.2	—
phenylboronic acid (1PB)	21	7.1	0.2	—
phenol	109	36	1	—
biphenyl	59	19	0.6	—
benzene	7.9	2.6	0.08	—
Al	316	105	3.03	7555
B	145	48.2	1.39	—
K	336	111	3.22	3449
Na	26000	20600	18000	128750
P	29	9.7	0.28	217
S	35	11.5	0.33	—
Si	15	5	0.14	84
Ti	118	39.3	1.14	—
Hg	12.5	13.8	14.5	5E-02
nitrite	16900	15500	14700	23003
nitrate	5840	4424	3740	125868
hydroxide	9190	8050	7500	35034
carbonate	11500	6630	4270	9001
sulfate	75	25	0.72	13448
chloride	52	17	0.5	851
fluoride	—	—	—	532
oxalate	228	76	2.2	704
formate	96	32	0.92	—
density (kg/L)	1.044	1.031	1.024	1.27
Total solids (wt %)	7.56	5.99	5.22	28.8

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[*] W.R. Grace, Daratard 17
[†] Dow-Corning, Q2-3183A

Table II. Premix Formulations for Processing.		
Premix	**Salt Solution**	**Water/Premix**
45% Class F Fly Ash (FA) 45% GGBFS[a] (Slag)	TPB	0.63
10% Cement	DSS	0.60

[a]Ground granulated blast furnace slag

TPB. To ensure that all of the KTPB was incorporated into each batch, individual salt solution simulant samples containing KTPB were prepared for each saltstone mix. The KTPB salt solution was added to a blender. Premix was added and the mix was blended for one minute, visually inspected, and blended for an additional two minutes. The resulting saltstone slurry was poured into vessels. Table III is the matrix of KTPB (calculated as TPB) concentrations and curing times evaluated. Additional samples were prepared covering a range of surface area to volume (SA/V) ratios of saltstone particle sizes.

TABLE III. Matrix of KTPB Concentrations and Cure Temperatures.	
TPB (mg/L) as KTPB	**Curing Temperature (°C)**
30 1000 3000	Ambient 55 75 95

Isopar® L. Premix was weighed and added to a glass jar with a Teflon® lid. The DSS was added to the same jar. The jar was closed and vigorously agitated by hand to prepare the saltstone slurry. Next, a volumetric aliquot of Isopar® L was added to the mixture. Table IV shows different Isopar® L concentrations and cure times evaluated. The jar was again sealed and further vigorously agitated by hand to ensure complete mixing. Finally, the saltstone slurry was poured into the test vessel and transported to the test oven.

Table IV. Isopar® L Concentrations and Saltstone Cure Temperatures.	
Isopar® L in DSS (µg/g)	**Curing Temperatures (°C)**
30	Ambient
50	55
61	75
100	95
200	

Curing

Each test vessel was placed into the oven and connected to a passive sampling system using Teflon lined tubing, Figure 1. To mimic the temperature rise associated with the heat-of-hydration in a mass pour, the oven was heated to the maximum temperature expected to be achieved during curing. Test vessels were sealed and, to represent the saltstone vault, vented only through the passive sampling system maintained at ambient laboratory temperatures. The sampling system contained a two-section activated carbon

sampling tube. Each tube contained 150 mg of activated coconut shell carbon (CSC) in two sections (100 mg front bed/ 50 mg back bed). The method utilized for quantifying the adsorbed benzene and Isopar® L is based upon the adapted NIOSH method (1501) used in previous testing [1].

Figure 1: Representative saltstone vessel and curing configuration.

Recovery

To determine the amount of benzene or Isopar® L released from a saltstone sample during a particular time period, the headspace of the sample vessel was purged with air for approximately 5 to 10 minutes at a flow rate of about 100 mL/min. The purpose of the air purge was to sweep the contents of the headspace through the CSC sampling tube prior to removing the sampling tube from the sample vessel. The front carbon bed (closest bed to the incoming airflow) of the sampling tube is designed to adsorb volatile organic compounds (VOCs) that pass through the tube. The back bed (that closest to the outgoing vent end) is designed to adsorb VOCs not retained on the front bed due to saturation of the front bed or due to volume breakthrough caused by excessive airflow.

After the air purge was complete, the CSC tube was removed and replaced with a fresh sampling tube. The CSC tube removed from the sample vessel was opened, and the front and back CSC beds were removed from the tube and each bed was placed into a separate 2-mL sample vial.

The CSC was transferred into the appropriate sample vials and the organic compounds were eluted from the CSC using 1 mL of carbon disulfide (CS_2). After the addition of CS_2 eluent, the sealed sample vials were gently agitated and allowed a minimum of 30 minutes to ensure complete elution of the CSC prior to analysis.

Analysis

Benzene. The analysis of the benzene recovered from the activated carbon tube uses a gas chromatograph equipped with a stainless steel capillary column and a flame ionization detector. The

benzene is separated in the gas chromatograph using a capillary column with a polydimethylsiloxane stationary phase (Restek MXT®-1, 30 meters, 0.53 mm ID, 3.0 micron film thickness). Primary identification is based on retention time. Confirmation analysis was obtained (when needed) by gas chromatography-mass spectrometry (GCMS) using both retention time and the peak's mass spectrum. The GC is calibrated daily with standards using the external standard technique. Three concentrations of benzene are used to develop the linear range of the GC. The detection limit of the gas chromatograph was approximately 1 ng/sample, which is roughly equivalent to 0.01 µg benzene/kg saltstone/h.

Isopar® L. Isopar® L is a complex mixture of organic compounds composed of multiple branched aliphatic (i.e., Isoparaffinic) hydrocarbons all sharing a distillation fraction. The mass spectra of all of the compounds are characterized by having significant signals at mass-to-charge ratio (m/e) of 57, 71 and 85 with the 57 signal generally the most significant. Isopar® L has a "fingerprint" chromatogram in that the chromatogram always consists of peaks of similar shape and area between two specific retention times. To quantify the results of Isopar® L analysis with a mass selective detector the summation of all integrated peak areas is used. All systems used similar method parameters for analysis to keep consistent retention times. All samples were analyzed using an Agilent 5973 GC-MS equipped with an Agilent 7683 automatic liquid autosampler. The Isopar® L is separated in the GC using an Agilent capillary column (DB-5MS, 30 meter, 0.25 mm ID, 0.25 micron film thickness).

Results and Discussion

Benzene

The sampling frequency for each vessel was adjusted so that measurable quantities of benzene would be collected on the carbon sampling tubes. In some cases, the amounts collected were much higher than anticipated, but not higher than the capacity of the sampling tube, as indicated by the absence of benzene (or any analyte) on the second bed.

For some sample tubes containing high amounts of benzene, the dynamic range of the GC-FID detector was exceeded, which resulted in signal saturation of the detector. These samples were reanalyzed using either a higher dilution or a reduced FID sensitivity.

The benzene release rate data reported herein shows the mean values of the benzene generation rate over specific time intervals. The actual measurements made are the total mass of benzene generated during the time interval that the sampling tube is installed on the vessel. Therefore, the amount of benzene measured is the amount evolved integrated over the time interval. Because the sample is integrated, the resulting rate (amount collected / collection time interval) is the average rate over the time interval.

Figure 2 compares the average benzene release rates from simulant monoliths at 95 °C. Release data at 95, 84, and 75 °C are compared in Figure 3. The rate at 95 °C and 1000 mg/L TPB is significantly higher than the rate at 84 °C and 1000 and 3000 mg/L TPB, so the effect of temperature (~10X) on the rate is stronger than the effect of the concentration (~3X). The average rate at 84 °C and 1000 mg/L TPB was higher than at 3000 mg/L TPB, which was unexpected. The rates at 84 °C are approximately 4-8 times higher than the rates at 75 °C for 3000 mg/L TPB.
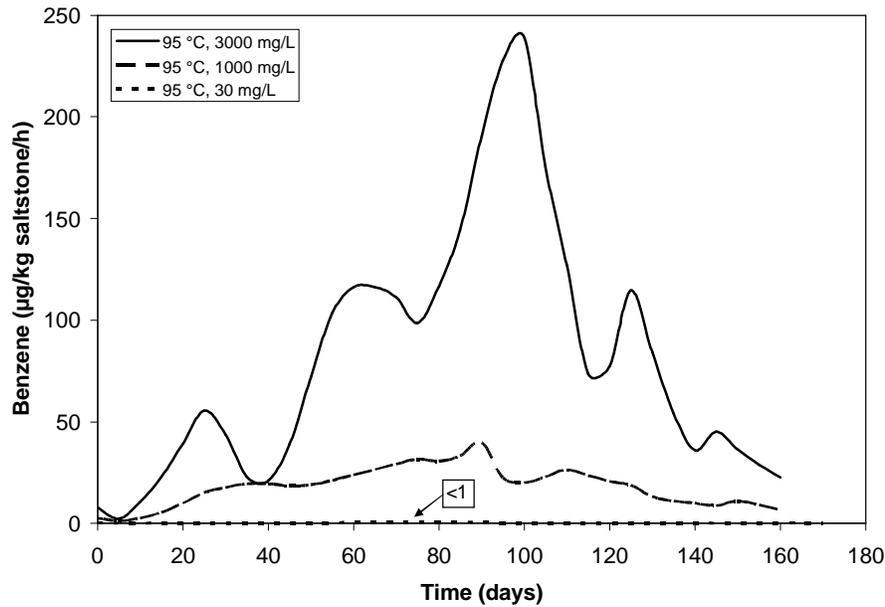
Figure 2: Average Benzene Release Rates from Simulant Monoliths at 95 °C.
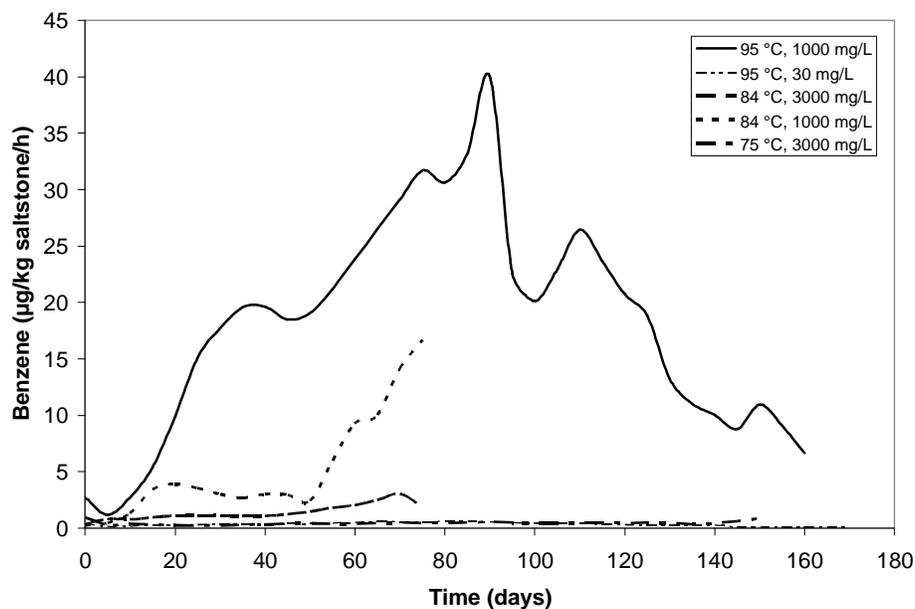

Figure 3: Average Benzene Release Rates from Simulant Monoliths at 75, 84, 95 °C.

The average cumulative benzene measured for the different TPB concentrations at 95 °C are shown in Figure 4. Here the average value is the average of three replicates. For the "theoretical" maximum from TPB, it was assumed that four moles of benzene could be formed from one mole of TPB. Note that these results are highly dependent on the accuracy of the initial concentration of TPB in the saltstone, which was possibly very inaccurate for the 30 mg/L tests as the salt solution used to make the samples contained only 0.7 g of Tank 48H. The slopes of these cumulative curves are the benzene release rates.

Figure 4 shows for the 95 °C tests that the measured percentage release of benzene appears to be a function of the initial TPB concentration. The total released benzene also appears to reach an asymptotic value, with this value being different for each initial TPB concentration. The 3000 mg/L data show that

about 29-52% of the TPB decomposed to form benzene that was released, while the 1000 and 30 mg/L tests gave 19-33% and 13-22%, respectively. Figure 5 shows that the cumulative release from crushed saltstone at 75 °C is lower but on the order of the 95 °C release from the monoliths. The release from monoliths at 75 °C is more that an order of magnitude less.

The effect of geometry at 75 °C and 3000 mg/L TPB in salt also is compared in Figure 5. The release from the crushed saltstone is an order of magnitude greater than both the standard monoliths and the higher surface area monoliths. The difference between the standard and flat monoliths was not very significant. The benzene release rates for the 25 and 55 °C samples are 1-2 orders of magnitude less than at 75 °C for the same geometry and TPB concentration.
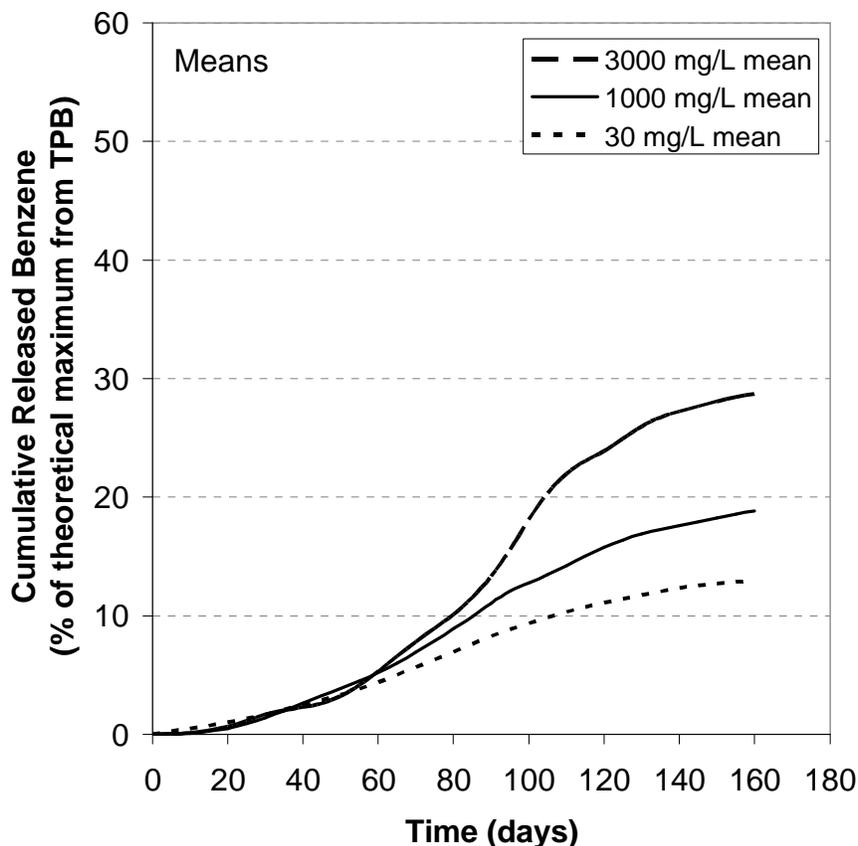

Figure 4: Cumulative Benzene Release from Simulant Monoliths at 95 °C.
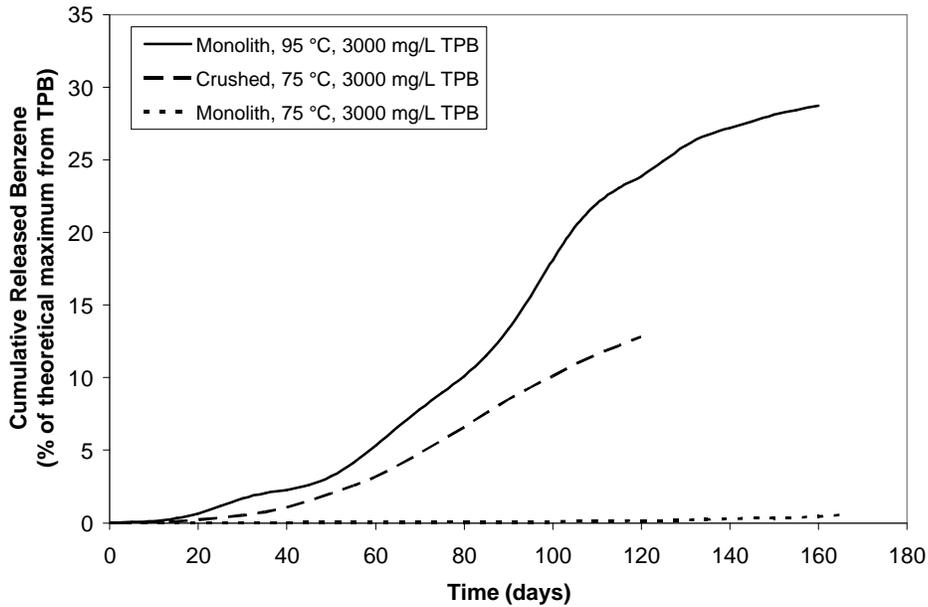
Figure 5: Comparison of Cumulative Release from Simulant at Several Temperatures.

Isopar® L

Samples were collected over a 28-day period. Samples were collected after approximately three hours and again at approximately twenty-four hours after preparing the saltstone. Following the initial two sampling times, all sampling times were at approximately seven-day intervals.

At 550 °C, the release of Isopar® L for the 50 µL/L (30 µg/g) concentration tests averaged 0.38 and 0.01 µg/g salt solution at 3 and 24 hours, respectively. Release of Isopar® L for the 100 µL/L (61 µg/g) concentration test averaged 0.90 and 0.39 µg/g salt solution at 3 and 24 hours, respectively. As seen in Figure 6, the cumulative release did continue in an upward trend throughout the testing, however, the amount of release per sample time nearly leveled off.
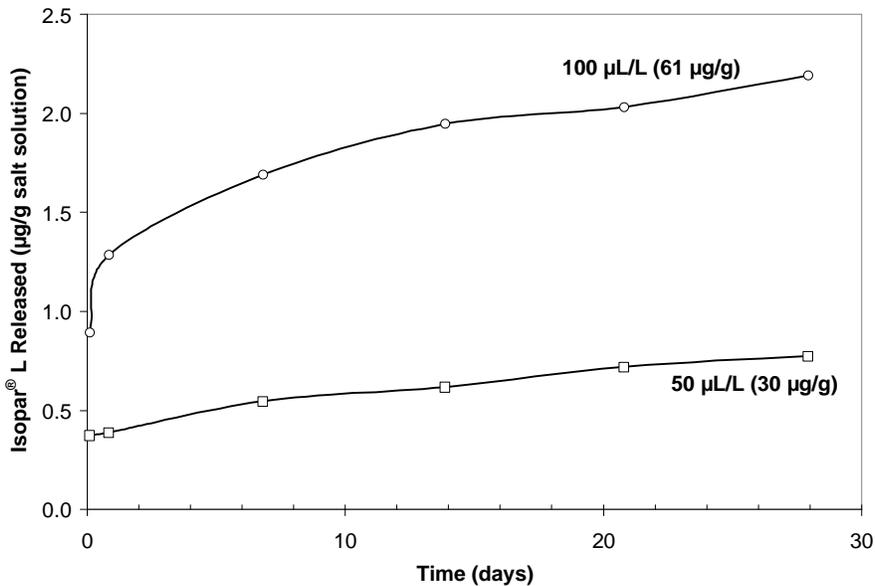

Figure 6: Cumulative release of Isopar® L from saltstone at 55 °C.

After the first 24 hours of curing, release rates were significantly reduced, Figure 7. This is in part due to the changing nature of the saltstone. As prepared, saltstone is a fresh slurry with a nominal effective viscosity of 60 centipoise. During this time, the Isopar® L can move easily through the fresh slurry and evaporate from the surface. As the hydration of the cementitious materials progresses, the slurry transforms from a self-leveling fluid to self-supporting structure. The development of a crystalline structure provides resistance to the transport of the Isopar® L, effectively reducing its availability at the surface for evaporation.
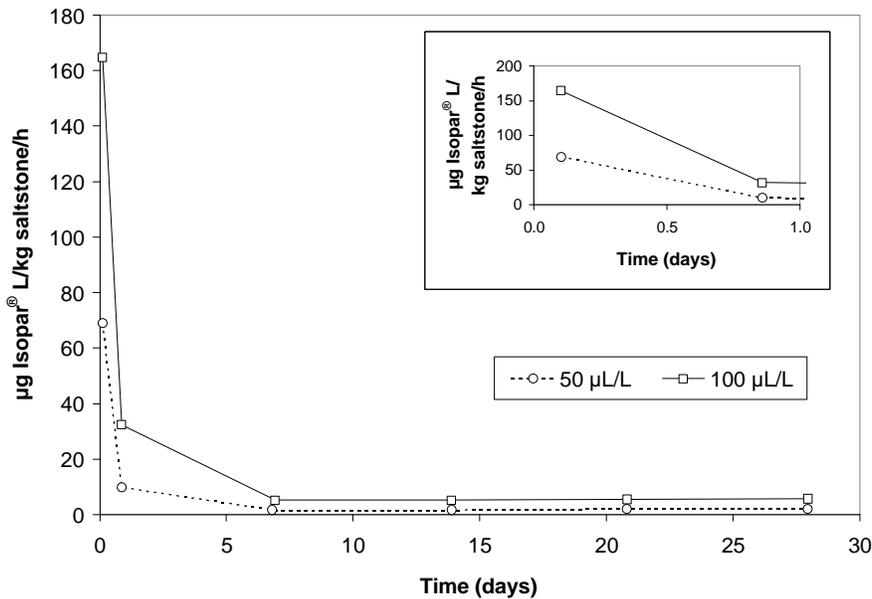

Figure 7: Release rate of Isopar® L from saltstone.

Conclusions

Benzene

A model for the generation and release of benzene from saltstone was developed to account for the observed S-shaped curvature of some of the data, the dependence of the release rate on the surface area to volume ratio, and the low accumulation of benzene within the saltstone. Actual data showed that, except for one sample, the benzene released was 7-50 times the amount retained. Therefore, a reasonable bounding model assumption was that the benzene accumulation within the saltstone was approximately zero. This assumption is equivalent to assuming that the diffusion rate of the benzene was much higher than the rate at which it was generated by the decomposition of TPB.

A hypothesis that is consistent with the results is that the effective volume in which the decomposition reactions forming benzene are occurring increases with time. One or both of the following would be consistent with this increasing volume hypothesis. For the decomposition reaction to occur:

The saltstone needs to become "drier" by evaporation of water from the pores.
Oxygen is required to initiate the TPB decomposition reaction.

For either 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. It is assumed that the crushed saltstone reactive volume will increase on a volume fraction basis more rapidly than the larger spheres, cylinders,

or especially the monolith due to the higher surface area available for mass transfer. If the TPB decomposition reaction only occurs in the reactive volume portion of the saltstone, then although the actual 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 can occur.

The model has two adjustable parameters: the benzene generation rate constant (h^{-1}) and the reactive volume increase rate, or drying rate (cm/h). Both of these parameters were found to be predictable functions of temperature. The reactive volume increase rate determines the increase in reactive volume as a function of time and temperature. With only these two parameters, the data at most temperatures, initial TPB concentrations, and saltstone shapes (crushed, spherical, cylindrical, monoliths) was reasonably fit.

The major implication of the model predictions is that there should be very little benzene generation within a large saltstone monolith such as the Saltstone Facility vaults. Significant reaction to form benzene appears to occur only at the surface interface of the saltstone with the surrounding air. Therefore, so long as a large amount of cracking of the saltstone does not occur while the temperature is elevated, there should be little accumulation or release of benzene. The model fits of the 75 and 84 °C data are shown in Figure 8.
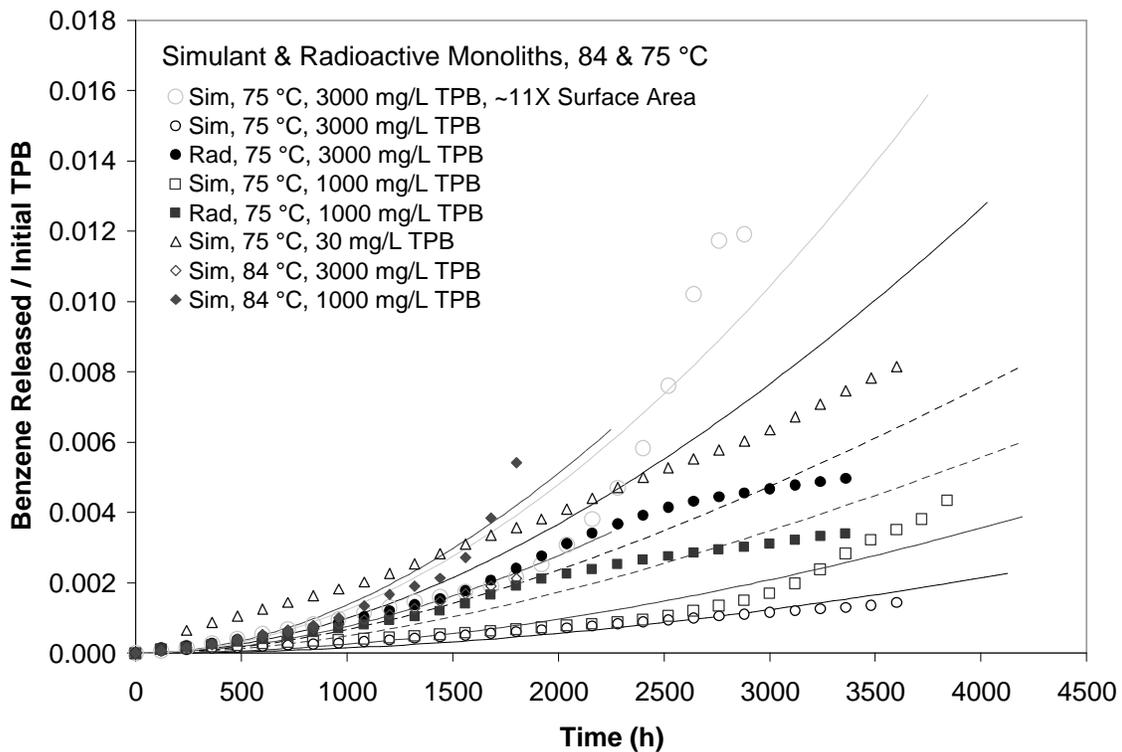

Figure 8: Simulant and Radioactive Data at 75 & 84 °C Fit by Reactive Volume Models.

Isopar® L

The release rate of Isopar® L from saltstone is related to the temperature (curing) of the saltstone. Moreover, the temperature of a system containing Isopar® L drives the vapor pressure of Isopar® L such that the temperature rise due to the heat of hydration would be the primary influence of the release rate of Isopar® L in the curing saltstone, Figure 9. The curve fit is forced through the origin (zero release for sample with zero vapor pressure) and allows for the estimation of release of Isopar® L from saltstone over a range of temperatures. It should be noted that the release curve resembles a curve that would be

expected for evaporation of a liquid (vapor pressure), indicating that the primary driving force for Isopar® L from saltstone is vapor pressure (temperature).
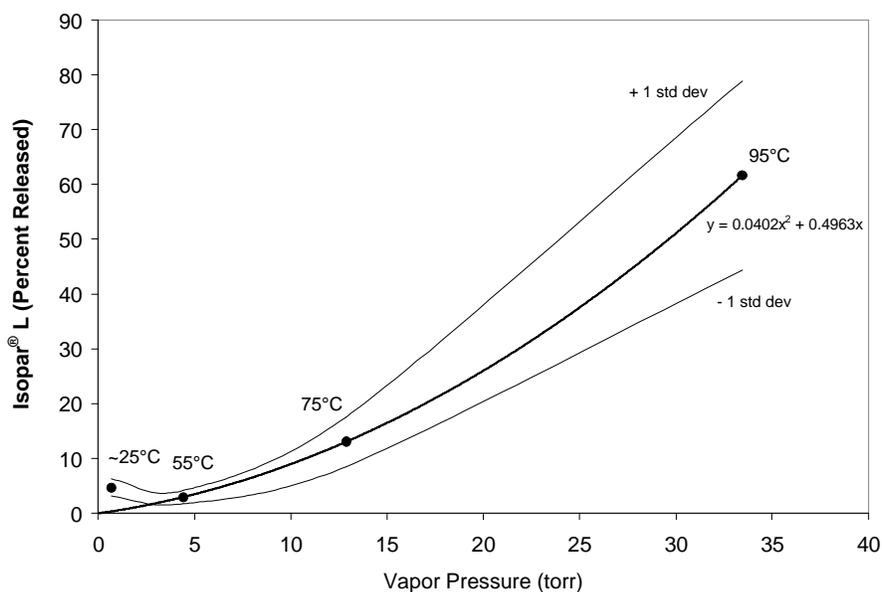

Figure 9: Percent of Isopar® L released as a function of vapor pressure.

References

1.   HYDROCARBONS, AROMATIC: METHOD 1501, Issue 3, *NIOSH Manual of Analytical Methods (NMAM)*. 4th ed., (2003).