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Benzene Evolution Rates from Saltstone Prepared with 2X ITP Flowsheet Concentrations of Phenylborates and Heated to 85° C (U)

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Summary

High Level Waste Engineering (HLWE) requested SRTC to determine the effect of tetraphenylborate (TPB) and its decomposition products (i.e., triphenylboron, diphenylborinic acid, and phenylboronic acid) on the saltstone process. As part of the task, HLWE requested SRTC to measure benzene evolution rates from saltstone prepared with 2X In-Tank Precipitation (ITP) process flowsheet concentrations of phenylborates and heated to 85° C for two days to determine the effect of curing temperature on benzene release.

SRTC prepared saltstone samples containing 2X ITP flowsheet levels of TPB, triphenylboron (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB). The samples were placed in glass kettles which were sealed. One end of kettle was connected to an air purge. An orbo tube was placed on the other end which discharged into a hood. The orbo tubes were changed periodically and analyzed to determine the amount of benzene released from the saltstone samples. One sample cured at ambient temperature. The other sample was heated to 85° C for two days and allowed to cool.

The results and conclusions of this test are:

- The saltstone sample which was heated to 85° C for two days released benzene at an average rate of 16 ug/L hr over 138 days. The maximum release rate (60 ug/L hr) occurred during the first seven days. The total benzene release was 27% of the theoretical maximum.
- The saltstone sample which cured at ambient temperature released benzene at an average rate of 10 ug/L hr over 138 days. The maximum release rate (17 ug/L hr) occurred after 70 days which is consistent with previous SRTC testing. The total benzene release was 18% of the theoretical maximum.
- The test shows the total amount of benzene released from saltstone samples during curing does not change much if the sample temperature increases to 85° C for a few days, but the increased temperature will cause the benzene to be released sooner and the peak release rate to be higher.

No further saltstone testing is recommended.

Introduction

The Saltstone Facility provides the final treatment and disposal of low level liquid waste streams. At the Saltstone Facility, the waste is mixed with cement, flyash, and slag to form a grout, which is pumped into large concrete vaults where it cures. The facility started radioactive operations in June 1990.

High Level Waste Engineering requested SRTC to determine the effect of TPB and its decomposition products (i.e., 3PB, 2PB, and 1PB) on the saltstone process.[1] Previous testing performed by SRTC determined saltstone benzene evolution rates as a function of ITP filtrate composition.[2] Testing by the Thermal Fluids Laboratory has shown at design operation, the temperature in the Z-area vaults could reach 85° C. Saltstone asked SRTC to perform additional testing to determine whether curing at 85° C could change saltstone benzene evolution rates. This document describes the test performed to determine the effect of curing temperature on the benzene evolution rates.

Tests

SRTC prepared a salt solution containing 48 g/L NaOH, 230 g/L $NaNO_3$, and 21 g/L $NaNO_2$. NaTPB, 3PB, 2PB, and 1PB were added to 100 ml samples of the salt solution. Table 1 shows the phenylborate concentrations in the solutions and compares them with the target concentrations and the ITP flowsheet.[3] The solutions were mixed and filtered with a 0.45µ filter. A 36.50 ml (44.16 g) sample of each salt solution was mixed with 5.18 g of cement, 23.33 g of slag, and 23.33 g of flyash. The samples were placed in glass kettles which had two ports and were sealed. One port was connected to an air purge. An orbo tube was placed on the other port which discharged into a hood. The orbo tubes were changed periodically and analyzed to determine the amount of benzene released from the saltstone samples. The saltstone prepared with salt solution 1 cured at ambient temperature for 138 days. The saltstone sample prepared with salt solution 2 was placed in a sand bath and heated to 85^{o} C for two days. After two days, the heater was turned off and the saltstone cured for another 136 days.

The 3PB and 2PB concentrations were within 20% of the target concentrations. The 1PB concentration was less than the detection limit. Since the 1PB target concentration was very close to the detection limit, the potential benzene from 1PB is about 2% of the total potential benzene, and previous testing has shown 1PB decomposition produces very little benzene in saltstone, the low 1PB concentration should not be a concern.

The TPB concentration in the samples is less than the target value. The reason for this result is probably the difficulty in dissolving the TPB into salt solution. The low TPB concentration should not be a concern. Previous SRTC testing has shown most of the benzene production in saltstone is from 3PB and 2PB decomposition.[5] Additionally, other testing has shown KTPB is stable to 200^{o} C which is much higher than the maximum temperature expected in Z-area. [6]

Table 1. Composition of Salt Solutions Used to Prepare Saltstone Samples[3]

Salt Solution	TPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Curing Temp.
Simulant #1	< 10	318	20	< 10	Ambient
Simulant #2	< 10	318	20	< 10	85° C
Target	766	364	24.2	10.8	N/A
Flowsheet[4]	383	182	12.1	5.4	N/A
12/96 test[5]	109	1689	161	71	Ambient

Results

Table 2 and Figure 1 show the benzene evolution data (the uncertainty in the measured evolution rates is ± 8%). The 12/96 test data was interpolated to calculate average benzene release rates over 138 days. The sample which was heated to 85° C showed a peak evolution rate of 60 μg/L hr (73,400 μg/mole 3PB hr) within the first seven days. After seven days, the evolution rate declined and averaged 16 μg/L hr (19,100 μg/mole 3PB hr) over 138 days. That sample released 27% of the theoretical maximum over the test. The peak release rate in the sample which was heated to 85° C was higher than the peak release rates in the samples which cured at ambient temperature. The peak release rate also occurred sooner. The average release rate from the sample which was heated to 85° C was within 10% of the average release rate of the 12/96 test. The average release rate was 50% higher in the sample which was heated to 85° C than the sample in the current test which cured at ambient temperature.

The sample which cured at ambient temperature showed a peak benzene evolution rate of 17 μg/L hr (20,800 μg/ mole 3PB hr) after 70 days which is consistent with previous SRTC testing. The average benzene evolution rate in this test was 10 μg/L hr (12,700 μg/mole 3PB hr). The sample released 18% of the theoretical maximum over 138 days. The peak release rate and average release rate are less than the rates measured in the 12/96 test. The differences could be due to differences in phenylborate concentrations in the saltstone samples or to experimental uncertainty.

Table 2. Composition of Salt Solutions Used to Prepare Saltstone Samples[3]

Salt Solution	Time (days)	Peak Release Rate (μg/mole 3PB hr)	Avg. Release Rate (μg/mole 3PB hr)	Yield (%)	Curing Temperature
Simulant #1	138	20,800	12,700	18	Ambient
Simulant #2	138	73,400	19,100	27	85° C

12/96 test[5]	328	53,300	15,600	31	Ambient
12/96 test[5]	138	53,300	17,400	25	Ambient

The test results show heating the saltstone sample to 85° C for two days does not significantly change the amount of benzene released, but causes the benzene release to occur sooner. The peak release rate of the sample which was heated to 85° C increased by 37% over the sample in the 12/96 test.

Conclusions

The results and conclusions of this test are:

- The saltstone sample which was heated to 85° C for two days released benzene at an average rate of 16 ug/L hr over 138 days. The maximum release rate (60 ug/L hr) occurred during the first seven days. The total benzene release was 27% of the theoretical maximum.
- The saltstone sample which cured at ambient temperature released benzene at an average rate of 10 ug/L hr over 138 days. The maximum release rate (17 ug/L hr) occurred after 70 days which is consistent with previous SRTC testing. The total benzene release was 18% of the theoretical maximum.
- The test shows the total amount of benzene released from saltstone samples during curing does not change much if the sample temperature increases to 85° C for a few days, but the increased temperature will cause the benzene to be released sooner and the peak release rate to be higher.

No further saltstone testing is recommended.

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Figure 1. Effect of Curing Temperature on Saltstone Benzene Evolution