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**DPST-86-390-72
LP-10374****Radiolysis effects,
benzene, in-tank
processing, salt
decontamination,
tetraphenylborate**

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January 15, 1987

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**TECHNICAL REPORT - BENZENE DISTRIBUTION IN PRODUCT STREAMS
FROM IN-TANK PROCESSING**

Attached is DPST-86-390, "Benzene Distribution in Product Streams from In-Tank Processing." This document summarizes the current information on the radiolytic decomposition of potassium tetraphenylborate and benzene production from in-tank processing. It includes information obtained from the full scale in-tank demonstration, subcontract work by the University of Florida, and small scale experiments at the Savannah River Laboratory. The amount of benzene which will be produced from in-tank processing and the composition of the slurry after storage can be estimated from the information provided. Areas in which further work is planned are also discussed.

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Radiolysis effects,
benzene, in-tank
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tetraphenylborate

DPST-86-390

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Benzene Distribution in Product Streams From In-Tank Processing

Summary

Benzene is the major product of radiolytic decomposition of tetraphenylborate salts during in-tank salt decontamination. Its production rate has been measured at the Savannah River Laboratory (SRL) and at the University of Florida under various conditions of importance to the in-tank process. Recent work has been concerned with the extent of decomposition for long storage periods, and the composition of the product streams from the process. The major results from this work are:

- The stored potassium tetraphenylborate precipitate will decompose at a rate of 7.3 ± 1.1 % per year.
- The major products of the decomposition are benzene, phenol, biphenyl, and phenylboric acid.
- Decomposition is directly proportional to the total dose and is unaffected by dose rate.
- The decomposition produces acidic compound which will cause a decrease in the pH of the storage tank.

The final report on the work done at the University of Florida is attached (see Appendix A). Although the subcontract with the University of Florida has ended, further work on the effects of radiation on tetraphenylborate solutions and slurries is still being pursued at SRL.

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Introduction

The in-tank process for decontaminating the Savannah River Plant's high activity soluble waste will use sodium tetraphenylborate to precipitate cesium-137 (Ref. 1). The precipitate slurry from this process will be stored for two years in the tank farm before it is sent to the Defense Waste Processing Facility (DWPF) where it will be incorporated in borosilicate glass. During the precipitation process and storage period, the precipitate slurry will be subjected to intense beta and gamma irradiation. As a result, some of the precipitate will decompose to smaller organic molecules such as benzene, phenol, and biphenyl. This decomposition has been studied at the Savannah River Laboratory and, by subcontract, at the University of Florida. Results of this work have been published previously (Ref. 2-6). The major product of the decomposition is benzene and it has been the cause of much concern because of its flammability and carcinogenicity. The amount of benzene produced is very important to safety and regulatory requirements in the Tank Farm where the precipitate is stored. Its presence in the product streams (decontaminated salt solution, recycled wash water, and concentrated slurry) is also important to the design of other facilities. In addition, the extent of the decomposition is important to the acid hydrolysis process for converting the precipitate into feed for the DWPF glass melter.

The results from the full scale in-tank demonstration (Ref. 7) and later small scale tests (Ref. 2-3), have shown that the decomposition products from radiolysis are of two kinds: "free" and "trapped". The free products are believed to be produced at the surface of the KTPB particles and are free to dissolve in the solution or evaporate into the air. The "trapped" products are formed on the inside of the KTPB particles and are held in the crystal lattice. The "trapped" products are released if the crystal is dissolved, such as occurs in the washing step of the in-tank process when the excess NaTPB is recovered in the wash water.

A calculation of the radiation dose expected for stored slurry is given in Appendix B. Normally, doses are expressed in rads. However, throughout this report the radiation doses will be given in terms of equivalent years of tank farm storage so that an easy comparison with planned tank farm operations can be made. During one year of storage, a slurry with the average level of Cs-137 (36 Ci/gal) will receive a dose of 1.45×10^8 rads. Currently, it is planned that the KTPB precipitate will be stored for approximately two years before it is sent to the DWPF.

Radiolytic Decomposition Rate for KTPB and Effect of Dose Rate

Previously, it was estimated that $12 \pm 5\%$ of the KTPB decomposed from a dose equivalent to two years of storage (Ref. 3). Further experiments have been completed at SRL and the University of Florida which have more accurately measured the rate of decomposition and which have given the overall product distribution. Based on the most recent data, $15 \pm 2\%$ of the stored KTPB is expected to decompose during two years of storage.

The decrease in KTPB after exposure to radiation is shown in Figure 1. This was measured at SRL on a 10 wt % KTPB slurry with a low dissolved salt concentration, simulating the washed precipitate. The nominal composition of the slurry is listed in Table I. The loss of KTPB is approximately linear with dose, similar to the behavior observed at the University of Florida (see Appendix A, Figure 7). The G-values for the loss of KTPB are given in Table II. There does not appear to be any significant trend due to dose rate. The average G-value ($0.13 \pm .02$ molecules/100eV) corresponds to $7.3 \pm 1.1\%$ decomposition of the KTPB per year of tank farm storage.

A lower limit on the rate of KTPB decomposition can be calculated from measurements of cesium release from the precipitate made in the full scale in-tank demonstration. That precipitate has been stored in Tank 48 for over three years, and, as it decomposes, the cesium-137 is released to the supernate. As long as there is excess sodium tetraphenylborate, the free cesium and potassium will be reprecipitated. When the excess sodium tetraphenylborate is all consumed, the cesium level in the supernate should increase at a rate related to the overall decomposition rate. However, since some of the cesium may be trapped within crystals, the rate of decomposition measured in this way should be less than the rate measured in the small scale experiments. The cesium levels measured in Tank 49 are given in Table III. The rate of accumulation of cesium has been constant over the time covered by the last four samples. This implies that the excess NaTPB has been consumed and, also, that the KTPB is decomposing at a constant rate. The rate of increase in cesium corresponds to a decomposition rate of 0.8% per year (see Appendix D). When corrected for the low cesium concentration in Tank 48, the decomposition rate would be 2.0% per year (for "average" slurry). This is only 27% of the decomposition predicted by the small scale experiments and is consistent based on the argument given above.

Decomposition Products

The major products from radiolytic decomposition of KTPB are benzene, phenol, biphenyl, and phenylboric acid (phenylboronic acid, $C_6H_5B(OH)_2$). The amounts of these compounds found at different radiation doses are shown in Figures 2 to 5. These results, obtained at SRL, reflect the total production of the compounds and do not distinguish "free" and "trapped" species.

The total amount of benzene produced in the SRL experiments is shown in Figure 2. From this data, the production of benzene appears to be linear with total dose and $G_{\text{benzene}} = 0.38$. These results contrast with the non-linear behavior observed by the University of Florida (Appendix A, Figure 5) and will be discussed further below.

Phenol is the second most abundant product from the decomposition of tetraphenylborate. At low doses, its production is linear with radiation dose (see Figure 3). At a dose equivalent to two years storage, the phenol yield is approximated by $G = 0.16$. However,

after two years, the level of phenol stops increasing. It may be that the phenol concentration has reached a steady state level, where its rate of formation is equal to its rate of reaction to form other products. In earlier work, the University of Florida noted the production of phenol when homogeneous solutions of NaTPB were irradiated (Ref. 2), but due to experimental complications, they were not able to measure phenol in their latest report (Appendix A).

The formation of biphenyl is similar to that of phenol (see Figure 4). Initially, it is almost linear with radiation dose, but then rapidly slows after about 1.5 years. At two years, the product yield is given by $G = 0.066$. Similar behavior was observed by the University of Florida (see Appendix A, Figure 6). The University of Florida experiments also distinguished between "free" and "trapped" biphenyl. The amount of "free" biphenyl was much lower than "trapped," and decreased slightly with increasing dose (see Appendix A, Figure 4). When the two contributions are added together, the behavior is very similar to that found at SRL, although about 35% less biphenyl was found (two year product yield of $G = 0.044$).

The major boron-containing product observed from the decomposition was phenylboric acid. Changes in its concentration with increasing radiation dose are shown in Figure 5. Its behavior is similar to phenol and biphenyl, accumulating rapidly at first, then becoming almost constant after a dose equivalent to two years of storage. The product yield at two years is given by $G = 0.090$. This compound was not measured in the experiments at the University of Florida.

Nitrobenzene was identified and quantified in the experiments at the University of Florida. All of the nitrobenzene was found in the aqueous phase ("free"). This is expected since the nitrate and nitrite ions in solution are required for its formation. The yield of this product was much lower than for the compounds mentioned above, although the general behavior was similar. The nitrobenzene increased until a radiation dose equivalent to two years of storage was reached, whereupon it began to decline slowly (see Appendix A, Figure 3). The yield of nitrobenzene was about 1% of that observed for phenylboric acid, with a product yield at two years of $G = 0.0013$. No attempt was made to detect nitrobenzene in the SRL work.

The three isomeric terphenyls were also detected in the University of Florida work but they were not quantified (see Appendix A). The yields were very low with estimated G-values less than 0.001.

Composition of Precipitate Slurry after Two Years of Storage

The expected composition of a slurry stored for two years may be calculated from the SRL data. A material balance of the products after a two year equivalent radiation dose is shown in Table IV. The accuracy of the balance is shown by summing the G-values:

$$\begin{aligned}
 4 \text{ } G_{(-\text{KTPB})} &= G_{\text{benzene}} + G_{\text{phenol}} + 2 \text{ } G_{\text{biphenyl}} + G_{\text{PBA}} \\
 4 \text{ } (0.16) &= (0.29) + (0.16) + 2 \text{ } (0.066) + (0.09) \\
 0.64 &\approx 0.67
 \end{aligned}$$

The KTPB and benzene G-values are calculated from the two year dose data only and are slightly different than the average data for all experiments.

The corresponding change in the slurry composition for 15% decomposition in two years is shown in Table V. The equivalent balanced chemical reaction is shown below:

Several assumptions have been used to obtain the reaction equation above. First, the products are written as their ionized forms at pH = 11 (Ref. 11). The pH changes in the system are described below, but the net effect is that radiolysis consumes hydroxide. Boric acid was assumed to be the final product for all of the boron not accounted for by the phenylboric acid and undecomposed KTPB.

The amount of hydrogen gas shown is simply that required to balance the equation. Experiments at the University of Florida (Ref. 2) have indicated that more hydrogen than this is actually formed. Of the decomposition products identified, four (phenol, biphenyl, terphenyl, and nitrobenzene) are oxidized relative to the tetraphenylborate ion. The latter two occur in such small amounts that they do not figure significantly in the balanced reaction. It is possible that hydrogen peroxide, an oxidation product from the radiolysis of water, may also be present (it was not analyzed for). There are several reduction reactions occurring in the system. In addition to the formation of hydrogen gas, it is known that nitrate ion is reduced to nitrite, and it is likely that dissolved oxygen gas is reduced to water, hydrogen peroxide, or phenol.

The composition given in Table V assumes that the volatile compounds are not lost in the storage tank ventilation system. The benzene shown is the sum of all that is formed, both "free" and "trapped," and the actual amount which accumulates in the storage tank will depend on how much evaporates over two years. Significant amounts of biphenyl, nitrobenzene, and phenol could also be lost by vaporization (Ref. 12). For phenol, this will depend greatly on the pH of the slurry, since at pH's above its pK_a it will be ionized and will not be volatile.

It should be noted that the loss of KTPB is linear with dose for at least 5 years of storage (Figure 1), but the formation of the major decomposition products is only approximately linear for two years, and is quite non-linear after two years. This implies that other products, as yet unidentified, are being made after two years.

pH Changes During Radiolysis

Radiolysis of KTPB slurries produces acidic decomposition products which neutralize the sodium hydroxide and cause a decrease in pH. In tests where carbon dioxide adsorption from the atmosphere was negligible, approximately 0.01 mole of caustic was consumed per 1.2×10^6 rads of gamma radiation dose (this corresponds to one month of storage under planned tank farm operations for a slurry of average composition). The changes in pH are shown in Figure 6. One curve is for a 10 wt % KTPB slurry in dilute salt solution containing approximately 0.075 molar NaOH initially. The second curve is for the dilute salt solution only. The pH of the salt solution changed very little during the irradiation, indicating no significant adsorption of carbon dioxide occurred. However, a large decrease occurred in the pH of the KTPB slurry. The pH of 9.5 at the end of the experiment is consistent with the formation of a solution buffered by phenol, phenylboric acid, and boric acid. In a separate experiment in which air (containing carbon dioxide) was circulated over the slurry, the pH dropped even faster than in the experiment shown in Figure 6.

The rate of hydroxide depletion can be calculated from the slope of the early portion of the curve for the KTPB slurry. This corresponds to approximately 0.01 molar/month. This is significantly faster than was calculated based on the decomposition equations given above. For 15% decomposition in two years, the rate of hydroxide depletion should be about 0.0025 molar/month due to the formation of acidic decomposition products. The reason for the much higher observed rate is not known. There may be a slight contribution from carbon dioxide adsorption (see Figure 6), but it does not account for all of the difference.

Previously, it had been reported that radiolysis of KTPB slurries caused the pH of the solution to increase (Ref. 2). In those experiments, the original slurry was in water with no dissolved salts or sodium hydroxide. The initial pH was near neutral. In that case, the production of phenol, phenylboric acid, and boric acid drove the pH up, producing the same buffer solution, but approaching the equilibrium from the acidic side.

Estimates of Benzene Production

Table VI lists the G-values found for benzene yields from different experimental sources. A considerable range has been observed, depending on the slurry composition and total radiation dose. However, the most recent G-values, measured at high doses and with dissolved salts present, only vary between 0.16 and 0.38. This may be compared to the maximum possible benzene production rate. The rate of loss of KTPB sets an upper limit on the amount of benzene

that can be formed. If $G_{(-KTPB)}$ is 0.13 (Table II), then G_{benzene} must be ≤ 0.52 (total of trapped and free benzene).

The variations in G_{benzene} within the range 0.38-0.16 agree qualitatively with the assumption that some of the benzene is "trapped" and some is "free." The largest value, $G = 0.38$, was obtained in the SRL experiment that measured the combined "trapped" and "free" benzene. The low G -value of 0.17 from the Tank 48 exhaust emissions is a measure of "free" benzene only. The University of Florida results for "trapped" benzene, which vary between 0.31-0.16 depending on total dose, are compatible with the other data within the experimental error. The earlier University of Florida results with G -values of 0.7-7.5 exceed the upper limit set by the loss of KTPB. These large rates were all measured at very low radiation doses and are not applicable to predictions of benzene production for long storage times.

Based on the most recent data from all three sources, the best G -values for predicting benzene production for long storage times are:

$$\begin{aligned} G_{\text{benzene}} (\text{total}) &= 0.4 \pm .1 \\ G_{\text{benzene}} (\text{free}) &= 0.2 \pm .1 \\ G_{\text{benzene}} (\text{trapped}) &= 0.2 \pm .1 \end{aligned}$$

There appears to be a significant effect on "free" benzene production due to the presence of dissolved salts. Compare the following results: $G = 0.71$ with no dissolved salts present (U. of F., Ref. 2), $G = 0.17$ for low levels of dissolved salt (Tank 48), and $G = 0$ with high dissolved salt levels (U. of F., Ref. 3). Although a strict comparison cannot be made from this data, it does suggest that higher salt concentrations reduce the amount of "free" benzene and this aspect should be studied in more detail. This is not a completely surprising trend, since nitrate ion, the major soluble anion, acts as a radical scavenger in aqueous systems (Ref. 13). The high "free" benzene yields observed with small doses ($G = 0.7$) may be applicable to the precipitation and filtration steps of the in-tank process. The current plans call for three consecutive batch precipitations prior to the washing step and the time required is 45 days. The experimental results imply that a higher benzene production rate should be observed with the fresh slurry during the initial exposure to radiation (ignoring any effect by dissolved salts). This was not corroborated by the full-scale in-tank demonstration. Prior to the washing step, less than 4 ppb benzene were found in the Tank 48 ventilation exhaust. Even with the low radioactivity level in that precipitate, benzene concentrations in the ppm range should have been observed if the G -value was 0.7. However, if dissolved salts greatly reduce this G -value, this apparent contradiction may not actually exist.

The amount of "trapped" benzene which will be released during slurry washing can be estimated from the data given in Reference 3 (see Figure 1 in that report), or from the data listed in Table VI ($G_{\text{initial}} = 6.7$, $G_{\text{half-year}} = 1.1$, and $G_{2\text{-year}} = 0.6$). The production

yield varies considerably with dose at doses equivalent to half a year of storage or less. An average over the first 45 days (equivalent storage) cannot be determined from the data at hand, but must lie between 1.6 and 6.7. The results from the in-tank demonstration suggest a G-value of 3.4, but this is a highly speculative number since only a very approximate estimate of the total benzene release can be made. In addition, the low dose received by this material may produce an overestimate of the G-value when compared to the larger doses the normal operations will involve.

Further Work

Several areas of interest still need further research. Some of these items are listed below.

- Radiolysis effects on nitrate and nitrite concentrations. A clear understanding of this process is needed to assure the storage tank is adequately protected against corrosion.
- Radiolysis of unwashed slurries for short storage times. The effect of high concentrations of nitrate and nitrite ions needs to be more closely examined since it may affect the amount of "free" benzene produced. This is most important in estimating the amount of benzene which will go to saltstone.
- Radiolysis of undissolved NaTPB. More data at short doses in the presence of high salt concentrations is needed to estimate "trapped" benzene. The results are applicable to benzene emissions during precipitate washing in Tank 48.
- Effect of nitrate and nitrite ion on product distribution. Most of the data discussed above were obtained at low salt concentrations. If nitrite ion concentration is increased to prevent tank corrosion, it could affect the product distribution from radiolytic decomposition. This would be important to the acid hydrolysis process in the salt cell of the DWPF.

Quality Assurance

Quality assurance of the new data reported here is covered by DPSTQA-85-2-25, Quality Assurance Review: Decontamination of Soluble Defense Waste by In-Tank Precipitation Processing." The data are recorded in Laboratory Notebook DPSTN-4274 and DPSTN-4443.

Experimental

For the radiolytic decomposition studies, 0.2 to 0.3 gram of 10 wt % KTPB slurry was sealed in a 9 ml glass vial with aluminum lined septum cap. Care was taken to avoid contacting the aluminum with the caustic slurry. The vials were irradiated in a Co-60 gamma

source with a dose rate of 3×10^6 rads/h. Following irradiation, the samples were dissolved by injecting 1 ml of propylene carbonate into the vial. Portions were then diluted in acetonitrile and injected into a Varian HPLC. The decomposition products were separated by reverse phase liquid chromatography using a water/acetonitrile elution system. The large tetraphenylborate peak was separated from the other product peaks by ion pairing it with 0.005 M tetrabutylammonium phosphate in the aqueous phase.

The 10 wt % precipitate slurry was prepared from reagent grade chemicals except for the sodium tetraphenylborate. The NaTPB was obtained from material left over from the 1983 full scale in-tank demonstration and is a mixture of products from Boulder Scientific, Raylo Chemicals, and AFF, Inc. A significant blank correction had to be made only for phenylboric acid.

For the pH studies, 12 to 15 grams of slurry were placed in a glass vial and capped. After irradiation, the samples were filtered in air and the pH of the filtrate measured immediately. It was not possible to obtain a steady pH reading in the presence of the KTPB precipitated, probably due to plugging of the electrode's ceramic junction.

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9. D. D. Walker and B. A. Hamm, "Sample Analyses from the Full Scale In-Tank Demonstration of the Precipitation Process," DPST-83-695, July 21, 1983.
10. Personal communication with D. T. Hobbs, results recorded in DPSTN-4379.
11. The pKa's for the decomposition products are: phenol, 9.9; phenylboric acid, 8.7 and 8.9; boric acid, 9.1, 12.7, and 13.8. See the CRC Handbook of Chemistry and Physics, 61st Ed., 1981, R. C. Weast, Ed., CRC Press, Inc., Boca Raton, Fla.
12. The vapor pressures of the more volatile compounds are: benzene, 100 mm at 26°C; nitrobenzene, 1 mm at 44°C; phenol, 1 mm at 40°C; biphenyl, 1 mm at 71°C. See the CRC Handbook of Chemistry and Physics, 61st Ed., 1981, R. C. Weast, Ed., CRC Press, Inc., Boca Raton, Fla.
13. N. E. Bibler, *J. Phys. Chem.*, **78**, 211 (1974).

TABLE I
Composition of 10 Weight % KTPB Slurry

<u>Component</u>		<u>Concentration</u>
Solids:	KTPB	9 ± 1 wt %
Solution:	Na ⁺	0.18 molar
	NO ₂ ⁻	0.026 molar
	NO ₃ ⁻	0.084 molar
	OH ⁻	0.072 molar

TABLE II
Rate of KTPB Decomposition

<u>Dose Rate (rads/hr)</u> ¹	<u>G(-KTPB) (molecules/100 eV)</u>
3.4x10 ⁶ (SRL)	0.12 ± .02
3.0x10 ⁵ (U of F) ²	0.12
1.0x10 ⁵ (U of F) ²	0.15

¹ The dose rate expected in the storage tank for average composition slurry is 1.7×10^4 rads/hr.

² See Appendix B for University of Florida data.

TABLE III
Cesium-137 Concentrations in Tank 48

<u>Date of sample</u>	<u>Cs-137</u> <u>(μCi/mL)</u>
4/20/83	0.2 ¹
11/11/84	12.
12/12/84	14.
1/1/86	22.2
5/4/86	25.2

1 Reference 9.
2 Reference 10.

TABLE IV
Material Balance for Two Year Equivalent Radiation Dose

<u>Component</u>	<u>Yield</u> <u>(μmoles/mL)</u>	<u>G-value</u> <u>(molecules/100 eV)</u>
benzene	87. $\pm$ 18.	0.29
phenol	47. $\pm$ 4.	0.16
biphenyl	20. $\pm$ 2.	0.066
phenylboric acid	27. $\pm$ 2.	0.090
KTPB (lost)	47. $\pm$ 2.	0.16

TABLE V
Change in Composition of 10 Wt % Precipitate Slurry
due to Radiolytic Decomposition

Component	Concentration (g/L)	
	<u>Fresh Slurry*</u>	<u>After 2 Years Storage</u>
KTPB	90.5	76.9
NH ₄ TPB	4.24	3.39
CsTPB	0.94	0.80
NaTi ₂ O ₅ H	4.21	4.21
(C ₆ H ₅) ₂ Hg	1.06	1.06
Benzene	--	5.4
Biphenyl	--	2.5
Phenol	--	3.6
Nitrobenzene	--	0.027
Phenylboric acid	--	2.6
Boric acid	--	1.2

* See Reference 8.

TABLE VI
Summary of G-Values for Benzene Production

<u>Source</u>	<u>Product</u>	<u>G</u>	<u>Comments</u>
SRL ¹	Total	0.38	washed precipitate, 10 wt % linear with dose to 5 yr
Tank 48 ²	Free	0.17	low dose rate, washed precipitate approx. 0.8 yr dose equivalent
UF ³	Trapped	0.31	washed precipitate, 6 wt % initial production rate
	Trapped	0.16	after 2-yr dose
UF ⁴	Free	0.71	low total dose, no dissolved salts 10 wt % KTPB
	Trapped	7.07	
	Free	0.67	25 wt % KTPB
	Trapped	7.53	
UF ⁵	Free	--	high soluble salts, high dose, 10 wt%
	Trapped	6.7	no increase in benzene with dose initial production rate
	Trapped	1.1	after half-year dose
	Trapped	0.6	after 2-yr dose

-
- ¹ This work.
² Appendix C.
³ Appendix A, p.11.
⁴ Reference 2.
⁵ Reference 3.

FIGURE 1
Loss of KTPB Due to Radiolysis

FIGURE 2
Benzene Formation in 10 Weight % KTPB Slurry

FIGURE 3
Phenol Formation in 10 Weight % KTPB Slurry

FIGURE 4
Biphenyl Formation in 10 Weight % KTPB Slurry

FIGURE 5
Phenylboric Acid (PBA) Formation in 10 Weight % KTPB Slurry

FIGURE 6
pH Changes During Radiolysis of a 10 Weight % KTPB Slurry

Appendix A
Report from University of Florida
Dated November 4, 1985

Report A

November 4, 1985

THE RADIOLYSIS OF WASHED TETRAPHENYLBORATE SLURRY CONTAINING
 Na^+ , OH^- , NO_2^- , and NO_3^- IONS

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In an earlier report (1) submitted February 1, 1985, and in the manuscript of the paper (2) presented at the 189th ACS National Meeting at Miami, Florida, April 28 - May 3, 1985, the results of the radiolysis of unwashed soluble and insoluble tetraphenylborate precipitate in the presence of NaOH , NaNO_2 , and NaNO_3 salt solution were submitted. The concentration of the ions were as follows Na^+ , 5.6M; NO_3^- , 3.3M; NO_2^- , 1.0M; and OH^- , 1.3M. The object of the current project was to identify qualitatively and quantitatively the products that are formed during the radiolysis of washed tetraphenylborate precipitate containing Na^+ , OH^- , NO_2^- , and NO_3^- ions. The washed slurry was sent by Dr. D.D. Walker from Savannah River Plant. The amount of tetraphenylborate precipitate left after irradiation was measured in both unwashed and washed tetraphenylborate precipitates. Experiments are in progress to study the effect of dose rate on the product yields in the radiolysis of washed tetraphenylborate slurries.

An ISCO high pressure liquid chromatograph with a V⁴ variable wavelength absorbance detector was used to identify the radiolysis products. Three new products that were previously unidentified have been identified in the radiolysis of unwashed tetraphenylborate precipitates in the presence of NaOH, NaNO₂, and NaNO₃ salt solution. These products are being separated using column chromatography and will be confirmed using NMR and mass-spectrometry.

EXPERIMENTAL

Radiolysis experiments were carried out on samples which were sent from Savannah River Plant by Dr. D.D. Walker. Samples consisting of 1 ml air saturated slurries of nominal 10 wt% (actually 6 wt% according to our measurements) washed tetraphenylborate precipitate containing Na⁺, OH⁻, NO₂⁻, and NO₃⁻ ions were taken in a 13 mm ground glass stoppered test tube using a hypodermic syringe. These samples were irradiated in a Co-60 gamma source for different time periods up to 60 days corresponding to a dose of about 450 mega rads. The calculated dose rate (higher) was 1.90×10^{19} eV ml⁻¹ hr⁻¹ in Fricke solution, on August 1, 1985. This dose rate will be referred to as the "Higher" dose rate value in contrast to other experiments conducted at a "Lower" dose rate, to be described later. The calculated dose rate (lower) was 6.5×10^{18} eV ml⁻¹ hr⁻¹, on August 1, 1985.

After irradiation, 1 ml of water was added to the radiolysis mixture. The mixture was then shaken with 1ml of cyclohexane, and 10 microliters of the cyclohexane extraction was injected into the ISCO high pressure liquid chromatograph. The aromatic products were separated using a Whatman ODS-3 (Octadecylsilane) column (25 cm x 4.6 mm i.d.). A guard column was used, the material of which was changed after every two analyses. A mixture of 75% acetonitrile in water was used as the mobile phase, the flow rate of which was adjusted to 1.1 ml/min. The ultraviolet absorbance detector was set to 254 nm; the output of the detector was fed to a 10 mV potentiometric recorder, with a chart speed of 2 cm/min.

The aqueous layer and the cyclohexane layer were decanted from the solid tetraphenylborate and the solid was dissolved in 5 ml of acetonitrile so as to release the trapped products into the solution. Ten microliters of this solution was then injected into the high pressure liquid chromatograph for analysis of the trapped products.

The tetraphenylborate peak that occurs in the experiment described in the previous paragraph is off scale. In order to analysis the amount of solid tetraphenylborate precipitate left after irradiation, 200 microliters of the dissolved tetraphenylborate solution was taken in a test tube and diluted with 1 ml of acetonitrile. Ten microliter of the diluted solution was then injected in the HPLC for analysis of the residual teraphenylborate.

Effect of Gamma Dose Rate

Experiments are in progress to study the effect of dose rate on the the yield of the products in the radiolysis of washed tetraphenylborate slurries. Samples consisting of 1 ml of the Fricke dosimeter solution were irradiated in 13 mm ground glass stoppered test tubes. An aluminum sample holder was used to assure reproducible positioning of the test tubes. The sample holder consists of a central 11/16 inch (1.7 cm) diameter hole for the gamma source rod surrounded by two concentric rings with six sample hole positions per ring. The inner ring of the sample positions is approximately on a 1¹/₄ inch (3.1 cm) diameter circle, while the outer holes are on a 2¹/₂ inch (6.4 cm) diameter circle. The sample holes accommodate 13 mm diameter (O.D.) test tubes (preferably -0.2 mm minimum size, +0.0 mm maximum size). Most of the experiments were done using the samples in the inner ring. To study the effect of dose rate the samples were also irradiated in the outer position of the sample holder. The dose rate at the outer position is one third the dose rate at the inner position. Irradiation of the Fricke solution was carried out in the absence and presence of NaCl, used to diagnose possible organic contamination. Optical densities were measured on a Beckman Spectrophotometer at a wavelength of 305 millmicrons.

Samples consisting of 1 ml of Fricke dosimeter solution were irradiated in 13 mm test tubes with ground glass stoppers. The samples were kept in the outer positions of the sample holder.

Figures 1 and 2 show the plots of the optical densities versus irradiation time in the presence and absence of NaCl. The calculated dose rate at the inner (higher dose rate) and outer (lower dose rate) positions of the sample holder were as follows, 1.9×10^{19} eV ml⁻¹ hr⁻¹ and 6.5×10^{18} eV ml⁻¹ hr⁻¹, respectively.

Radiolysis experiments at a lower dose rate were carried out in the same fashion as the radiolysis experiments at a higher dose rate, as explained earlier in the experimental section.

RESULTS

Experiments were carried out to study the effect of long term gamma irradiation on the 6 wt% washed slurries. Irradiation was carried out at a higher dose rate for a period of approximately 60 days, equivalent to a maximum dose of about 450 mega rads which corresponds to a storage period of the tetraphenylborate precipitate at the Savannah River Plant for 3.1 years.

Figures 3 and 4 show the yields of nitrobenzene and biphenyl analyzed from the cyclohexane extraction of the aqueous layer as a function of irradiation time at the higher and lower dose rate. At the higher dose rate the yield of nitrobenzene reaches a maximum value of 4.0×10^{-7} moles/ml at about 40 days and then drops off. Irradiation time of 40 days at a higher dose rate corresponds to a dose of about 300 mega rads. At the lower dose

rate the yield of nitrobenzene is linear with absorbed dose up to at least 100 mega rads. The yield of nitrobenzene at the lower dose rate is greater than that at the higher dose rate. The yield of biphenyl drops off as the irradiation time increases, and as seen from figure 4 the yield of biphenyl at the lower dose rate is much higher than the yield at higher dose rate. Experiments corresponding to higher (total) doses at the lower dose rate are in progress.

The remaining solid was then dissolved in 5 ml acetonitrile and analyzed. Benzene and biphenyl were the major products. Figures 5 and 6 show plots of the yields of trapped benzene and trapped biphenyl as a function of irradiation time, when the solid is dissolved in acetonitrile. Initially, at the higher dose rate, the yield of trapped benzene increases with irradiation time, reaches a maximum yield of 50 micromoles/ml at 30 days and then falls off. Irradiation time of 30 days corresponding to a dose of about 220 mega rads. At the lower dose rate the yield of benzene is linear with dose up to at least 100 mega rads. At the higher dose rate the yield of trapped biphenyl increases linearly with irradiation time up to about 40 days corresponding to a dose of 300 mega rads and then remains essentially constant with a maximum yield of 12.1 micromoles/ml. At the lower dose rate the yield of trapped biphenyl is almost linear with dose up to at least 60 mega rads. Table 1 shows the G-values of the products formed in the radiolysis of 6 wt % tetraphenylborate at the two values of the dose rate.

Figure 7 shows the yield of residual tetraphenylborate versus irradiation time. The amount of tetraphenylborate irradiated in each of the radiolysis experiments was 1.4×10^{-4} moles/ml. At a higher dose rate the amount of residual tetraphenylborate left after 60 days, corresponding to a total dose of about 450 mega rads was 0.90×10^{-4} moles/ml, indicating that 38% of the solid tetraphenylborate was converted into various products. At a lower dose rate the amount of residual tetraphenylborate left after 40 days corresponding to a total dose of about 100 mega rad was 1.30×10^{-4} moles/ml, indicating that 11% of the solid tetraphenylborate was converted into various products. Table 2 compares the amount of tetraphenylborate converted into products using higher and lower dose rates. Table 3 shows a comparison of the G-values of the products (immediate release and trapped in crystal) in the radiolysis of unwashed and washed tetraphenylborate slurries at high and low dose rates.

Earlier results had much higher OH^- , NO_3^- , and NO_2^- concentrations therefore the yields of the products in the earlier experiments and the present experiments are considerably different. Also, the unwashed precipitate that was irradiated was 10 wt% as compared to the 6 wt% washed precipitate that was irradiated in the present experiments. Solutions resulting from long term irradiation of the unwashed precipitate had a much darker yellow color when dissolved in acetonitrile indicative of larger yields of nitrate or nitrite species. Also, product yields at the lower dose rate are somewhat different than the

product yields at the higher dose rate except for the total destruction of KTPB at both the dose rates are the same.

The three new minor products, previously unidentified are o-terphenyl, m-terphenyl, and p-terphenyl. G-values are estimated as not greater than 0.001.

Table 1

G-Value of Products (Immediate Release) in the Radiolysis
of 6 wt % Tetraphenylborate Slurries.

Product	Higher Dose Rate	Lower Dose Rate
Nitrobenzene	$G_{\text{initial}} = 0.0019$	$G = 0.0064$
Biphenyl	$G_{\text{initial}} = >0.033$	$G = 0.060$

G-Value of Products (Trapped in Crystal) in the Radiolysis
of 6 wt % Tetraphenylborate Slurries.

Product	Higher Dose Rate	Lower Dose Rate
Benzene	$G_{\text{initial}} = 0.31$	$G = 0.47$
Biphenyl	$G_{\text{initial}} = 0.044$	$G_{\text{initial}} = 0.079$

Table 2

Comparison of the Amount of Tetraphenylborate Converted into
Products in the Radiolysis of 6 wt % Tetraphenylborate
Slurries Using Higher and Lower Dose Rates.

Dose Rate	Total Dose Mega Rads	% Conversion
Higher	~450	38
Lower	~100	11

Table 3

Comparison of the G-Values of the Products (Immediate Release and Trapped in Crystal) in the Radiolysis of Unwashed and Washed Tetraphenylborate Slurries at High and Low Dose Rates.

Product	Unwashed Precipitate Higher Ion Concentration (10 wt% Solid)			Washed Precipitate Lower Ion Concentration (6 wt% Solid)			
	High Dose Rate			High Dose Rate		Low Dose Rate	
	(a) G _{Initial} 1 hour	(b) G _{Initial} 10 days	(b) G _(40 days)	(b) G _{Initial} 10 days	(b) G _(40 days)	(c) G _{Initial} 10 days	(c) G _(40 days)
Nitrobenzene (d)	0.40	>0.028	0.0021	0.0019	0.0013	0.0064	0.0064
Biphenyl (d)	1.6	0.20	0.20	>0.033	0.0050	>0.27	0.060
Benzene (e)	6.7	1.08	0.60	0.31	0.16	0.47	0.47
Biphenyl (e)	0.44	0.12	0.060	0.044	0.038	0.079	0.068

- (a) Short term irradiation. Maximum irradiation time 8 hours corresponding to a maximum dose of 2.7 megarads.
- (b) Long term irradiation. Maximum irradiation time 60 days corresponding to 450 megarads at higher dose rate.
- (c) Long term irradiation. Maximum irradiation time 40 days corresponding to a maximum dose of 100 megarads at lower dose rate.
- (d) Immediate release
- (e) Trapped in crystal

REFERENCES

- 1) A.K. Gupta and R.J. Hanrahan, "The Radiolysis of Tetraphenylborate in the Presence of Alkaline NaOH, NaNO_2 , and NaNO_3 Salt Solution". Report 2, February 1, 1985.
- 2) A.K. Gupta, R.J. Hanrahan, and D.D. Walker, "Use of Co-60 Gamma Irradiation to Simulate the Decomposition of Tetraphenylborate Precipitates from High Level Radioactive Waste". Report 3, Presented at the 189th ACS National Meeting, Miami, Florida, April 28 - May 3, 1985.

Fig. 1 Dosimetry: Optical density versus irradiation time (1 ml solution). Outer position of the Co-60 irradiator sample holder.

Fig. 2 Dosimetry: Optical density versus irradiation time (1 ml solution). Outer position of the Co-60 irradiator sample holder.

Fig. 3 Production of nitrobenzene versus radiolysis time in the radiolysis of tetraphenylborate. Nitrobenzene extracted from aqueous layer into cyclohexane for analysis.

Fig. 4 Production of biphenyl versus irradiation time in the radiolysis of tetraphenylborate. Biphenyl extracted from aqueous layer into cyclohexane for analysis.

Fig. 5 Production of benzene versus irradiation time in radiolysis of tetraphenylborate. Benzene was analyzed after dissolving the solid in 5 ml acetonitrile.

Fig. 6 Production of biphenyl versus irradiation time in the radiolysis of tetraphenylborate. Biphenyl was analyzed after dissolving the solid in 5 ml acetonitrile.

Fig. 7 Residual tetraphenylborate versus irradiation time in the radiolysis of tetraphenylborate. The tetraphenylborate was analyzed after dissolving the solid in actonitrile.

Appendix B

Calculation of Dose Rate to Stored KTPB Precipitate Slurry

The following assumptions are made in the calculation of the radiation dose to the stored slurry:

- The radiation dose can be approximated by considering only the Cs-137 in the precipitate. The Sr-90 is ignored since it contributes very little to the total number of curies in the slurry.
- All of the decay radiation is absorbed by the precipitate. This ignores any radiation energy deposited in the walls or airspace of the storage. For a large diameter tank filled several feet deep with slurry, this is a good approximation.
- The Cs-137 concentration is 36 Curies/gallon of 10 weight % slurry. This estimate is obtained from the current material balance for the DWPF process (Ref. 8).
- The decay of Cs-137 and Ba-137 produces 4.84 watts per kilocurie.
- A 10 weight % slurry has a density of 1.0 g/mL.

The method of calculation is:

$$\begin{aligned}
 \text{Dose (rads)} &= \left(\frac{36. \text{ Ci Cs-137}}{\text{gal}} \right) \times \left(\frac{4.84 \text{ watts}}{10^3 \text{ Ci}} \right) \times \left(\frac{1 \text{ eV/sec}}{1.602 \times 10^{-19} \text{ watts}} \right) \times \\
 &\quad \left(\frac{1 \text{ rad}}{6.24 \times 10^{13} \text{ eV/g}} \right) \times \left(\frac{1 \text{ mL}}{1 \text{ g}} \right) \times \left(\frac{1 \text{ gal}}{3,785.4 \text{ mL}} \right) \times \\
 &\quad \left(\frac{3.1536 \times 10^7 \text{ sec}}{\text{yr}} \right) \\
 &= 1.45 \times 10^8 \text{ rads/yr}
 \end{aligned}$$

Appendix C Calculation of Dose Rate in Tank 48

A major uncertainty in the interpretation of data from the Tank 48 demonstration has been the calculation of the dose rate and how it compares to the CPES "average" slurry composition. In a previous report, a G-value was calculated for the benzene production in that tank using 130,000 Ci of Cs-137 and 10,000 pounds of KTPB. An error in the cesium concentration in the Tank 24 salt solution used for the Tank 48 demonstration has recently been found, and a higher estimate of the Tank 48 dose rate has been calculated.

The previous estimate in the cesium in Tank 48 was based on the volume of salt solution transferred from Tank 24 and the Cs-137 concentration in the liquid. The volume was 427,000 gallons, measured to ± 300 gallons using reel tapes in Tank 24 (Ref. 7). The concentration of cesium in the salt solution was obtained by averaging the Cs-137 found in samples 1AP and 1BP, as reported in Reference 9. These two samples were taken from Tank 24 or the transfer line during the actual transfer to Tank 48. However, an error in one of the reported numbers has been found after a recheck of the original analyses, recorded in "In Tank Demonstration, Data Book #3" and maintained by B. A. Hamm. The originally reported and the new values are listed below:

Sample	Cesium-137 Concentration (nCi/mL)	
	<u>Reported in Ref. 9</u>	<u>Corrected value</u>
1AP	$1.3 \pm .1 \times 10^5$	$1.3 \pm .1 \times 10^5$
1BP	$3.5 \pm .3 \times 10^4$	$1.41 \pm .03 \times 10^5$

The number of curies of Cs-137 in Tank 48 is obtained by the following calculation:

$$\begin{aligned} \text{Curies of Cs-137} &= (427,000 \text{ gal}) \times \frac{(3785.4 \text{ mL})}{\text{gal}} \times \frac{(1.35 \times 10^{-4} \text{ Ci})}{\text{mL}} \\ &= 2.2 \times 10^5 \text{ Curies } (\pm 0.1 \times 10^5) \end{aligned}$$

The amount of Cs-137 removed from Tank 48 in the decontaminated filtrate and wash water can also be calculated from information in References 7 and 9. However, this is a negligably small portion, amounting to only 10 Ci.

The radiation dose to the slurry, assuming no energy losses to the walls or airspace, is given by:

$$\begin{aligned} \text{Dose rate} &= (2.2 \times 10^5 \text{ Ci of Cs-137}) \times \frac{(4.84 \text{ watts})}{\text{kCi of Cs-137}} \times \frac{(1 \text{ eV/sec})}{1.6 \times 10^{-19} \text{ watts}} \\ &= 6.7 \times 10^{21} \text{ eV/sec} \end{aligned}$$

There are currently 62,000 gallons of slurry stored in Tank 48. The configuration of the slurry is approximately a disk 85 feet in diameter and 17.7 inches thick. Calculations of the fraction of energy lost to the walls and airspace using infinite cylinder and

infinite slab models indicate that more than 95% of the beta and gamma energy from the decay of Cs-137 is absorbed by the solution.

Using the dose rate above and the known evolution rate for benzene from Tank 48 (Ref. 3), it is possible to calculate a G-value for "free" benzene. This calculation was made in Reference 3 but using the incorrect cesium concentration. The correct calculation is:

(Note: 2.7 ± 1.0 ppm benzene by volume is 0.0027 mL/L)

$$\begin{aligned}
 G(\text{benzene}) &= \frac{(0.0027 \text{ mL}) \times (330 \text{ ft}^3) \times (1 \text{ mole}) \times (28.3 \text{ L})}{1000 \text{ mL} \quad \text{min} \quad 22.4 \text{ L} \quad \text{ft}^3} \times \\
 &\quad \frac{(6.02 \times 10^{23} \text{ molecules/mole}) \times (1 \text{ min})}{6.7 \times 10^{21} \text{ eV/sec} \quad 60 \text{ sec}} \\
 &= 0.17 \frac{\text{molecules}}{100 \text{ eV}} (\pm 0.06)
 \end{aligned}$$

An easy way to compare the Tank 48 results with those expected from full scale operations is to estimate the equivalent amount of 10 wt % KTPB slurry currently in the tank. This may be obtained from a material balance from the In-Tank Demonstration, given in Table C. At the end of the third wash, there was approximately 9500 lbs of NaTPB which had been converted to 9900 lbs of KTPB in Tank 48. There were also 2100 lbs of sodium titanate in the tank (Ref. 7). Assuming it was concentrated to 10 wt % solids, there would be 14,400 gallons of 10 wt % slurry and it would contain 15 Ci of Cs-137 per gallon (42% of the CPES "average" slurry). Although the original Tank 24 salt solution was 6X lower than "average" in Cs-137, it was also 2X lower in potassium, so the precipitate is only 2-3X lower in Cs-137.

This equivalent amount of slurry can be used to calculate the benzene release expected in full-scale operations (based on the Tank 48 data):

$$\begin{aligned}
 \text{Benzene release (ppm)} &= (2.7 \text{ ppm}) \times \frac{(1,050,000 \text{ gal}) \times (36 \text{ Ci/gal})}{14,400 \text{ gal} \quad 15 \text{ Ci/gal}} \\
 &= 470 \text{ ppm (at ventilation flowrate = 330 cfm)}
 \end{aligned}$$

The corresponding release for a full year is:

$$\begin{aligned}
 \text{Benzene release (tons)} &= \frac{(0.472 \text{ mL}) \times (1 \text{ mole}) \times (330 \text{ ft}^3) \times (0.0781 \text{ kg})}{1000 \text{ mL} \quad 22.4 \text{ L} \quad \text{min} \quad \text{mole}} \\
 &\quad \times \frac{(28.3 \text{ L}) \times (525,600 \text{ min}) \times (1 \text{ ton})}{\text{ft}^3 \quad \text{year} \quad 907 \text{ kg}} \\
 &= 8.9 \text{ tons/year } (\pm 3.1 \text{ tons})
 \end{aligned}$$

The error in this number is the same as the error in the G-value ($\pm 35\%$).

TABLE C
Sodium Tetrphenylborate Material Balance
for the Full Scale In-Tank Demonstration

	<u>Volume</u> <u>(gal)</u>	<u>NATPB</u> <u>Concentration</u> <u>(molar)</u>	<u>NATPB</u> <u>Amount</u> <u>(lbs)</u>
I. NaTPB into Tank 48			
a) Cold Chemical Run-in Tests			3,200
b) Full-scale Test			<u>32,800</u>
Total in			36,000
II. NaTPB removed from Tank 48			
a) Cold Chemical Filtrate (to Tank 49)	47,000	.014 (est)	1,900
b) Decontaminated Salt Solution (to Tank 50)	518,000	.0016	2,400
c) First Wash Filtrate (to Tank 49)	78,000	.067	14,900
d) Second Wash Filtrate (to Tank 49)	88,000	.025	6,300
e) Third Wash Filtrate (to Tank 49)	7,000	.0088	<u>200</u>
Total			25,700
III. NaTPB left in Tank 48			
a) Cold Chemical Precipitate (300# KNO ₃)			1,000
b) Potassium in Tank 24 Salt Solution	427,000	.007	8,500
c) Solution Remaining in Tank 48	53,000	.0084	<u>1,300</u>
Total			10,800
Total accounted for (sum of II and III):			36,500

Appendix D Calculation of Decomposition of KTPB

It is possible to calculate the extent of the decomposition of KTPB expected in two years of tank farm storage using the G(-KTPB)-values listed in Table II. This calculation requires the assumption that the loss of KTPB is not dependent on wt % KTPB but only on the amount of energy deposited in the sample. Evidence supporting this was given in Reference 2.

The % decomposition per year is given by:

$$\begin{aligned} \% \text{ Decomposition} &= \frac{\text{moles of KTPB lost (per mL)}}{\text{moles of KTPB initially (per mL)}} \\ &= \frac{(0.13 \text{ molecules}) \times (1.45 \times 10^8 \text{ rads}) \times (1 \text{ mole})}{100 \text{ eV} \quad \text{year} \quad 6.02 \times 10^{23} \text{ molecules}} \\ &\quad \times \frac{(6.24 \times 10^{13} \text{ eV/g}) \times (1 \text{ g}) \times (1 \text{ mL of slurry})}{1 \text{ rad} \quad \text{mL} \quad 0.000267 \text{ moles TPB-}} \times 100 \\ &= 7.3 \pm 1.1\% \text{ (per year)} \end{aligned}$$

The number of moles of tetraphenylborate per mL of 10 wt % slurry is obtained by adding together the cesium, potassium, and ammonium TPB given in the CPES material balance (Ref. 8). The estimate of the error is based on the error in the G-value.

A similar calculation can be made for the decomposition occurring in Tank 48. If one assumes that the rates of decomposition of potassium and cesium salts are equal, then the rate of accumulation of cesium in the Tank 48 supernate is equal to the decomposition rate. The calculation is:

$$\begin{aligned} \% \text{ Decomposition} &= \frac{\text{change in soluble Cs-137 curies}}{\text{total Cs-137 curies}} \\ &= \frac{(0.65 \text{ } \mu\text{Ci Cs-137}) \times (62,000 \text{ gal}) \times (12 \text{ months}) \times (3785.4 \text{ mL})}{\text{mL-month} \quad \text{year} \quad \text{gal}} \\ &\quad \times \left(\frac{1}{2.2 \times 10^5 \text{ Curies}} \right) \times 100 \\ &= 0.83\% \text{ (per year) for current Tank 48 slurry.} \end{aligned}$$

This may be corrected for the low cesium-137 concentration in Tank 48 and then compared to the decomposition rate expected in Tank 48 under full scale operations with "average" slurry:

$$\begin{aligned} \% \text{ Decomposition} &= 0.83\% \times \frac{(36 \text{ Ci/gal})}{15 \text{ Ci/gal}} \\ &= 2.0\% \text{ (per year) for "average" slurry.} \end{aligned}$$

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