

**WSRC-TR-99-00156**

**KEYWORDS:** Saltstone,  
Tetraphenylborate

**RETENTION:** Permanent

## **Benzene TCLP Results from Saltstone Prepared with 2X ITP Flowsheet Concentrations of Phenylborates (U)**

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**May 21, 1999**

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

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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 determine if saltstone prepared with 2X In-Tank Precipitation process (ITP) flowsheet concentrations of phenylborates and heated to 85° C for two days passes the 28 day benzene Toxic Characteristic Leaching Procedure (TCLP) test. The TCLP test is a standard method to determine if solid waste must be disposed of in accord with SCDHEC/EPA hazardous waste regulations.

SRTC prepared saltstone samples containing 2X ITP flowsheet levels of TPB, triphenylboron (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB). One sample cured at ambient temperature. The other sample was heated to 85° C for two days and then allowed to cool. After curing for 28 days, the samples were submitted to ADS for a benzene TCLP test.

The results and conclusions of this test are:

- The benzene concentration in the TCLP extract of a saltstone sample containing 2X ITP flowsheet concentrations of 3PB, 2PB, and 1PB which cured at ambient temperature was 9.5 µg/L versus a regulatory limit of 500 µg/L.
- The benzene concentration in the TCLP extract of a saltstone sample containing 2X ITP flowsheet concentrations of 3PB, 2PB, and 1PB which was heated to 85° C for two days was 55 µg/L versus a regulatory limit of 500 µg/L.
- Since the benzene concentration in the TCLP extract was well below the regulatory limit for both samples, these test results provide confidence that saltstone prepared with flowsheet concentrations of phenylborates will pass the benzene TCLP test.

No further TCLP 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.<sup>1</sup> Previous testing performed by SRTC showed saltstone prepared with bounding concentrations of phenylborates and cured at ambient temperature will pass the TCLP test for benzene.<sup>2</sup> 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 cause the benzene concentration in the TCLP extract to exceed the regulatory limit. This document describes the test performed to determine the effect of heating a saltstone sample to 85° C on the TCLP benzene results.

## Tests

SRTC prepared a salt solution containing 48 g/L NaOH, 230 g/L NaNO<sub>3</sub>, and 21 g/L NaNO<sub>2</sub>. Different amounts of 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.<sup>3</sup> 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 solutions were mixed, poured into a saltstone container, and cured for 28 days. The saltstone prepared with salt solution 1 cured at ambient temperature for 28 days. The saltstone sample prepared with salt solution 2 was placed in a sand bath and heated to 85° C for two days. After two days, the heater was turned off and the saltstone cured for another 26 days.

After curing, the samples were frozen in liquid nitrogen for six hours and crushed. Samples of the crushed saltstone (2 - 2.5g) were placed in a zero-headspace extractor and extracted with acetic acid for 18 hours. The extract was then analyzed by Gas Chromatography/Mass Spectrometry. ADS performed the extraction consistent with the test protocol provided in federal regulations, and performed the analysis according to ADS procedure 2656. ADS is not a certified laboratory for TCLP testing.

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.

**Table 1. Composition of Salt Solutions Used to Prepare Saltstone Samples<sup>3</sup>**

| <u>Salt Solution</u>       | <u>TPB (mg/L)</u> | <u>3PB (mg/L)</u> | <u>2PB (mg/L)</u> | <u>1PB (mg/L)</u> | <u>Curing Temperature</u> |
|----------------------------|-------------------|-------------------|-------------------|-------------------|---------------------------|
| Simulant #1                | < 10              | 318               | 20                | < 10              | Ambient                   |
| Simulant #2                | < 10              | 318               | 20                | < 10              | 85° C                     |
| Target Concentration       | 766               | 364               | 24.2              | 10.8              | N/A                       |
| ITP Flowsheet <sup>4</sup> | 383               | 182               | 12.1              | 5.4               | N/A                       |

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.<sup>5</sup> Additionally, other testing has shown KTPB is stable to 200° C<sup>6</sup> which is much higher than the maximum temperature expected in Z-area.

## Results

Table 2 shows these TCLP results<sup>7</sup> as well as the TCLP results from other SRTC tests<sup>2,8,9</sup>. The benzene concentration in the TCLP extract of saltstone simulant #1 was 9.5 µg/L versus a regulatory limit of 500 µg/L. The benzene concentration in the TCLP extract of saltstone simulant #2 was 55 µg/L versus a regulatory limit of 500 µg/L. The results show heating the saltstone to 85° C while it cured increased the benzene concentration in the TCLP extract, but the concentration was still well below the regulatory limit.

In other tests performed by SRTC with real and simulated ITP filtrate, all saltstone samples passed the benzene TCLP test, except for simulant #2 in December 1996. That sample contained phenylborates well in excess of the expected flowsheet concentrations. The Tank 48H filtrate sample contained a large excess of TPB, and would be expected to have high 3PB and 2PB concentrations. The benzene concentration in TCLP extract was well below the regulatory limit. Simulant #1 prepared in December 1996 contained phenylborate in excess of the ITP flowsheet concentrations. The benzene concentration in TCLP extract was below the regulatory limit.

Since the saltstone samples in this test contained 2X ITP flowsheet concentrations of 3PB, 2PB, and 1PB and the benzene concentrations in the TCLP extract were less than 11 % of the regulatory limit, saltstone prepared with ITP flowsheet concentrations of phenylborates is expected to pass the TCLP test for benzene.

**Table 2. Benzene TCLP Results**

| <u>Sample</u>         | <u>TPB (mg/L)</u> | <u>3PB (mg/L)</u> | <u>2PB (mg/L)</u> | <u>1PB (mg/L)</u> | <u>Pot. Benz. (mg/L)</u> | <u>TCLP (mg/L)</u> | <u>Reg. Limit (mg/L)</u> | <u>Curing Temp</u> |
|-----------------------|-------------------|-------------------|-------------------|-------------------|--------------------------|--------------------|--------------------------|--------------------|
| Tank 50H <sup>8</sup> | 246               | N/A               | N/A               | N/A               | > 240                    | 0.05               | 0.5                      | Ambient            |

|                                 |      |      |      |      |        |        |     |         |
|---------------------------------|------|------|------|------|--------|--------|-----|---------|
| Tank 48H Filtrate <sup>9</sup>  | 2038 | N/A  | N/A  | 1256 | > 2795 | 0.027  | 0.5 | Ambient |
| Simulant #1 12/96 <sup>2</sup>  | 515  | 1591 | 787  | 204  | 2883   | 0.36   | 0.5 | Ambient |
| Simulant #2 12/96 <sup>2</sup>  | 988  | 2944 | 2044 | 423  | 5933   | 0.96   | 0.5 | Ambient |
| Simulant #1 6/97 <sup>3,7</sup> | < 10 | 318  | 20   | < 10 | 340    | 0.0095 | 0.5 | Ambient |
| Simulant #2 6/97 <sup>3,7</sup> | < 10 | 318  | 20   | < 10 | 340    | 0.055  | 0.5 | 85° C   |
| ITP Flowsheet <sup>4</sup>      | 383  | 182  | 12.1 | 5.4  | 564    |        |     |         |

## Conclusions

The results and conclusions of this test are:

- The benzene concentration in the TCLP extract of a saltstone sample containing 2X ITP flowsheet concentrations of 3PB, 2PB, and 1PB which cured at ambient temperature was 9.5 µg/L versus a regulatory limit of 500 µg/L.
- The benzene concentration in the TCLP extract of a saltstone sample containing 2X ITP flowsheet concentrations of 3PB, 2PB, and 1PB which was heated to 85° C for two days was 55 µg/L versus a regulatory limit of 500 µg/L.
- Since the saltstone samples contained 2X flowsheet concentrations of 3PB, 2PB, and 1PB and the benzene concentrations were less than 11 % of the regulatory limit, saltstone prepared with flowsheet concentrations of phenylborates is expected to pass the TCLP test for benzene.

No further TCLP testing is recommended.

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