Tetraphenylborate Solids Stability Tests

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TETRAPHENYLBORATE SOLIDS STABILITY TESTS (U)

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TETRAPHENYLBORATE SOLIDS STABILITY TESTS (U)

By D. D. WALKER and T. B. EDWARDS

SUMMARY

Tetraphenylborate solids provide a potentially large source of benzene in the slurries produced in the In-Tank Precipitation (ITP) process. The stability of the solids is an important consideration in the safety analysis of the process and we desire an understanding of the factors that influence the rate of conversion of the solids to benzene. This report discusses a statistically designed set of tests that measured the effects of four variables: sodium ion concentration, pH (or hydroxide ion concentration), irradiation dose prior to test, and continuous radiation during test. The appearance of soluble potassium indicates the loss of potassium tetraphenylborate solids (KTPB). The following points summarize the test results.

- The rates of increase in soluble potassium vary from 1 to 178 mg/L/day at 45 °C. This range exceeds that expected from previous tests at 40 and 50 °C and is similar to the range observed when the temperature varied from 40 to 70°C.

- The highest rates (>35 mg/L/day) occur at the worst case combination of variables and reflect an artifact of the statistical experimental matrix. These conditions will not occur in ITP operations.

- The higher rates largely result from the five-fold higher sludge and catalyst concentrations in these tests. The rate of increase in potassium is directly proportional to the amount of sludge and noble metal catalyst present.

- The two-mechanism model that correlated previous tests predicts lower K^+ rates than were measured in 10 of the 14 tests. The model worked only for those tests that reacted slowly. This result suggests that the model is incomplete (i.e., an additional mechanism exists).

- Statistical analysis of the results determined low pH and high sodium ion concentration are significant factors in promoting the decomposition of KTPB.

- Continuous radiation is a significant factor in retarding the decomposition rate.

- The statistical model provided poor reproduction of the measured values. The R^2 measure of the fit (i.e., the

fraction of the variability of the measurements explained
by the model) was 0.58. The lack of fit suggests an
additional variable affected the reaction rate.

- The experimental method used to adjust the pH (addition of
nitric acid) did not affect the rates of decomposition.

Recommendations are made for additional work to improve
definition of the decomposition rate within the ITP operating
window and improve our understanding of the reaction
mechanism. The additional experimental work in progress will
determine reaction rates at the edges of the ITP waste
composition operating window and identify basic features of
the reaction mechanism. With the additional rate
measurements and understanding, a better predictive model can
be constructed.

INTRODUCTION

Previous measurements of the rate of increase in soluble
potassium and cesium from the decomposition of KTPB slurries
suggested temperature as a possible major controlling factor.[1]
The slurry compositions used in those radioactive and
simulant tests had compositions similar to the waste in the
first ITP operations.[2] Based on that earlier work,
researchers developed a two-mechanism model for changes in
potassium concentration. The two mechanisms included
radiolytic degradation of solid and catalytic decomposition
of soluble tetraphenylborate ion (TPB^-). Results from the
model were compared to the observations from facility
operations and from laboratory tests with radioactive waste
and simulants. The model adequately predicted the waste tank
observations and the low temperature laboratory work. In
this most recent study, additional simulant tests over a
range of waste compositions and radiolysis rates were
undertaken at 45 °C to expand the data base for the model and
to search for additional factors that affect the rate of
decomposition. The design and results of these tests are
described in this report.

The results of these tests are summarized in reaction rates
for the appearance of soluble potassium in solution. One use
of these results is to estimate the rate of production of
benzene. The relationship between the two rates can be
easily calculated from the assumption that complete
decomposition of one mole of potassium tetraphenylborate
(KTPB) produces one mole of potassium ions and four moles of
benzene. This calculation provides a conservative estimate
of benzene production since some phenyl groups convert to
pehnol and other products. Also, the subsequent reactions
involve an additional delay. To convert a potassium rate
(mg K^+/L/day) to a benzene rate (mg benzene/L/hour), simply
divide by 3.

$$\left(\frac{1 \text{ mg } K^+}{L\text{-day}}\right)\left(\frac{1 \text{ mmole } K^+}{39.1 \text{ mg } K+}\right)\left(\frac{4 \text{ mmoles benzene}}{1 \text{ mmole } K+}\right)\left(\frac{78.12 \text{ mg benzene}}{1 \text{ mmole benzene}}\right)$$

$$\frac{1 \text{ day}}{24 \text{ hours}} = 0.333 \frac{\text{mg benzene}}{L\text{-hour}}$$

This work fulfills a request from A. W. Wiggins, "TPB Solids Stability,"Technical Task Request #HLE-TTR-97015, Rev.0, November 14, 1996. The work was performed in accordance with the following plan: M. J. Barnes, R. A. Peterson, and D. D. Walker, "Technical Task Plan for Solids Stability Studies of Tetraphenylborate Slurries (U)," WSRC-RP-96-602, Rev.2, October 24, 1997.

DISCUSSION

The initial test matrix included 10 experiments statistically designed to explore the effects of salt concentration, hydroxide ion concentration, radiation dose rate, and total irradiation dose. The matrix also included four exploratory tests on the effects of uranium, solids concentration, oxygen, and very large radiation dose. Table I lists the fixed parameters; Table II lists the variables and their ranges. Table III lists the test matrix. Subsequently, additional tests explored the effect of the pH adjustment step used in the statistically designed experiments, the effect of the sludge and noble metal concentration, and the effect of pH between pH 10 and pH 12. Table III also lists these additional tests (Runs 15-29).

Selection of Variables and Fixed Parameters for Statistically Designed Tests

The following paragraphs examine the process conditions and waste components in Tables I and II that could affect the rate of appearance of soluble K^+. The text discusses the potential effect of each, and indicates whether each was treated as a single valued parameter or 2-value variable_in the statistically designed test.

Temperature

Increasing the temperature accelerates the reaction. This effect has been experimentally established in numerous tests.[1] All experiments reported below occurred at 45 °C, a temperature that exceeds the highest expected in future Tank 48H and Tank 49H operations.

Sludge

Several experiments suggest the presence of sludge increases the rate of decomposition of tetraphenylborate ion.[1,2,3] Other evidence suggests the decomposition occurs as a homogeneous reaction between a soluble sludge component and soluble TPB⁻.

TABLE I.   Summary of Fixed Conditions for Statistically Designed Test

KTPB	5 wt %
Initial [TPB⁻]	0-100 mg/L
Sludge*	1 wt %
Organics	500 mg/L 3PB
	250 mg/L 2PB, 1PB, phenol
	750 mg/L benzene
	150 mg/L diphenylmercury
Temperature	45 °C
Atmosphere	sealed under air
Mixing	no mixing
Vessels	glass

*See Table A-3, Appendix A.

TABLE II.   Summary of Variables for Statistically Designed Test

Variable	Value		
	Low	Midpoint	High
[Na⁺] (molar)	0.5	2.75	5.0
[OH⁻]	pH=10	pH=12	3.0 molar
Dose rate (rad/h)	0	1E4	2E4
Pre-test dose (Mrad)	0	2.5	5

Nevertheless, the data to date do not exclude existence of a heterogeneous reaction (i.e., solid catalyst and soluble tetraphenylborate). Depending on the mechanism (i.e., heterogeneous or homogeneous), addition of sludge should either show no affect or increase the rate of reaction. Therefore, the tests included sludge at nominally 1 wt % in the slurry (1.2 g/L), the highest level expected in the process.[4] This sludge concentration is approximately five-fold higher than used in previous testing. Noble metal concentrations (i.e., Ru, Rh, and Pd) were increased proportionally with the sludge.

For a homogeneous reaction, the sludge composition would have no effect if it contained all of the catalytically active components and enough of each to saturate the solution. If a heterogeneous reaction occurs, the composition of the sludge could have an effect on the rate. Ideally, the simulated sludge should contain maximum levels of the active components at the expense of the inactive components.

These tests used a catalyst system described previously.[2] Noble metals (i.e., Ru, Rh, and Pd) and copper were added as both insoluble and soluble forms. Mercury was added as mercuric nitrate (forming HgO in the alkaline slurry) and as

diphenylmercury. Diphenylmercury accounted for 97% of the total mercury. Mercury concentrations were not increased in proportion to the amount of sludge. Since researchers suspected no active role for uranium in the reaction system, and because of experimental difficulties in handling radioactive samples, uranium was included in only one experiment. The uranium concentration was 344 mg/L, double the maximum amount expected in 1 wt % sludge with highest uranium content.[5]

Weight Percentage KTPB Solids

Potassium tetraphenylborate provides the source of reactant (either TPB⁻ or KTPB solids) and therefore increasing its concentration should either increase the reaction rate or have no effect. The presence of KTPB solids has been demonstrated experimentally to increase the rate of decomposition of TPB⁻. In unstirred systems, Barnes[6] measured higher rates of reaction for TPB⁻ with solids present, although the rate does not increase with increasing KTPB content in the range 1-8 wt %. Tests with Tank 48H slurries[1] that varied KTPB and sludge simultaneously showed increased reaction rates at higher concentrations. However, this result could reflect either the higher KTPB content or the higher sludge content.

For a homogeneous reaction (i.e., soluble catalyst and soluble tetraphenylborate), additional KTPB might have no effect if the lowest concentration tested is sufficient to maintain the solution saturated with TPB⁻. For a heterogeneous reaction (i.e., solid KTPB and soluble catalyst), increasing the KTPB solids concentration could increase the rate of reaction by providing more surface area. A third possibility, the reaction between solid catalyst and solid KTPB is highly unlikely because the reaction zone (solid-solid contact points) is too limited to support a significant reaction rate. Therefore, to obtain conservatively high reaction rates, the KTPB solids concentration should be included at the highest expected level. Current operating plans include concentrating to 10 wt %. A slightly higher concentration (12 wt %) would bound experimental and tank uncertainties.

However, preparing, handling, and sampling unirradiated 12 wt % slurry proves very difficult due to its high viscosity and yield strength. Most previous testing used slurries near 5 wt %. Therefore, to provide better comparison to the current data base and to alleviate experimental problems, 5 wt % slurry was used. An additional test run was made at 2.5 wt % KTPB to determine if there is a significant effect from the KTPB solids concentration.

Oxygen

The presence of oxygen has been shown to delay or suppress the decomposition of tetraphenylborate.[2,7,8] Some evidence to the contrary has been observed for decomposition of other components (i.e., presence of oxygen speeds decomposition of 2PB and 1PB). The presence of oxygen also tends to produce phenol rather than benzene as the final product. Thus, the conservative approach to these tests (i.e., to maximize benzene generation) suggests that oxygen should be excluded. However, due to experimental difficulties inherent in maintaining samples inerted, the tests were run under air but in sealed vessels. Two exploratory experiments under nitrogen was included to provide insight on the effect of this parameter.

Initial [TPB⁻]

Previous testing in the Shielded Cells with Tank 48H slurry samples targeted 100 and 400 mg/L excess NaTPB as an initial condition.[1] Actual initial conditions ranged from 33 to 360 mg/L. This initial condition did not affect the eventual rate of increase, although higher values delay the onset of the increases in soluble potassium. The initial [TPB⁻] was included as a variable because its presence might be required to "condition" the catalyst (i.e., provide a reducing agent to obtain a lower oxidation state). These tests targeted >10 but <100 mg/L of NaTPB for the initial condition. In several cases, the initial NaTPB was less than detectable (<10 mg/L).

Mixing

Mixing normally enhances chemical reactions, but recent test results indicate that continuous mixing in a sealed system does not significantly affect the rate of decomposition of TPB⁻. Barnes' results indicate a 20% increase in rate when sludge solids in a salt solution are continuously mixed (compared to unmixed).[9] However, if KTPB solids are present, mixing a sludge/slurry does not affect the rate measurably. The slurries were not mixed in these tests.

Benzene, organic intermediates, and diphenylmercury

Experimental evidence exists that indicates the presence of triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB) influence TPB⁻ and 3PB decomposition.[10] These organics appear to consume oxygen, possibly leading to reduction of the catalytic metal ion to the active oxidation state.[8] This explains an induction effect but implies that the final decomposition rate remains unchanged. Benzene is also implicated in the catalytic system.[10] It may form a non-aqueous phase that promotes the decomposition, but experimental support is lacking. In any

rapid reaction in a sealed system, these compounds will accumulate even if not present initially. However, their absence may slow the onset of the reaction. Because of the potential induction effect, benzene and organic intermediates were included at high initial levels. Concentrations of intermediates (3PB, 2PB, and 1PB) double those used in previous catalyst testing were targeted (250 mg/L of 3PB, 2PB, 1PB, and phenol). Benzene was held the same as previous testing (750 mg/L).

Diphenylmercury was added as a fixed component of the slurry at the same level used in catalyst identification testing (150 mg/L).

Total radiation dose

The effect of a large adsorbed radiation dose on the rate of appearance of soluble K^+ is not known. Barnes has shown that a dose of 200 Mrad does not accelerate decomposition of *soluble* TPB^-.[11] Comparison of Crawford's tests (no dose)[12] and other tests (Tk 48H samples, irradiated simulants)[1] and the agreement of the model with Tank 48H results[1] suggest little impact from doses in the range 5 to 200 Mrad. Since a direct investigation of the effect of radiation dose on solids stability is not available, pre-irradiation was included as a 2-level variable.

The Tank 48H solids have received an estimated average dose of 200 Mrad. Rate differences between simulated slurries irradiated to 5 Mrad and Tank 48H slurries prove minimal.[1] However, the rheological properties of slurries change significantly with doses of 15 to 30 Mrad.[13] Thus, pre-irradiation to doses of 0 and 30 Mrad was used to encompass the rheological changes. In addition, a single exploratory experiment with a slurry irradiated to 200 Mrad was included at the centerpoint composition (2.8 M Na^+, pH 12) and radiation conditions (15 Mrad adsorbed dose, 1.5×10^4 rad/h continuous dose) to provide insight on the effect of long storage times.

Salt concentration

The salt (or total sodium ion) concentration can affect the rate in three ways, two of which have been experimentally verified. First, increasing the salt concentration decreases the solubility of tetraphenylborate compounds.[14] This will decrease the rate of a reaction involving TPB^- ion but might have no effect on a reaction involving NaTPB or KTPB solids. Second, experimental evidence indicates the rate constant for decomposition of TPB^- ion increases with salt concentration,[6] possibly due to an ionic strength affect. Third, if a salt component is part of the catalytic system, then increasing its concentration could affect the rate of appearance of soluble K^+. Work by Barnes has not identified any salt

components active in the catalytic system in TPB⁻ decomposition.[6] Since the first two effects oppose one another, it is not clear whether the fastest rates will occur at low or high salt concentrations. Total sodium ion concentration was treated as a 2-level variable at 0.1 and 5.5 molar to bound salt concentrations expected in Tank 48H, Tank 49H, and the Late Wash Facility.

OH⁻ or pH

Hydroxide ion or pH is an important factor in stabilizing TPB⁻ purchased from vendors. Although the metal-catalyzed decomposition mechanism for TPB⁻ ion appears independent of OH⁻ in the range 0.5 to 3 molar,[6] a general acid catalyzed mechanism is rapid at low pH.[15] The current ITP process requirements[16] include the possibility for storage of washed precipitate in Tank 49H under conditions where the pH will drop to approximately 10.3. The irradiated slurry is buffered at pH 10 by a mixture of phenol and carbonate so Late Washing will not reduce the pH significantly. It is possible that the acid catalyzed mechanism may be important at this pH. However, the solubility of Cu and other metal ions decrease as the pH drops from 14 to 10.[17] Thus, the metal-catalyzed reaction could be slower at the lower pH. Since these two effects oppose each other, the hydroxide concentration was tested pH 10 to pH 14.5 (3 M NaOH).

Radiation dose rate

Radiation affects the appearance of K⁺ in solution due to the degradation of KTPB solids and TPB⁻ ion.[1] At dose rates expected in ITP operations, decomposition of TPB⁻ from radiation is negligible compared to the catalyzed reaction.[11] However, in the absence of the rapid catalytic reaction, radiation will contribute significantly to the total decomposition rate. Thus, radiation was included as a 2-level variable to determine how changes in the dose rate affect the total decomposition rate.

Statistical Test Design

Several options for statistically designed tests for four variables were considered, including a full factorial with centerpoints (18 runs). A partial factorial design was selected to reduce the time. From statistical considerations, a linear model of the variables can be tested in 8 runs with two centerpoints. This design provides main effects and insight on 2-way interactions. Additional runs outside of the statistical design were included to investigate effects of nitrogen inerting, weight percentage KTPB, uranium, and very large radiation dose. Table III lists the test matrix.

The centerpoint conditions in a linear model are normally taken as the arithmetic average of the high and low values.

TABLE III. Statistically Designed Test Matrix

Run	[Na$^+$]	[OH$^-$]	Preirrad.	Dose rate
1*	+1	+1	-1	-1
2*	+1	+1	+1	+1
3*	+1	-1	-1	+1
4*	+1	-1	+1	-1
5*	0	0	0	0
6*	0	0	0	0
7 (Uranium)	0	0	0	0
8 (High pre-dose)	0	0	0	0
9*	-1	+1	-1	+1
10*	-1	+1	+1	-1
11*	-1	-1	-1	-1
12 (N$_2$ inerted)	-1	-1	-1	-1
13*	-1	-1	+1	+1
14 (2.5 wt % KTPB)	-1	-1	+1	+1
15 (Run 5/6 repeat at pH10)	0	-1	0	0
16 (Run 5/6 repeat at pH10)	0	-1	0	0
17 (N$_2$ inerted)	0	-1	0	-1
18 (2.5 wt % KTPB)	0	-1	0	+1

* Indicates tests that are part of the statistical design.
+1, 0, and -1 indicate high, centerpoint, and low values for
the variables. See Table II for numerical values. Other
tests are not part of the statistical design.

In this test, the center point values for three of the
variables (salt concentration, dose rate, and total dose)
were the arithmetic averages. However, the fourth variable
(pH) very likely has a nonlinear response, so the centerpoint
value was pH = 12 rather than [OH$^-$] = 1.5 M.

The experiment at high [OH$^-$] and low sodium is not physically
accessible. In this case, the experimental parameters were
selected as close as possible to the desired point.

Appendix A details the preparation of slurries for the
experiments. The tests ran for eight weeks. Samples were
taken initially and every seven days. Potassium and pH
measurements were made on all samples. Soluble catalytic
metals (Cu, Ag, Rh, Pd) were measured only on initial and
final samples. The NaTPB, 3PB, 2PB, 1PB, and phenol
concentrations were analyzed on all initial samples and
during the first several weeks of the test, but were
terminated during the fourth or fifth week because little
information was gained from them.

Tests of the Effect of pH Adjustment Step and pH

In the statistically designed set of 10 tests, concentrated nitric acid was used to adjust the pH. The amount of acid used was inversely proportional to the desired pH, with several milliliters required for pH 10 slurries and none required for pH 14 slurries. Thus, the correlation between pH and decomposition rate was confounded with the same correlation between the amount of acid used and decomposition rate. Since an effect due to acid is not representative of the ITP process, four of the statistically designed tests (Table III, Run 3, 4, 11, and 13) were repeated using carbon dioxide to adjust the pH. The nitric acid adjustment method was repeated at the same time.

Four other tests (Run 15-18) at the midpoint sodium concentration were run at pH 10 using the carbon dioxide pH adjustment method. These tests provide additional data on the effect of the method of adjustment and on the effect of a hydroxide change between pH 10 and pH 12. In particular, Runs 15 and 16 at pH 10 can be compared to Runs 5 and 6 at pH 12. Runs 17 and 18 changed more than one variable, so direct comparisons with other runs are not possible. However, the results were used in the statistical evaluation of the data.

Effect of Sludge/Catalyst Concentration

Three runs at 0.2, 1.0 and 2.0 wt % sludge and noble metals examined the effect of these components with other variables constant. The slurries for these tests contained 4.5 M Na^+. The results of these tests were not included in the statistical analysis of the effects of sodium ion, pH, pre-irradiation, and dose rate.

Test Results

Potassium

The appearance of soluble potassium ion was used as a measure of the loss of tetraphenylborate solids (KTPB and CsTPB). Figure 1 graphs the potassium ion concentrations in the first 14 tests listed in Table IV. Modeling results for each test are also shown in Figure 1 and discussed in the Modeling Results section. Tables IV and V summarize the test conditions and the observed rates of increase in soluble potassium. The following points summarize test observations.

- The rates of increase in soluble potassium vary from 1 to 178 mg/L/day at 45 °C. This range is similar to the range observed in previous tests over a range of temperatures from 40 to 70 °C (i.e., 0.1 to 130 mg/L/day).[1]

- The higher rates largely result from the five-fold higher sludge and catalyst concentrations in these

FIGURE 1.   Changes in Soluble Potassium Concentrations

Note: The vertical scales on these graphs differ.   Use care when comparing different experiments.
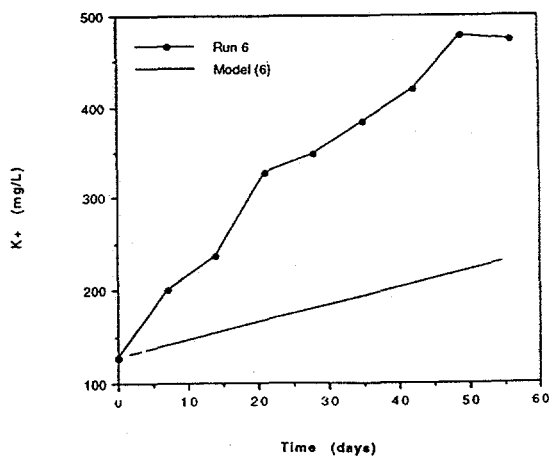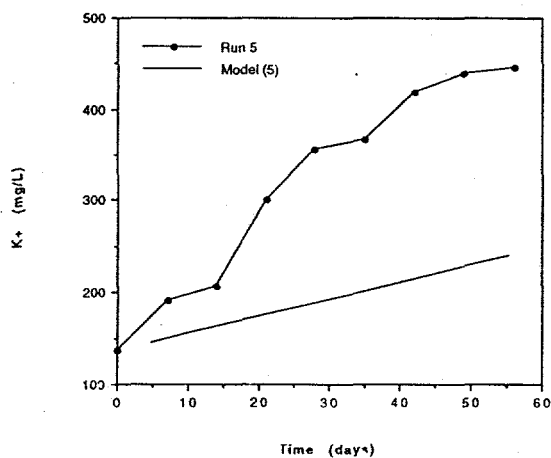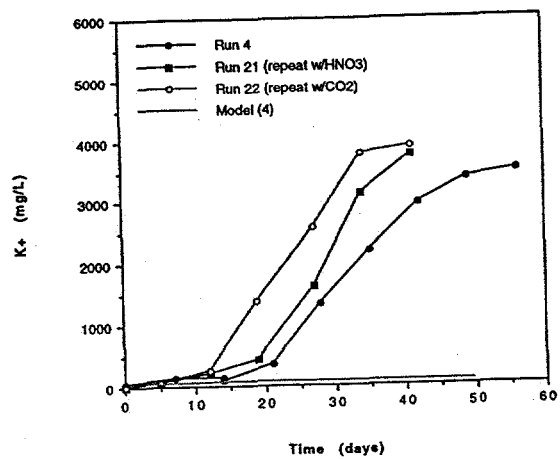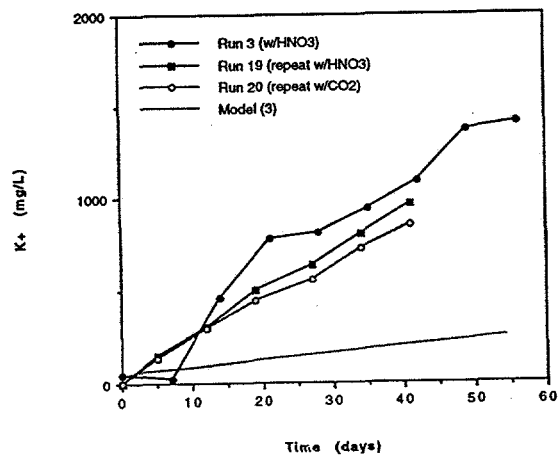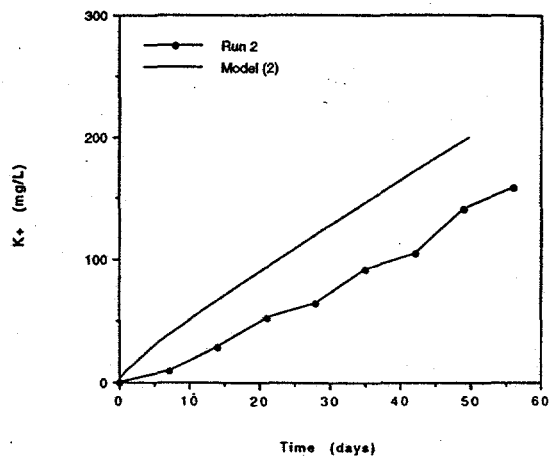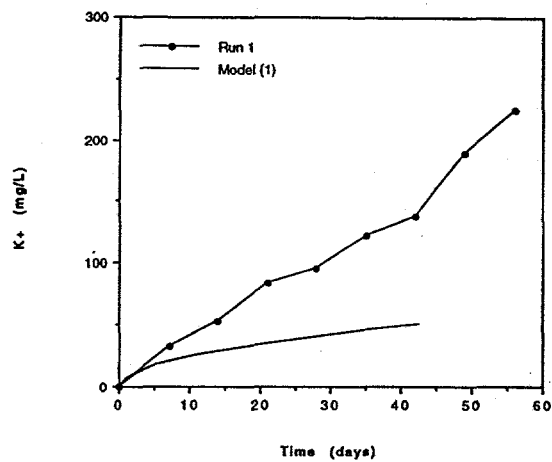
FIGURE 1 (continued). Changes in Soluble Potassium Concentrations

Note: The vertical scales on these graphs differ. Use care when comparing different experiments.
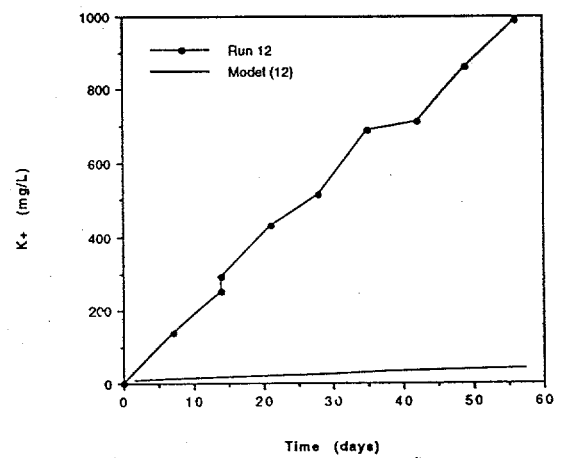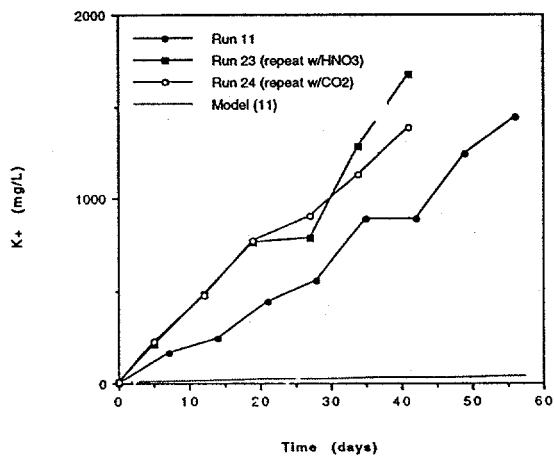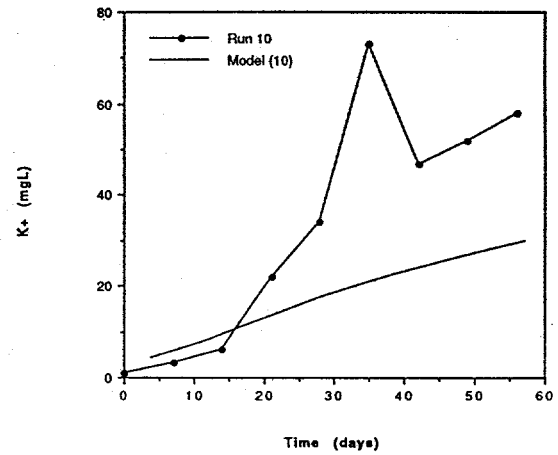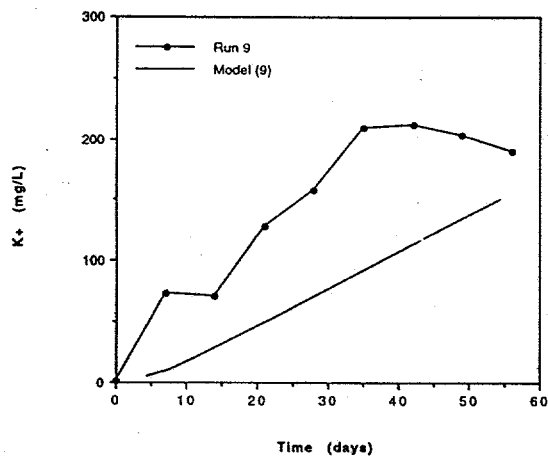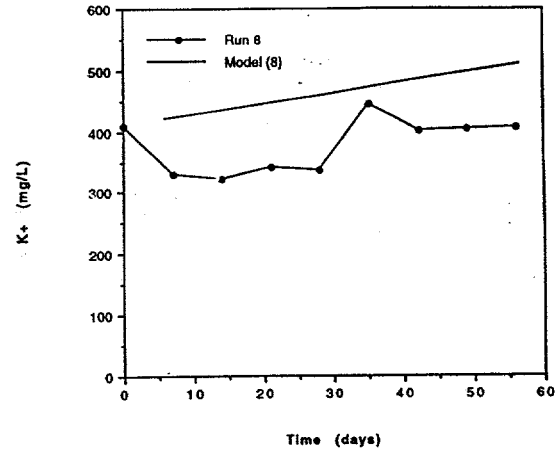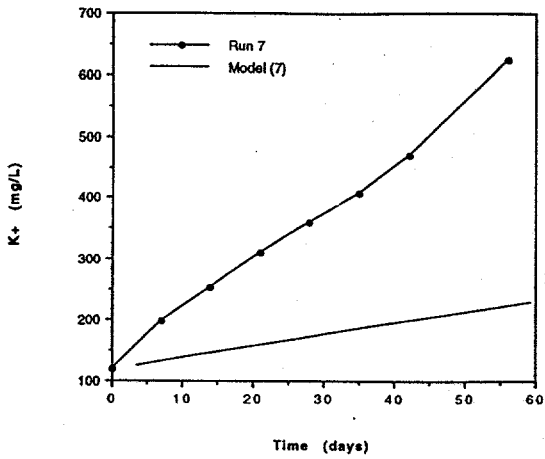
FIGURE 1 (continued).   Changes in Soluble Potassium Concentrations

Note: The vertical scales on these graphs differ.   Use care when comparing different experiments.
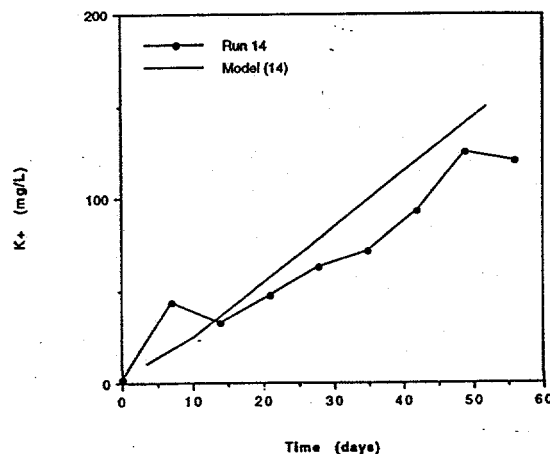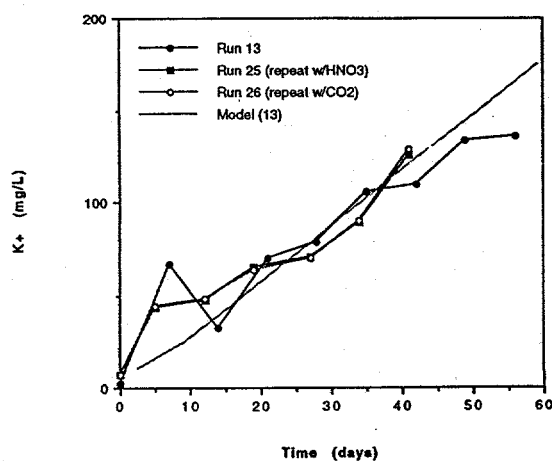
TABLE IV.   Summary of Test Conditions and Potassium Rates

Run	[Na⁺] (molar)	pH	Pre-test dose (Mrad)	Dose rate (rad/h)	Other	Soluble K⁺ Rate (mg/L/day)
1	5.5	14.5	0	0		3.8
2	5.5	14.5	30	2.8×10^4		2.9
3	5.5	10.5	0	2.8×10^4		26.
4	5.5	10.7	30	0		124.
5	2.8	12.2	15	1.5×10^4		5.9
6	2.8	12.2	15	1.5×10^4		6.3
7	2.8	12.0	15	1.5×10^4	Uranium	8.5
8	2.8	11.8	200	1.5×10^4	Large dose	1.1
9	0.65	13.7	0	2.8×10^4		5.0
10	0.65	13.7	30	0		1.2
11	0.10	10.3	0	0		26.
12	0.10	10.4	0.	0	N_2 inerted	17.
13	0.10	10.2	30	2.8×10^4		2.2
14	0.10	10.1	30	2.8×10^4	2.5 wt % KTPB	2.0
15	2.8	10.2	15	1.5×10^4		15
16	2.8	9.9	15	1.5×10^4		14
17	2.8	10.5	15	0	N_2 inerted	19
18	2.8	10.2	15	2.9×10^4	2.5 wt % KTPB	22

tests. The rate of increase in potassium is directly proportional to the amount sludge and noble metal catalyst present.

- The highest rates (>35 mg/L/day) are caused by worst case combination of variables and are an artifact of the statistical experimental matrix. They will not occur in ITP operations.

In 17 of the 18 tests, a significant increase in the soluble potassium occurred. In Run 8, the change in potassium was not significantly larger than the sampling and analytical errors. In the other tests, the potassium concentration typically increased with time. Although potassium usually increased linearly, clear exceptions are Run 4 and Run 9 and possible exceptions include Runs 3, 5, 6, and 13. In Run 4, the rate increased at 21 days, then slowed near the end of the test. The same response was observed when this run was repeated to test for an effect of the pH adjustment method. Although other explanations are possible, the slowdown was probably due to the extreme loss of solids; by the end of the test, more than 70% of the solids decomposed. Decreases in the concentration of soluble palladium does not appear to explain the curvature and slowing of the reaction rate. Although soluble palladium decreased during Run 4 and Run 3, it increased in the other runs that showed or suggested slowing of the rate (see Appendix A, Table A-4).

The rates of increase in soluble potassium varied between 1 and 178 mg/L/day (Table IV and V). This range is similar to results from previous tests.[1] However, the large range in previous tests was attributed to differences in temperature. In previous tests, rates larger than 2 mg/L/day were observed only above 50 °C. The present set of tests indicate that there is a factor that can promote rates greater than 2 mg/L/day at 45 °C. The higher concentrations of sludge and catalytically active metals used in the current tests contribute to the higher rates. These tests used five times as much sludge and metals as previous tests. If the potassium rate is directly proportional to the amount of sludge and metals, then rates as high as 10 mg/L/day are expected. The measurement of rates much higher than 10 mg/L/day suggests that an additional factor is present.

Effect of pH adjustment method

The use of nitric acid to adjust pH did not cause the high potassium rates observed at low pH. Table V lists the results of the comparison tests. In the repeat measurements, there was no significant difference between the nitric acid method and the carbon dioxide method. The difference in rates between the initial and repeat runs gives an estimate of ±30% for the average reproducibility of the experiments.

TABLE V.   Effect of pH Adjustment Method

Run	[Na$^+$]	[OH$^-$]	Pre-irrad.	Dose rate	pH Method	Amount† of HNO$_3$	K$^+$ rate (mg/L/day)
3	+1	-1	-1	+1	HNO$_3$*	4.8	26
19					HNO$_3$**	5.0	23
20					CO$_2$	0	20
4	+1	-1	+1	-1	HNO$_3$*	4.4	124
21					HNO$_3$**	4.6	178
22					CO$_2$	0	159
11	-1	-1	-1	-1	HNO$_3$*	0.5	26
23					HNO$_3$**	0.2	38
24					CO$_2$	0	32
13	-1	-1	+1	+1	HNO$_3$*	0	2.2
25					HNO$_3$**	0.2	2.4
26					CO$_2$	0	2.4

†Milliliters of 7.5 M HNO$_3$ added per 100 mL of slurry.
*Test results from initial runs listed in Table III.
**Repeat runs using nitric acid.

Other observations

Several other measurements were made during the tests, including total soluble boron, pH, soluble organics, and soluble metals (i.e., Cu, Ag, Ru, Rh, and Pd). The analytical results are listed in Appendix A and summarized briefly in the following paragraphs.

Total Soluble Boron
If KTPB decomposes to yield soluble K$^+$ and soluble boron-containing products, then the rate of appearance of boron in solution should equal the rate of appearance of potassium. An increase in soluble boron confirms that the reaction includes decomposition of tetraphenylborate since other analyses show that tetraphenylborate is not accumulating in solution. Table VI lists the changes in potassium and boron for five of the runs. There is a strong correlation between the change in boron and potassium, although the yield of boron is slightly greater than expected. The difference could be due to either analytical bias in the potassium and boron measurements or the presence (and simultaneous decomposition) of solid NaTPB. The discrepancy was small and its source will be pursued in future work.

Benzene
Benzene from the decomposition reaction was measured in a few cases to confirm that the potassium found in solution indicated loss of tetraphenylborate. The analytical method

TABLE VI. **Comparison of Yields of Soluble Potassium and Boron**

Run**	Change (mmoles/L)*	
	K^+	B
4	88	110
5	7.9	13.9
10	1.5	4.7
11	37	47
12	25	34

*Difference between initial and final measurements on filtered samples. The elapsed time was 56 days.
**See Tables IV and V.

TABLE VII. **Benzene Yields**

Run*		Change in Concentration (mmoles/L)**	
		K^+	Benzene
25	repeat of Run 13 with HNO_3	1.6	0.2
26	repeat of Run 13 with CO_2	1.6	0.01
19	repeat of Run 3 with HNO_3	16.	0.7
20	repeat of Run 3 with CO_2	14.	4.
23	repeat of Run 11 with HNO_3	20.	12.
24	repeat of Run 11 with CO_2	23.	12.
21	repeat of Run 4 with HNO_3	42.	280
22	repeat of Run 4 with CO_2	66.	320

*From Table V.
**Changes calculated between initial and 27-day samples.

used for benzene is known to be inaccurate, but it can show trends if the differences between samples are large.[18] Table VII lists the results for the eight repeat experiments listed in Table V. Benzene concentrations increase with the amount of K^+ found in solution (Table VII). In the six slowest reactions, the amount of benzene produced was less than expected from the theoretical yield of four moles of benzene per mole of potassium. In the two fastest reactions (Runs 21 and 22), more than the theoretical yield of benzene was measured. These results could be due to errors in the benzene measurements, loss of small amounts of benzene from the reaction container, contribution from the decomposition of NaTPB, or to a change in reaction stoichiometry between slow and fast reactions.

Solution pH.
The pH of the solutions changed very little during the test. In most cases, the pH varied randomly by ±0.25 pH units, with

only one varying by more than 0.5 pH units. In Run 8, the pH
decreased by 1.1 pH units from 12.0 to 10.9. The large
change may reflect the 200 Mrad radiation dose that the
slurry received prior to the test. Large radiation doses are
known to cause the pH to decrease, although the change
typically is observed within a few days after receiving the
dose.[13]

Soluble organics (NaTPB, 3PB, 2PB, 1PB, and phenol).
One or more of the phenyl borate decomposition products
(i.e., 3PB, 2PB, and 1PB) promote the rapid decomposition of
soluble TPB$^-$.[10] Since these compounds may also promote the
decomposition of solid tetraphenylborates, the following
target values for the initial test conditions were set: 3PB,
500 mg; 2PB and 1PB, 250 g/L. Phenol was also targeted for
250 mg/L but a report subsequent to the start of these tests
found that phenol does not affect the catalytic reaction.[7] In
22 of the 29 experiments reported in this document, one of
the three phenyl borate compounds was more than 20% below the
target. In one case (i.e., Run 26), two compounds were more
than 20% below the target. In those cases where the
experiments were repeated, the variation in starting
concentrations does not appear to have significantly affected
the final rate. In almost all runs, the rate of appearance
of soluble K$^+$ was linear from the start, *even though the
concentrations of the phenyl borate compounds varied
drastically*. This result implies that although some amount
of at least one of the phenyl borate compounds is required to
initiate the decomposition reaction, it does not appear
important in sustaining the reaction. Therefore, the
variation in the starting concentrations probably did not
affect the measured rates. However, this conclusion should
be revisited when the identity and role of the significant
phenyl borate compounds are determined. The lack of
precision in achieving the target values was due to formation
of the intermediates by irradiation (yielding values higher
than target), formation and destruction during the pH
adjustment step (yielding high and low values), and
inaccuracies in adding small amounts of the compounds during
slurry preparation. Future preparations will include steps
to minimize these sources of error.

The other organics (3PB, 2PB, and 1PB) typically decreased
during the tests. In all but one case, 3PB disappeared
completely by the fourth week. The 2PB and 1PB concentrations
typically decreased, but in most cases they were still
present in measurable amounts after four weeks. The rapid
loss of 3PB is unexpected from previous measurements of the
3PB reaction rate.[19] If 3PB is produced but does not
accumulate, it must be decomposing at least as fast as the
tetraphenylborate. Based on the rate of loss of tetraphenyl-
borate and the previously measured rate constants for 3PB,
the 3PB concentration should be observable in many of the

experiments. The increase in soluble boron indicates that 3PB is not precipitating as it forms. The missing 3PB suggests that either the decomposition of tetraphenylborate occurs by concerted loss of two phenyl groups bypassing 3PB and forming 2PB directly, or the estimated rate constants for decomposition of 3PB are too low. The concerted loss of two phenyl groups is unlikely since the decomposition of soluble TPB⁻ does not proceed by that mechanism. It is more likely that extension of the 3PB rate constants (measured at 0.5 M NaOH or higher) to the low pH used in the solids stability tests may introduce significant error.

Phenol concentrations increased in the majority of the tests and remained constant in the others. This is expected since phenol does not decompose or decomposes slowly in the presence of radiation. The phenol yields (normalized to loss of tetraphenylborate) are generally low for the rapid decomposition reactions and higher for slow decomposition reactions. Low phenol yields imply benzene is the major product similar to Tank 48H experience.[3]

Transition Metals.
Transition metals were measured in the aqueous phase at the beginning and end of the test using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Consistent trends were not observed. Since the initial samples were obtained within a few hours of mixing the metals into the slurries, the solutions probably had not reached equilibrium. Therefore, changes in metals between the start and end may only reflect attainment of equilibrium. Each metal was found to increase in some cases and decrease in others, but instances where the metals increased in solution predominated. One possibly significant observation was that for palladium, all four of the fastest reactions showed decreases in the soluble Pd. This could reflect either adsorption on solids or extraction into a nonaqueous phase bound to the solids.

Modeling Results

The appearance of soluble potassium was predicted for the conditions in the first fourteen tests in Tables III and IV using the dual mechanism model described previously.[1] The model includes two decomposition pathways: radiolytic and catalytic. Table VIII lists the values of parameters used in the modeling calculations. The results of the calculations are plotted along with the experimental data in Figure 1.

The two-mechanism model predicts slower rates of increase in soluble potassium than measured in ten of the 14 tests modeled. The model worked only for those tests that showed very little reactivity. This result strongly suggests an additional mechanism for decomposition, or that one of the two mechanisms already included is incorrectly formulated.

TABLE VIII.   Values of Parameters Used in Modeling Calculations

Run	k (h^{-1})	K_1 $(molar^2)$	K_2 $(molar^2)$	R (eV/s)	Initial NaTPB $(mmolar)$	K^+ $(mmolar)$
1	1.5	5.34E-10	9.68E-13	0	0.11	–
2	1.5	5.34E-10	9.68E-13	2.56E21	0.21	–
3	1.5	5.34E-10	9.68E-13	2.56E21	–	1.2
4	1.5	5.34E-10	9.68E-13	0	–	1.3
5	0.1	8.64E-9	1.57E-11	1.25E21	–	3.5
6	0.1	8.64E-9	1.57E-11	1.25E21	–	3.2
7	0.1	8.64E-9	1.57E-11	1.25E21	–	3.0
8	0.1	8.64E-9	1.57E-11	1.25E21	–	10.5
9	0.005	6.60E-8	1.20E-10	2.16E21	1.20	–
10	0.005	6.60E-8	1.20E-10	0	0.97	–
11	0.004	1.41E-7	2.55E-10	0	0.90	–
12	0.004	1.41E-7	2.55E-10	0	0.90	–
13	0.004	1.41E-7	2.55E-10	2.10E21	0.81	–
14	0.004	1.41E-7	2.55E-10	2.10E21	0.96	–

The results do not suggest a synergistic effect between the two mechanisms, since the model also predicts lower rates than measured in tests that did not include radiation (Runs 1,11, and 12).

The rate constants shown in Table VIII were derived from experiments on the decomposition of soluble TPB⁻.[6,9] The rates were corrected for the higher sludge and catalyst concentration in these tests by assuming the rate proportional to the weight of sludge and catalyst added.

The solubility constants for KTPB and CsTPB were calculated as described previously.[1]

The radiation dose to the solids was calculated differently than the method used in previous tests with radioactive slurries. In the present tests, the radiation source was external to the samples so the entire sample was irradiated in a uniform field. No correction is necessary for separation of the solids by settling or floating. The fraction of the total dose adsorbed by the solids was assumed to equal the weight fraction of the solids (either 5% or 2.5%).

Statistical Analysis

The results of the 18 tests listed in Table III and the eight repeat tests listed in Table IV were statistically analyzed with the details described in Appendix B. The following observations summarize the statistical analysis.

- The best linear model using all of the data (including the highest, or "accelerated" rate measurements) was:

$$K^+ \text{ rate} = 166.0 + 11.70[Na^+] - 12.7[pH]$$
$$+ 0.016[\text{Total dose}] - 0.00188[\text{Dose rate}]$$

  where K^+ rate = rate of increase in soluble K^+ (mg/L/day)
  $[Na^+]$ = total sodium ion concentration (molar)
  $[pH]$ = hydrogen ion concentration (pH units)
  $[\text{Total dose}]$ = pre-test adsorbed dose (Mrad)
  $[\text{Dose rate}]$ = continuous dose rate during test (rad/h)

- Low pH and high sodium ion concentration were significant factors in promoting the appearance of soluble K^+.

- Continuous radiation dose rate during the tests was a significant factor in retarding the appearance of soluble K^+.

- Pre-test irradiation was not a significant factor in predicting the rate of appearance of soluble K^+.

- The fit of this model to the data was not good. The R^2 measure of fit was 0.58.

- Other, non-linear dependencies on $[Na^+]$ and pH did not significantly improve the fit (i.e., $\exp([Na^+]^{1/2})$, $[OH^-]$, and $[OH^-]^{-1}$).

The absence of a good fit to the data suggests that the rate is either affected by an additional factor not kept constant during these tests, or the dependence of the potassium rate is more complicated than the linear and non-linear models examined in the statistical analysis.

Effects of Other Variables

Effect of Sludge Concentration

The rate of appearance of soluble potassium is directly proportional to the concentration of sludge and noble metal catalysts. Table IX and Figure 2 show the results of separate experiments in which the effect of sludge concentration was measured at 0.24, 1.2, and 2.4 g of sludge per liter of slurry. The total ruthenium, rhodium, and palladium in the slurries increased in proportion to the sludge. The graph of the rate constant and sludge concentration (Fig. 2) shows that the relationship is approximately linear in the range tested with an intercept near zero, as expected when the sludge and metal catalysts are absent.

TABLE IX.   Effect of Sludge Concentration*

Sludge (g/L)*	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	K$^+$ Rate (mg/L/day)
0.24	6.3	1.7	3.2	0.11
1.2	28.4	7.4	13.7	8.5
2.4	56.0	14.6	26.9	11.9

*Other significant conditions: temperature, 45 °C; 5 wt % KTPB, 4.5 M Na$^+$. The sludge concentrations are approximately 0.2, 1 and 2 wt % of the slurry.

FIGURE 2.   Effect of Sludge and Noble Metals on Tetraphenylborate Decomposition Rate
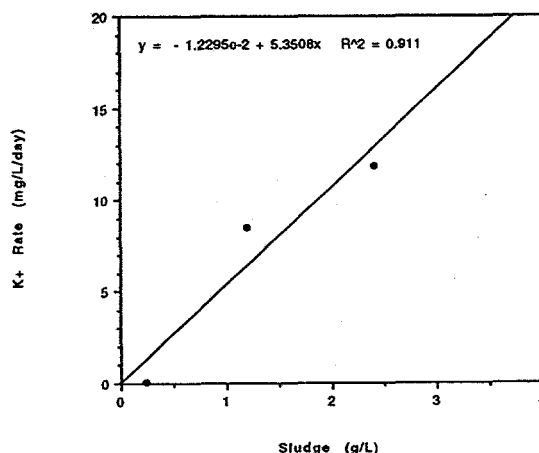
Experiments on the decomposition of soluble tetraphenylborate used 0.2 wt % sludge similar to the amount in Tank 48H during ITP first batch operations.[3] Previous solids stability tests with radioactive waste and simulated slurries used 0.2 to 0.9 wt % sludge.[1] A sludge concentration of 1 wt % was used in the statistically designed tests.

Effect of pH

Increasing the pH of the slurry decreases the rate of the decomposition of potassium tetraphenylborate. The two midpoint tests at pH 12 (Runs 5 and 6, Table IV) were repeated at pH 10 (Runs 14 and 15, Table IV) to directly determine the effect of pH in the absence of changes in other variables. The rate of decomposition of KTPB more than doubles when the pH decreases from 12 to 10. The results agree with the results of the statistical analysis of all of the data.

Uranium

Addition of uranyl nitrate to simulate the uranium in sludge increased the rate of appearance of potassium by 30%. This is shown by comparing Runs 5 and 6 to Run 7 in Table IV. Although significant compared to the reproducibility of the duplicate centerpoints (Run 5 and Run 6), it is a minor effect compared to salt concentration and pH. The relative insensitivity to uranium is also true of the reaction of soluble TPB[-].[11]

Very High Radiation Dose

A large absorbed radiation dose significantly reduces the rate of appearance of soluble potassium. This is shown by comparing Runs 5 and 6 to Run 8 in Table IV. The 200 Mrad dose reduced the rate of appearance of potassium by 80% compared to a dose of 15 Mrad. Thus, the absorbed dosed received by the precipitate during extended outages in Tank 48H will decrease the rate of catalytic decomposition.

Nitrogen Inerting

Nitrogen inerting reduced the rate of decomposition by 35% in the one test in which the effect was measured. This is shown by comparing Run 11 with Run 12. This result supports the assertion that tests run under air yield conservatively high reaction rates compared to inerted tests.

KTPB Solids Concentration

Reducing the concentration of KTPB solids from 5 to 2 wt % did not significantly change the rate of appearance of potassium. This is shown by comparing Run 13 with Run 14. Although the reaction rate for the 2.5 wt % slurry was 10% slower, this weak dependence on a primary reactant is smaller than expected.

RECOMMENDATIONS FOR FURTHER ACTIVITIES

The results of the experiments and modeling suggest the following additional areas of investigation.

- Determine the rate of decomposition under compositions more closely related to expected ITP operating conditions.

    The range of variables used in the statistically designed experiment were chosen to maximize the composition space investigated while assuming that high decomposition rates were largely caused by higher temperatures. The results suggest that combinations of low pH and high sodium that will not occur in the ITP process also cause high decomposition rates.

- Determine the catalytically active components for the decomposition reaction.

  The design of the present set of tests was based on the assumption that the catalytic system for loss of KTPB solids is the same as for the decomposition of soluble NaTPB. This should be verified to insure that the proper variables are controlled in future tests. The test methodology would be similar to the catalyst identification tests for soluble NaTPB. If the catalytic system is similar, then the test series could be considerably shortened compared to the earlier work.

- Determine the phase in which the metal catalyst acts.

  Assuming that the catalyst system for the decomposition of KTPB is similar to soluble NaTPB, knowledge of the location of the catalyst metal can help determine if the right variables are being controlled in the tests.

- Determine the relative decomposition rates for potassium and sodium tetraphenylborate solids.

  A major feature of the Tank 48H reaction was the rapid decomposition of NaTPB (soluble and excess solids) but not the KTPB. The KTPB solids appear to decompose at a slow rate attributable to radiolysis. The difference in stability of the two compounds towards the catalytic decomposition reaction should be experimentally established to help explain why the Tank 48H reaction did not consume the KTPB.

- Investigate other statistical models.

  The linear model described in this document is a good starting place when other information about the reacting system is absent. Additional testing will reveal the functional dependence for each variable which will lead to a more accurate model.

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APPENDIX A
Experimental

Preparation of Slurries

Researchers prepared six simulated KTPB slurries (nominally 2.5 or 5 wt %) with the compositions shown in Table A-1. The statistically designed tests used Slurries A through E. The repeat tests investigating the effect of the pH adjustment method and additional low pH tests used second batches of the slurries. The experiment measuring the effect of sludge and noble metals concentration used Slurry F. Researchers precipitated the KTPB in the presence of a low sodium ion concentration with the soluble sodium salts added after precipitation. Researchers prepared the 0.1 M Na^+ Slurry E at 2.5 wt % solids, then concentrated to 5 wt % solids. Researchers irradiated all or portions of the slurries (except Slurry F) in Co-60 gamma sources at the dose rates and to the doses listed in Table A-2. After irradiation, the slurries were analyzed for potassium ion and adjusted with 0.55 M NaTPB solution (0.5 to 8.6 mL) to obtain TPB^- ion in solution. On the day the test began, 100 mL portions of slurry were placed in Erlenmeyer flasks. The components of the catalyst system were added next (Table A-3). Since some potassium was present in the catalyst components, another small addition of 0.55 M NaTPB solution was made (approximately 0.3 mL). The slurries were stirred at room temperature for one hour, then the pH of each was adjusted. During the initial tests, the pH adjustment used nitric acid or sodium hydroxide. During the repeat tests, either nitric acid or carbon dioxide was used. Carbon dioxide was obtained from evaporating dry ice. The amounts of nitric acid or sodium hydroxide required for the adjustments are shown in Table A-2. The pH adjustment step was not required for the

TABLE A-1. Simulant Slurry Compositions

Component	A	B	C	D	E	F
KTPB (g/L)	60	60	60	60	30	60
(~wt %)	5	5	5	5	2.5	5
			Concentration (molar)			
Na^+	5.5	5.5	2.8	0.65	0.1	4.5
OH^-	3.0	<.01	0.01	0.50	<.01	2.6
NO_3^-	1.36	3.00	1.51	0.15	0.075	0.64
NO_2^-	0.50	1.10	0.56	–	–	0.69
AlO_2^-	0.21	0.47	0.24	–	–	0.17
CO_3^{2-}	0.10	0.22	0.11	0.25	–	0.17
SO_4^{2-}	0.093	0.20	0.10	–	–	0.009
Cl^-	0.016	0.036	0.018	–	–	0.013
F^-	0.010	0.022	0.011	–	–	0.007
PO_4^{3-}	0.006	0.014	0.007	–	–	0.006

TABLE A-2. Slurry Irradiation and pH Adjustment

Slurry	Composition*	Total Dose (Mrad)	pH Adjustment (target)
1	A	0	none required (3 M OH⁻)
2	A	30	none required (3 M OH⁻)
3	B	0	4.85 mL of 7.5 M HNO_3 (pH 10)
4	B	30	4.35 mL of 7.5 M HNO_3 (pH 10)
5	C	15	1.25 mL of 7.5 M HNO_3 (pH 12)
6	C	15	1.25 mL of 7.5 M HNO_3 (pH 12)
7	C	15	1.50 mL of 7.5 M HNO_3 (pH 12)
8	C	15	2.70 mL of 4 M NaOH (pH 12)
9	D	0	none required (0.5 M OH⁻)
10	D	30	none required (0.5 M OH⁻)
11	E	0	0.5 mL/7.5 M HNO_3 and 0.1 mL of 4 M NaOH (pH 10)
12	E	0	0.25 mL/7.5 M HNO_3 and 0.1 mL of 4 M NaOH (pH 10)
13	E	30	0.5 mL of 4 M NaOH (pH 10)
14	E	30	none required (pH 10)
15	C	15	CO_2 (pH 10)
16	C	15	CO_2 (pH 10)
17	C	15	CO_2 (pH 10)
18	C	15	CO_2 (pH 10)
19	B	0	5.0 mL of 7.5 M HNO_3 (pH 10)
20	B	0	CO_2 (pH 10)
21	B	30	4.6 mL of 7.5 M HNO_3 (pH 10)
22	B	30	CO_2 (pH 10)
22	E	0	0.25 mL of 7.5 M HNO_3 (pH 10)
24	E	0	CO_2 (pH 10)
25	E	30	0.25 mL of 7.5 M HNO_3 (pH 10)
26	E	30	CO_2 (pH 10)
27	F	0	none required (2.6 M OH⁻)
28	F	0	none required (2.6 M OH⁻)
29	F	0	none required (2.6 M OH⁻)

*See Table A-1.

TABLE A-3.   Catalyst Components in Simulant Slurries

Insoluble Components (wt % of slurry)*
       1.2 g/L (~1 wt %) sludge
       1.2 g/L (~1 wt %) monosodium titanate

Sludge composition (wt % of dry sludge):

Al	4.8	Cu	0.1
Fe	18.8	Mg	0.1
Mn	5.9	Ni	2.5
Ru	0.23	Pb	0.3
Pd	0.11	Zn	0.2
Rh	0.06	Zr	2.5
Cr	0.2		

Metal Additives (mg/L)

Ca(II)	12.2	Ru(III)	0.8	Cd(II)	0.4
Sr(II)	0.1	Co(II)	0.04	Hg(II)	2.2
La(III)	0.05	Rh(III)	0.2	Si(IV)	16
Ce(IV)	0.3	Pd(II)	0.4	Sn(III)	2.1
Cr(VI)	60	Cu(II)	1.7	Pb(II)	1.2
Mo(VI)	12.	Ag(I)	0.6	As(IV)	0.04
Fe(III)	2.6	Zn(II)	8.8	Se(VI)	1

Organic Additives (mg/L)

3PB	500	Diphenylmercury	150
2PB	250	Methanol	4
Phenol	250	Isopropanol	40
Benzene	750		

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* The experiment measuring the effect of sludge and noble metals concentration used 0.2, 1.0, and 2.0 wt % of these components (sludge and monosodium titanate). The other components were not varied.

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experiment measuring the effect of sludge and noble metal concentration (Slurry F). Approximately 65 mL of slurry were placed in 70-mL glass serum bottles. Uranyl nitrate (51 mg) was added to Slurry 7 and all the vials were capped. The vapor space above Slurry 12 was flushed gently with nitrogen for 5 minutes. The vials were then placed in an oven or thermostated Co-60 gamma irradiation source at 45 °C (±3 °C). The gamma source contained two shelves, once of which was partially shielded. The dose rates for the two shelves were 1.5×10^4 and 2.8×10^4 rad/h. The vials were sampled by syringe once a week for eight weeks. The samples were filtered using disposable nitrocellulose filters (0.45 micron nominal pore size).

Analytical Results

The filtered samples were analyzed for potassium ion, organic compounds (NaTPB, 3PB, 2PB, 1PB, and phenol), and pH. A few

filtrate samples were analyzed for total boron and a few
slurry samples were analyzed for benzene. The initial and
final filtrate samples were also analyzed for the potentially
catalytic metals (Cu, Ag, Ru, Rh, and Pd). The analytical
results from all experiments are listed in Table A-4.

Several of the initial samples showed high results for both K^+
and NaTPB, in excess of the amount expected from the
solubility of KTPB. Analyses of two of these initial samples
(Runs 4 and 8) were repeated six weeks later along with one
initial sample (Run 12) in which the potassium and NaTPB
appeared consistent with the solubility of KTPB. Table A-5
summarizes the results. The repeat analyses confirmed the
original potassium results but failed to confirm the high
NaTPB results. Soluble NaTPB is relatively stable once it is
separated from the precipitate and sludge solids, as shown by
the results of the Run 12 sample (no loss of NaTPB in 6
weeks). The loss of NaTPB was not reflected by increases in
3PB and 2PB, although they might have decomposed also. No
precipitate was observed in the stored samples indicating
that the decrease in NaTPB was not caused by precipitation of
KTPB during storage (also confirmed by the fact that K^+ did
not change). The initial K^+ results agree with the trend in
potassium shown in subsequent samples. These results imply
the NaTPB results were erroneously high.

Analytical Methods

The following analyses were performed by the Analytical
Development Section of SRTC.

Phenylboronic acid (1PB) and phenol were measured by high
performance liquid chromatography (HPLC) on a Hewlett Packard
LC with a 2.1x250 mm Dychrom Chemosorb 5-ODS-UH column using
acetonitrile-water eluent. The HPLC instrument methods are
described in Manual L16.1, Procedure #ADS-2655. The
methodology of sample preparation, standards, and standard
preparation for HPLC analyses is described in SRT-ADS-96-0438.
A control solution was submitted with each set of samples to
verify consistent performance of the HPLC method. The control
samples contained NaTPB, 1PB and phenol. The results for the
controls were consistently within ±10% of the average.

Potassium ion concentrations were measured by flame atomic
absorption using a Varian SpectrAA-400 spectrometer. The
samples were first digested in nitric acid by microwave
heating. Each digested sample was diluted
1:4(sample:suppressant) in a suppressant solution of 2000
μg/mL cesium. For more concentrated samples, additional
dilutions were made with 1600 μg/mL cesium. The method is
described in Manual L16.1, Procedure #ADS-1549.

Copper and boron concentrations were measured by Inductively
Coupled Plasma Emission Spectroscopy (ICPES) using an ARL

3580 instrument. Samples for copper were diluted 10X and acidified to a pH less than or equal to 2 using 5 wt % nitric acid. Spiked samples were analyzed with each sample to verify that there was no loss of copper. A 1000 mg/L copper standard purchased from High Purity, Inc. was used to prepare the spikes. Samples for boron analysis were first digested by heating in nitric acid. The methods are described in Manual L16.1, Procedure #ADS-1509 and in Reference 20.

Silver, ruthenium, rhodium, and palladium were measured using a Fisons PQS-974 ICPMS according to the method described in Manual L16.1, Procedure #ADS-1553. The salt solution samples were diluted by a factor of 100 with dilute nitric acid prior to analysis.

The pH was measured using a Radiometer autotitration system equipped with a standard size combination pH electrode (Orion). For alkaline samples, the system was calibrated using at two points using pH 7 and pH 10 standardized buffer solutions (Fisher Scientific).

Dose rates for the sample geometry used in the Co-60 gamma sources were measured with nylon film dosimeters by Waste Processing Technology personnel.[21]

Benzene was analyzed by gas chromatography by Waste Processing Technology personnel. Samples were prepared by injecting ~0.2 mL of slurry into 0.1-L glass bulbs. The benzene was allowed to evaporate into the vapor space, then portions of the vapor space were injected into an HNU Model 301 gas chromatograph with 10.2 eV photoionization detector and 1/8 inch diameter x 3 ft long column packed with 3 wt % SP-2100 on Chromosorb 120/140 (Whatman Co.). The methods used are described in Manual L12.1, Procedure ITP-006,Rev.3 (12/20/94) and Procedure ITP-OP-005, Rev.3(12/20/94).

TABLE A-4. Analytical Results for Solids Stability Tests

Note: All results are soluble concentrations in filtered samples.

Run 1 — 5.5 M Na+ | 3 M OH- | Unirrad. | No continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<.09	-	0.11	1.70	0.77	2.85	3.6	0.4	<.03	0.8	0.2	7.4	-	-
7	32	-	<.03	<.04	<.06	1.02	5.6	-	-	-	-	-	-	-
14	52	-	<.03	0.05	0.12	0.30	7.6	-	-	-	-	-	-	-
21	84	-	<.03	<.04	<.06	0.20	7.7	-	-	-	-	-	-	-
28	96	-	-	-	-	-	-	-	-	-	-	-	-	-
35	122	-	-	-	-	-	-	-	-	-	-	-	-	-
42	138	-	-	-	-	-	-	-	-	-	-	-	-	-
49	139	-	-	-	-	-	-	-	-	-	-	-	-	-
56	225	-	-	-	-	-	-	5.2	<.03	1.7	1.3	0.2	-	-

Run 2 — 5.5 M Na+ | 3 M OH- | 30 Mrad | High continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<.005	-	0.21	2.1	0.89	2.85	3.7	0.4	0.01	0.5	0.2	3.1	-	-
7	9.7	-	<.03	0.48	0.42	0.87	6.3	-	-	-	-	-	-	-
14	29	-	<.03	0.05	0.12	0.29	6.6	-	-	-	-	-	-	-
21	53	-	<.03	<.04	0.17	0.24	4.9	-	-	-	-	-	-	-
28	65	-	-	-	-	-	-	-	-	-	-	-	-	-
35	92	-	-	-	-	-	-	-	-	-	-	-	-	-
42	105	-	-	-	-	-	-	-	-	-	-	-	-	-
49	141	-	-	-	-	-	-	-	-	-	-	-	-	-
56	159	-	-	-	-	-	-	2.6	0.1	3.1	1.6	10.2	-	-

Run 3 — 5.5 M Na+ | pH 10 | Unirrad. | High continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	48	10.55	0.14	1.10	3.1	3.3	2.8	0.1	<.03	0.4	0.2	4.9	-	-
7	23	10.62	<.03	<0.4	1.9	4.2	2.0	-	-	-	-	-	-	-
14	463	10.50	<.03	<.04	3.7	7.2	2.3	-	-	-	-	-	-	-
21	783	10.50	<.03	<.04	4.1	0.29	<.1	-	-	-	-	-	-	-
28	812	10.44	<.03	<.04	3.2	-		-	-	-	-	-	-	-
35	940	10.34	<.03	<.04	2.0	-		-	-	-	-	-	-	-
42	1094	10.30	-	-	-	-		-	-	-	-	-	-	-
49	1373	10.29	-	-	-	-		-	-	-	-	-	-	-
56	1410	10.19	-	-	-	-		0.4	<.03	0.9	1	3.6	-	-

Run 4 — 5.5 M Na+ | pH 10 | 30 Mrad | No continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	52	10.50	0.46	0.71	2.6	2.7	4.1	1.0	0.8	0.5	0.2	13.5	11.8	-
7	155	10.66	0.30	0.05	1.9	3.7	2.2	-	-	-	-	-	-	-
14	145, 102	10.61	<.03	0.02	2.2	6.8	5.6	-	-	-	-	-	-	-
21	353	10.80	<.03	<.04	1.5	0.94	5.5	-	-	-	-	-	-	-
28	1341	10.90	<.03	<.04	1.4	-	-	-	-	-	-	-	-	-
35	2210	10.97	<.03	<.04	1.0	-	-	-	-	-	-	-	-	-
42	2959	10.80	-	-	-	-	-	-	-	-	-	-	-	-
49	3373	11.04	-	-	-	-	-	-	-	-	-	-	-	-
56	3482	10.98	-	-	-	-	-	0.5	<.03	1.4	1.2	1.2	122	-

Run 5 — 2.8 M Na+ | pH 12 | 15 Mrad | Low continuous dose rate (duplicate midpoint)

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	136	12.23	0.22	2.3	3.3	0.89	3.5	0.1	0.2	0.4	0.05	5.9	7.0	-
7	191	12.28	0.20	0.04	1.4	2.2	2.9	-	-	-	-	-	-	-
14	207	12.16	<.03	<0.4	2.0	2.8	4.3	-	-	-	-	-	-	-
21	300	12.30	<.03	<.04	2.5	1.7	3.8	-	-	-	-	-	-	-
28	357	12.23	<.03	<.04	2.8	-	-	-	-	-	-	-	-	-
35	367	12.17	<.03	<.04	2.5	-	-	-	-	-	-	-	-	-
42	419	12.14	-	-	-	-	-	-	-	-	-	-	-	-
49	439	12.09	-	-	-	-	-	-	-	-	-	-	-	-
56	446	11.98	-	-	-	-	-	0.2	0.3	0.3	0.7	9.6	20.9	-

Run 6 — 2.8 M Na+ | pH 12 | 15 Mrad | Low continuous dose rate (duplicate midpoint)

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	127	12.24	0.21	2.3	3.1	2.9	3.3	0.9	0.08	0.2	0.04	6.3	-	-
7	200	12.29	0.20	0.02	1.4	3.2	3.2	-	-	-	-	-	-	-
14	237	12.14	<.01	<.04	2.1	3.6	4.4	-	-	-	-	-	-	-
21	328	12.30	<.01	<.04	2.5	3.0	4.0	-	-	-	-	-	-	-
28	349	12.20	<.01	<.04	2.7	-	-	-	-	-	-	-	-	-
35	383	12.15	<.01	<.04	2.7	-	-	-	-	-	-	-	-	-
42	419	12.12	-	-	-	-	-	-	-	-	-	-	-	-
49	478	12.07	-	-	-	-	-	-	-	-	-	-	-	-
56	473	12.07	-	-	-	-	-	0.2	0.4	0.2	0.7	10.0	-	-

TABLE A-4. Analytical Results for Solids Stability Tests (Continued)

Note: All results are soluble concentrations in filtered samples.

Run 7 — 2.8 M Na+ | pH 12 | 15 Mrad | Low continuous dose rate | UO2 added

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	118	12.09	0.20	2.4	2.8	2.8	3.5	0.1	0.2	0.2	0.05	6.0	-	-
7	199	12.03	0.19	<.04	1.5	3.5	3.4	-	-	':	-	-	-	-
14	253	12.04	<.03	<.04	1.6	3.8	4.2	-	-	-	-	-	-	-
21	310	12.10	<.03	0.07	2.1	-	-	-	-	-	-	-	-	-
28	358	11.99	<.03	<.04	2.9	-	-	-	-	-	-	-	-	-
35	406	11.96	<.03	<.04	2.9	-	-	-	-	-	-	-	-	-
42	467	11.93	-	-	-	-	-	-	-	-	-	-	-	-
49	-	11.97	-	-	-	-	-	-	-	-	-	-	-	-
56	623	11.85	-	-	-	-	-	0.1	0.2	0.1	0.5	6.9	-	-

Run 8 — 2.8 M Na+ | pH 12 | 200 Mrad | Low continuous dose rate/Very high pre-dose)

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	409	12.00	0.73	2.0	1.09	5.0	4.1	1.2	0.3	0.2	0.2	9.8	-	-
7	329	12.00	0.68	0.64	0.71	3.4	4.7	-	-	-	-	-	-	-
14	322	11.73	<0.3	0.24	0.46	5.8	8.5	-	-	-	-	-	-	-
21	342	11.60	<.03	0.14	0.24	3.5	8.2	-	-	-	-	-	-	-
28	338	11.62	-	-	-	-	-	-	-	-	-	-	-	-
35	444	11.42	-	-	-	-	-	-	-	-	-	-	-	-
42	401	11.27	-	-	-	-	-	-	-	-	-	-	-	-
49	404	11.13	-	-	-	-	-	-	-	-	-	-	-	-
56	406	10.88	-	-	-	-	-	2.6	0.3	0.3	0.9	8.9	-	-

Run 9 — 0.65 M Na+ | 0.50 M OH- | Unirrad. | High continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	0.8	-	1.2	0.22	1.62	3.6	3.9	0.1	<.03	0.1	0.01	3.3	-	-
7	73	-	<.03	<.04	0.63	3.1	7.0	-	-	-	-	-	-	-
14	70	-	0.006	<0.4	0.97	2.8	10.2	-	-	-	-	-	-	-
21	128	-	<.03	0.04	0.46	1.4	10.6	-	-	-	-	-	-	-
28	158	-	-	-	-	-	-	-	-	-	-	-	-	-
35	209	-	-	-	-	-	-	-	-	-	-	-	-	-
42	211	-	-	-	-	-	-	-	-	-	-	-	-	-
49	203	-	-	-	-	-	-	-	-	-	-	-	-	-
56	190	-	-	-	-	-	-	0.4	<.03	0.3	0.2	5.3	-	-

Run 10 — 0.65 M Na+ | 0.50 M OH- | 30 Mrad | No continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	1.1	-	0.97	2.7	0.95	2.6	4.2	0.2	1.0	0.3	0.01	5.8	14.2	-
7	3.3	-	0.59	2.5	1.13	2.5	3.9	-	-	-	-	-	-	-
14	5.9	-	0.18	1.8	1.52	3.0	5.2	-	-	-	-	-	-	-
21	22	-	0.10	1.2	1.39	3.3	5.7	-	-	-	-	-	-	-
28	34	-	<.03	0.79	1.27	-	-	-	-	-	-	-	-	-
35	73	-	-	-	-	-	-	-	-	-	-	-	-	-
42	47	-	-	-	-	-	-	-	-	-	-	-	-	-
49	52	-	-	-	-	-	-	-	-	-	-	-	-	-
56	58	-	-	-	-	-	-	0.2	<.03	0.7	0.3	5.3	19.0	-

Run 11 — 0.1 M Na+ | pH 10 | Unirrad. | No continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	1.5	10.07	0.90	0.79	1.26	2.3	2.8	0.1	<.001	<.1	0.007	0.008	6.6	-
7	168	10.39	<.03	<.04	0.63	5.0	6.3	-	-	-	-	-	-	-
14	250	10.24	0.012	<.04	0.31	4.2	7.5	-	-	-	-	-	-	-
21	447	10.40	<.03	<.04	0.38	3.9	8.0	-	-	-	-	-	-	-
28	556	10.36	-	-	-	-	-	-	-	-	-	-	-	-
35	893	10.28	-	-	-	-	-	-	-	-	-	-	-	-
42	894	10.28	-	-	-	-	-	-	-	-	-	-	-	-
49	1247	10.36	-	-	-	-	-	-	-	-	-	-	-	-
56	1446	10.20	-	-	-	-	-	0.2	<.03	<.1	<.05	0.3	53.4	-

Run 12 — 0.1 M Na+ | pH 10 | Unirrad. | No continuous dose rate | N2 flush

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	1.5	10.22	0.90	1.9	1.21	2.3	2.9	0.1	<.03	<.02	0.007	0.12	6.5	-
7	140	10.55	<.03	0.02	0.84	5.5	5.6	-	-	-	-	-	-	-
14	251, 292	10.36	0.006	<0.4	0.47	4.7	6.7	-	-	-	-	-	-	-
21	431	10.60	<.03	0.01	0.42	4.3	7.4	-	-	-	-	-	-	-
28	515	10.51	-	-	-	-	-	-	-	-	-	-	-	-
35	690	10.45	-	-	-	-	-	-	-	-	-	-	-	-
42	712	10.44	-	-	-	-	-	-	-	-	-	-	-	-
49	861	10.08	-	-	-	-	-	-	-	-	-	-	-	-
56	989	10.46	-	-	-	-	-	0.1	<.03	<.02	<.007	0.03	40.1	-

TABLE A-4. Analytical Results for Solids Stability Tests (Continued)
Note: All results are soluble concentrations in filtered samples.

Run 13 | 0.1 M Na+ | pH 10 | 30 Mrad | High continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	2	10.10	0.81	2.2	0.64	2.19	3.1	0.5	0.01	0.02	0.01	5.7	-	-
7	67	10.22	<.03	0.39	<.06	1.26	6.7	-	-	-	-	-	-	-
14	33	9.99	0.05	0.01	<.06	<.08	9.5	-	-	-	-	-	-	-
21	70	10.20	<.03	0.05	<.06	<.08	7.8	-	-	-	-	-	-	-
28	79	10.14	-	-	-	-	-	-	-	-	-	-	-	-
35	106	10.03	-	-	-	-	-	-	-	-	-	-	-	-
42	110	10.00	-	-	-	-	-	-	-	-	-	-	-	-
49	134	10.10	-	-	-	-	-	-	-	-	-	-	-	-
56	136	9.80	-	-	-	-	-	4.6	0.2	0.2	0.3	7.5	-	-

Run 14 | 0.1 M Na+ | pH 10 | 30 Mrad | High continuous dose rate, 1/2 solids (vs. Run 13)

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	1.7	10.06	0.96	1.90	0.64	2.16	3.2	0.5	<.03	0.04	0.02	3.8	-	-
7	44	10.19	<.03	0.39	<.06	1.30	6.5	-	-	-	-	-	-	-
14	33	9.94	0.08	<.04	<.06	<.08	7.9	-	-	-	-	-	-	-
21	48	10.08	0.10	<.04	<.06	<.08	6.0	-	-	-	-	-	-	-
28	63	10.04	0.04	<.04	0.06	-	-	-	-	-	-	-	-	-
35	72	9.82	-	-	-	-	-	-	-	-	-	-	-	-
42	93	9.69	-	-	-	-	-	-	-	-	-	-	-	-
49	125	9.70	-	-	-	-	-	-	-	-	-	-	-	-
56	120	9.67	-	-	-	-	-	5.1	0.6	0.1	0.3	8.5	-	-

Run 15 | 2.8 M Na+ | pH 10 (CO2) | 15 Mrad | Low continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<1	10.2	2.1	1.72	5.3	1.48	0.5	-	<.05	0.03	0.01	3.8	-	-
7	209	-	<.03	<.05	0.32	7.5	3.2	-	-	-	-	-	-	-
14	250	-	<.03	<.05	0.41	3.8	3.7	-	-	-	-	-	-	-
21	338	-	<.03	<.05	0.55	3.5	4.8	-	-	-	-	-	-	-
28	457	-	<.03	<.05	0.57	3.0	5.8	-	-	-	-	-	-	-
35	727	-	<.03	<.05	0.41	2.6	5.8	-	-	-	-	-	-	-
42	617	10.12	<.03	<.05	0.26	2.7	5.7	-	<.02	0.43	0.81	1.81	-	-

Run 16 | 2.8 M Na+ | pH 10 (CO2) | 15 Mrad | Low continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1P3 (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<1	9.94	2.2	1.81	5.5	1.15	0.6	-	<.05	0.02	0.01	3.4	-	-
7	235	-	<.03	<.05	0.18	5.5	2.9	-	-	-	-	-	-	-
14	270	-	<.03	<.05	0.21	2.7	4.6	-	-	-	-	-	-	-
21	366	-	<.03	<.05	0.22	1.76	5.6	-	-	-	-	-	-	-
28	498	-	<.03	<.05	0.19	1.68	7.5	-	-	-	-	-	-	-
35	627	-	<.03	<.05	0.18	1.72	6.3	-	-	-	-	-	-	-
42	709	9.95	<.03	<.05	0.07	1.23	5.7	-	<.02	0.52	0.85	1.66	-	-

Run 17 | 2.8 M Na+ | pH 10 (CO2) | 15 Mrad | N2 inerted, no continuous dose rate.

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<1	10.30	2.1	1.72	5.5	1.74	0.6	-	<.05	0.03	0.01	4.1	-	-
7	252	-	<.03	0.066	0.76	10.0	2.5	-	-	-	-	-	-	-
14	345	-	<.03	<.05	0.79	10.7	2.0	-	-	-	-	-	-	-
21	494	-	<.03	<.05	0.76	10.2	3.5	-	-	-	-	-	-	-
28	653	-	<.03	<.05	0.68	11.6	5.0	-	-	-	-	-	-	-
35	783	-	<.03	<.05	0.66	11.0	4.5	-	-	-	-	-	-	-
42	910	10.62	<.03	<.05	0.58	10.2	5.3	-	<.02	0.59	0.76	0.2	-	-

Run 18 | 2.8 M Na+ | pH 10 (CO2) | 15 Mrad | 2.5 wt % solids, high continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<1	10.30	2.0	1.63	5.1	1.66	0.6	-	<.05	0.02	0.01	3.8	-	-
7	137	-	<.03	<.05	0.71	5.6	1.3	-	-	-	-	-	-	-
14	256	-	<.03	<.05	1.54	4.8	0.7	-	-	-	-	-	-	-
21	378	-	<.03	<.05	1.64	3.7	0.7	-	-	-	-	-	-	-
28	502	-	<.03	<.05	1.89	3.8	0.6	-	-	-	-	-	-	-
35	650	-	<.03	<.05	1.69	4.5	0.6	-	-	-	-	-	-	-
42	949	10.05	<.03	<.05	1.12	4.2	2.0	-	>19	0.46	0.77	6.6	-	-

Run 19 | 5.5 M Na+ | pH 10 (5.0 mL HNO3) Unirrad. High continuous dose rate. | Rate (mg/L/day)

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Fhenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	2	10.60	<.03	1.12	3.1	2.3	1.6	-	<.05	0.38	0.13	3.0	4.0	-
5	154	-	<.03	<.05	2.3	5.5	2.4	-	-	-	-	-	-	-
12	305	-	<.03	<.05	2.4	5.9	1.1	-	-	-	-	-	-	-
19	503	-	<.03	<.05	3.2	7.0	1.0	-	-	-	-	-	-	-
27	635	-	<.03	<.05	3.6	8.6	0.8	-	<.05	0.83	0.87	1.8	23.3	-
34	808	-	<.03	<.05	2.6	10.4	0.9	-	-	-	-	-	-	0.7
41	965	9.99	<.03	<.05	1.5	10.8	1.8	0.79	<.05	0.76	0.87	2.7	-	-

TABLE A-4. Analytical Results for Solids Stability Tests (Continued)

Note: All results are soluble concentrations in filtered samples.

Run 20 — 5.5 M Na+ | pH 10 (CO2) | Unirrad. | High continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	2	10.30	<.15	0.81	1.86	2.4	2.9	-	<.05	0.33	0.11	3.3	3.3	-
5	139	-	<.03	<.05	1.23	5.9	3.3	-	-	-	-	-	-	-
12	291	-	<.03	<.05	1.41	5.8	1.0	-	-	...	-	-	-	-
19	444	-	<.03	<.05	1.51	5.2	0.5	-	-	-	-	-	-	-
27	554	-	<.03	<.05	2.2	6.5	0.6	-	<.05	1.00	1.1	2.0	21.6	-
34	725	-	<.03	<.05	1.25	7.3	0.9	-	-	-	-	-	-	3.9
41	850	10.10	<.03	<.05	0.66	7.4	1.4	0.078	<.05	1.04	0.125	2.9	-	-

Run 21 — 5.5 M Na+ | pH 10 (4.6 mL HNO3) | 30 Mrad | No continuous dose rate.

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<1	10.30	0.77	1.17	3.2	2.5	2.8	-	0.31	0.37	0.13	6.8	9.0	-
5	73	-	<.03	<.05	5.2	7.6	4.0	-	<.05	0.98	0.67	8.8	-	-
12	209	-	<.03	<.05	2.8	11.4	4.1	-	<.05	1.2	0.91	8.3	-	-
19	441	-	<.03	<.05	1.76	16.1	4.7	-	<.05	1.4	1.1	7.3	-	-
27	1626	-	<.03	<.05	0.88	50	6.8	-	<.05	1.4	1	3.4	62	-
34	3124	-	<.03	<.05	0.48	73	7.6	-	-	-	-	-	-	284
41	3756	10.60	<.03	<.05	0.12	79	10.2	0.3	<.05	1.5	1.1	1.5	-	-

Run 22 — 5.5 M Na+ | pH 10 (CO2) | 30 Mrad | No continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<1	10.20	0.58	0.79	1.66	2.8	3.6	-	0.52	0.03	0.02	2.3	8.2	-
5	75	-	0.058	<.05	5.1	8.4	4.9	-	<.05	1.1	0.86	9.3	-	-
12	263	-	<.03	<.05	1.90	13.4	5.1	-	<.05	1.4	1.1	8.6	-	-
19	1397	-	<.03	<.05	0.91	40	6.5	-	<.05	1.7	1.3	4.7	-	-
27	2593	-	0.26	<.05	0.31	69	7.4	-	<.05	1.6	1.1	2.1	92	-
34	3783	-	<.03	<.05	0.09	70	7.9	-	-	-	-	-	-	316
41	3892	10.50	<.03	<.05	<.06	63	10.9	0.29	<.05	1.8	1.3	1.5	-	-

Run 23 — 0.1 M Na+ | pH 10 (5 drops HNO3) | Unirrad. | No continuous dose rate.

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	5	9.96	0.33	<.05	1.42	3.6	2.9	-	<.05	0.03	0.02	2.3	4.7	-
5	217	-	<.03	<.05	1.48	5.8	5.5	-	-	-	-	-	-	-
12	486	-	<.03	<.05	0.60	7.1	8.3	-	-	-	-	-	-	-
19	768	-	<.03	0.054	0.87	8.6	9.5	-	-	-	-	-	-	-
27	791	-	<.03	<.05	0.49	8.8	11.1	-	<.05	0.14	0.03	0.03	33	-
34	1283	-	<.03	<.05	0.91	8.4	16.4	-	-	-	-	-	-	11.8
41	1672	10.20	<.03	0.057	1.06	14.2	24	0.023	<.05	0.19	0.043	0.058	-	-

Run 24 — 0.1 M Na+ | pH 10 (CO2) | Unirrad. | No continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	4	10.10	0.35	<.05	1.42	1.67	3.0	-	<.05	0.04	<.01	2.9	3.0	-
5	231	-	<.03	<.05	2.3	5.4	5.1	-	-	-	-	-	-	-
12	476	-	<.03	<.05	0.68	7.4	7.9	-	-	-	-	-	-	-
19	775	-	<.03	0.070	0.91	9.0	9.5	-	-	-	-	-	-	-
27	912	-	<.03	<.05	0.59	9.1	10.5	-	<.05	0.16	0.03	<.02	34	-
34	1132	-	<.03	<.05	0.59	7.9	12.3	-	-	-	-	-	-	11.7
41	1386	10.30	<.03	<.05	0.58	9.4	19.4	0.025	<.05	0.22	0.05	0.03	-	-

Run 25 — 0.1 M Na+ | pH 10 (5 drops HNO3) | 30 Mrad | High continuous dose rate.

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	7	9.97	0.20	1.72	1.05	2.2	1.9	-	0.21	0.03	0.02	3.3	8.2	-
5	44	-	<.03	0.43	0.24	1.23	5.0	-	-	-	-	-	-	-
12	48	-	<.03	<.05	<.06	<.2	6.1	-	-	-	-	-	-	-
19	65	-	<.03	<.05	<.06	<.1	5.3	-	-	-	-	-	-	-
27	71	-	<.03	<.05	<.06	<.1	3.8	-	0.54	0.12	0.14	6.9	14.2	-
34	89	-	<.03	<.05	<.06	<.1	2.7	-	-	-	-	-	-	0.17
41	126	9.61	<.03	<.05	<.06	<.1	3.1	3.9	0.95	0.19	0.25	6.8	-	-

Run 26 — 0.1 M Na+ | pH 10 (CO2) | 30 Mrad | High continuous dose rate

Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	7	9.98	0.20	1.62	0.98	1.84	2.0	-	0.18	0.03	0.02	3.5	8.5	-
5	45	-	<.03	0.42	0.29	1.16	5.3	-	-	-	-	-	-	-
12	49	-	<.03	<.05	<.06	0.29	7.0	-	-	-	-	-	-	-
19	64	-	<.03	<.05	<.06	<.1	6.3	-	-	-	-	-	-	-
27	70	-	<.03	<.05	<.06	<.1	4.7	-	0.44	0.12	0.14	6.7	14.1	-
34	90	-	<.03	<.05	<.06	<.1	<.1	-	-	-	-	-	-	0.01
41	129	9.70	<.03	<.05	<.06	<.1	3.6	3.9	1.03	0.19	0.22	7.2	-	-

TABLE A-4. Analytical Results for Solids Stability Tests (Continued)

Note: All results are soluble concentrations in filtered samples.

Run 27	4.5 M Na+	2 wt % sludge, 2 wt % MST, Full ECC cat.												
Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<3	.	0.57	1.69	1.18	1.86	1.86	0.34	<.05	1:4	0.32	7.2	-	-
5	<3	.	<.03	0.07	3.7	-	-	-	<.05	4.2	0.88	0.07	-	-
11	71	.	<.03	<.05	0.13	-	-	-	<.05	4.3	1.1	0.016	-	-
18	138	.	<.03	<.05	0.05	-	-	-	<.05	4.3	1.3	0.23	-	-
26	200	.	<.03	<.05	<.06	-	-	-	0.073	4.0	1.4	0.14	-	-
33	277	.	<.03	<.05	0.06	-	-	-	<.05	4.0	1.4	0.29	-	-
40	322	.	<.03	<.05	0.09	2.8	5.7	-	<.02	4.0	1.2	0.40	-	-
47	427	.	<.03	<.05	0.09	-	-	-	<.02	4.6	1.8	0.18	-	-
54	636	.	<.03	<.05	0.15	1.68	14.7	1.41	<.02	4.51	2.0	0.34	-	-
Run 28	4.5 M Na+	0.2 wt% sludge, 0.2 wt % MST, Full ECC cat.												
Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<3	.	0.56	1.69	1.23	1.79	2.9	0.39	<.05	0.33	0.22	0.67	-	-
5	<3	.	0.36	5.0	4.6	-	-	-	<.05	1.2	0.47	0.12	-	-
11	6	.	0.31	6.4	2.9	-	-	-	<.05	1.2	0.48	0.17	-	-
18	<2	.	0.105	5.4	2.9	-	-	-	<.05	1.2	0.49	0.15	-	-
26	<2	.	<.03	4.2	4.5	-	-	-	<.05	1.3	0.5	0.042	-	-
33	7	.	<.03	2.8	3.1	-	-	-	<.05	1.25	0.47	0.020	-	-
40	3	.	<.03	1.53	1.60	<.1	14.3	-	<.02	1.14	0.34	0.046	-	-
47	5	.	<.03	0.96	0.56	-	-	-	<.02	1.3	0.46	0.063	-	-
54	9	.	<.03	0.86	0.18	1.16	19.2	2.2	<.02	1.33	0.51	0.127	-	-
Run 29	4.5 M Na+	1.0 wt % sludge, 1.0 wt % MST, full ECC cat.												
Elapsed Time (days)	K+ (mg/L)	pH	NaTPB (mmolar)	3PB (mmolar)	2PB (mmolar)	1PB (mmolar)	Phenol (mmolar)	Cu (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	B (mmolar)	Benzene (mmolar)
0	<3	.	0.56	1.63	1.16	1.76	2.8	0.35	<.05	0.74	0.27	1.8	-	-
5	<3	.	0.032	0.70	9.1	-	-	-	<.05	2.8	0.79	0.056	-	-
11	19	.	<.03	<.05	2.3	-	-	-	<.05	2.9	0.90	0.083	-	-
18	39	.	<.03	<.05	0.35	-	-	-	<.05	2.9	1.00	0.087	-	-
26	106	.	<.03	<.05	0.11	-	-	-	<.05	2.9	1.10	0.041	-	-
33	117	.	<.03	<.05	0.10	-	-	-	<.05	2.7	1.03	0.09	-	-
40	167	.	<.03	<.05	0.09	0.36	9.4	-	<.02	2.8	1.12	0.27	-	-
47	279	.	<.03	<.05	0.21	-	-	-	<.02	3.3	1.30	0.15	-	-
54	412	.	<.03	<.05	0.34	1.98	15.4	1.32	<.02	3.32	1.41	0.29	-	-

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TABLE A-5. Comparison of Initial and Repeat Analyses of Samples Showing High K+ and NaTPB

Sample		Concentration (mg/L) K+	NaTPB	3PB	2PB
Run 4	Day 0	52	156	173	475
	Day 0 (repeat)*	45	<10	201	20
Run 8	Day 0	409	249	495	199
	Day 0 (repeat)*	404	<10	521	174
Run 12	Day 0	1.5	308	452	220
	Day 0 (repeat)*	5	315	505	252

*The Day 0 (initial) filtrate samples were re-analyzed after 6 weeks storage at room temperature.

APPENDIX B
Statistical Analysis

Experimental Design

A designed experimental plan was developed to study the influence of four factors (Na^+ molar concentration, pH, pre-irradiation in Mrad, and dose rate in rad/hr) on the stability of the solids in solutions typical of those processed at ITP. This designed experiment consisted of ten experiments. Subsequently, additional experimental trials were conducted. The results from all of these experiments are presented in Table 1.

Note that pH column is expressed as two additional columns: OH^- molar concentration and its reciprocal.

Table B-1: Experimental Design and Results

Notes	Flask #	Na^+ (molar)	pH	OH^- molar	$1/OH^-$ l/molar	Pre-irrad (Mrad)	Dose Rate (rad/hr)	Response: K+ (mg/L/day)
original design	1	5.5	14.5	3.00000	0.333333	0	0	3.8
original design	2	5.5	14.5	3.00000	0.333333	30	28000	2.9
original design	3	5.5	10.4	0.00025	4000	0	28000	26
original design	4	5.5	10.8	0.00060	1666.667	30	0	11 (124)
original design	5	2.8	12.2	0.01600	62.5	15	15000	5.9
original design	6	2.8	12.2	0.01600	62.5	15	15000	6.3
	7	2.8	12.0	0.01000	100	15	15000	8.5
	8	2.8	11.5	0.00300	333.3333	200	15000	1.1
original design	9	0.65	13.7	0.50000	2	0	28000	5
original design	10	0.65	13.7	0.50000	2	30	0	1.2
original design	11	0.1	10.3	0.00020	5000	0	0	26
	12	0.1	10.4	0.00025	4000	0	0	17
original design	13	0.1	10.1	0.00013	7692.308	30	28000	2.2
	14	0.1	9.9	0.00010	10000	30	28000	2
Repeat of #3 (HNO_3)	15	5.5	10.3	0.00008	12500	0	28000	23
Repeat of #3 (CO_2)	16	5.5	10.2	0.00020	5000	0	28000	20
Repeat of #4 (HNO_3)	17	5.5	10.4	0.00016	6250	30	0	23 (178)
Repeat of #4 (CO_2)	18	5.5	10.4	0.00025	4000	30	0	22 (159)
Repeat of #11 (HNO_3)	19	0.1	10.1	0.00025	4000	0	0	38
Repeat of #11 (CO_2)	20	0.1	10.2	0.00013	7692.308	0	0	32
Repeat of #13 (HNO_3)	21	0.1	9.8	0.00016	6250	30	28000	2.4
Repeat of #13 (CO_2)	22	0.1	9.8	0.00006	16666.67	30	28000	2.4
	23	2.8	10.2	0.00006	16666.67	15	15000	15
	24	2.8	9.9	0.00016	6250	15	15000	14
	25	2.8	10.5	0.00008	12500	15	0	19
	26	2.8	10.2	0.00016	6250	15	29000	22

The ten original design points are indicated in this table. Four flasks (7, 8, 12, and 14) were added to the experimental plan to investigate the following specific conditions: for flask # 7, UO_2 was added; flask # 8 was subjected to a very high pre-irradiation dose; for flask # 12, the solution was under nitrogen instead of oxygen, and the solids concentration for flash # 14 was low (2.5 wt%). Some of these original design points (as indicated in Table 1) were subsequently repeated, twice, once using HNO_3 and then using CO_2, to help attain the target pH.

The experimental plan was designed to generate data for the estimation of linear effects for the four factors. Flasks 5 and 6 are center points of the design region and were added to provide an opportunity for assessing the adequacy of such a linear model.

The solids stability was measured by the milligrams of K^+ precipitated per liter of solution per day. Note that for three of the experiments (flasks 4 and its repeats, flasks 17 and 18) two different response rates are provided in Table 1. For these experiments, there appeared to be two rates of potassium precipitation. An initial slow rate followed by an accelerated rate (shown in parentheses in Table 1) later. Many of the analyses that follow are conducted twice, first with the initial rates representing these experiments and then using the accelerated rates.

Statistical Models

A number of statistical models were explored to investigate the relationship between these precipitated K+ values and the factors of Table 1. As noted above, in the analyses that follow, the data from Table 1 will used to explore the various statistical models in two ways:

  (a) flasks 4, 17, and 18 represented by their initial rates (init) and
  (b) these flasks represented by their accelerated rates (accel).

Also, the factors Na+, Pre-irradiation, and dose rate were consistently included in the models that follow.

The pH factor was introduced into these models in one of several forms, either as pH, OH^-, or $1/OH^-$. These models were analyzed using JMP®, a statistical software package from SAS Institute in Cary, NC, and they are summarized in Table 2.

Table B-2: Results From Fitting The Statistical Models

Model	Table 1 Data	Intercept Term	Na+		Pre-irrad	Dose Rate		Effect of pH Term	Estimate	R^2
1	init	61.7 *	1.18	*	-0.100 *	-0.00033	*	pH	-4 *	0.578
	accel	166.0 *	11.70	*	0.016	-0.00188	*	pH	-12.7 *	0.580
2	init	18.4 *	1.32		-0.116 *	-0.00029	*	OH^-	-5.92 *	0.467
	accel	28.2 *	12.64	*	-0.040	-0.00178	*	OH^-	-22.85 *	0.566
3	init	15.2 *	0.839		-0.095 *	-0.00034	*	$1/OH^-$	0.00058	0.357
	accel	19.3	10.54	*	0.028	-0.00191	*	$1/OH^-$	0.00164	0.459

An * after a value indicates that the estimate was statistically significant at the 10%; init and accel represent the use of the data in Table 1 as indicated above.

The R^2 value for each of the fitted models is given. This value for a fitted model represents the fraction of the variability of the response data explained by the model. The R^2 values for these models indicate that they explain only about 36 to 58% of the variation in the K^+ rates. The best model (in terms of these R^2 values) appears to be Model 1 which may be expressed as

(for the "init" data)

$$Response^+ (mg/L/day) = 61.7 + 1.18 \left(Na^+_{molar} \right) - 4.00(pH) - 0.100 \left(Pre\text{-}irrad_{Mrad} \right) - 0.0003 \left(Dose\ Rate_{rad/hr} \right)$$

and

(for the "accel" data)

$$Response^+ (mg/L/day) = 166.0 + 11.7 \left(Na^+_{molar} \right) - 12.7(pH) + 0.016 \left(Pre\text{-}irrad_{Mrad} \right) - 0.0018 \left(Dose\ Rate_{rad/hr} \right)$$

Other Functional Forms for the Factors

Several other functional forms for the factors (a quadratic term for $1/OH^-$, sodium represented by $exp\left(\sqrt{Na^+_{molar}} \right)$), were explored for the data ("init" and "accel") of Table 1. The explanatory capabilities of these models, as indicated by their R^2 values, are comparable to the models summarized in Table 2. The results of fitting these special functions are provided in Table 3.

Table B-3: Results From Fitting Additional Statistical Models

Model	Table 1 Data	Intercept Term	f(Na)	Pre-irrad	Dose Rate	Effect of pH Term	Estimate	R^2
4	init	60.9 *	0.704 *	-0.099 *	-0.00033 *	pH	-4 *	0.579
	accel	158.4 *	7.198 *	0.030 *	-0.00188 *	pH	-12.8 *	0.600
5	init	17.4 *	0.817 *	-0.115 *	-0.00029 *	OH^-	-6.02 *	0.472
	accel	18.4	7.911 *	-0.026	-0.00178 *	OH^-	-23.96 *	0.595
6	init	14.6 *	0.507	-0.094 *	-0.00034 *	$1/OH^-$	0.00058	0.358
	accel	11.1	6.518 *	0.042	-0.00191 *	$1/OH^-$	0.00168	0.477
7	init	8.9 *	0.562	-0.071	-0.00032 *	$1/OH^-$	0.00321 *	
						$(1/OH^-)^2$	-1.767e-7 *	0.554
	accel	-6.4	6.684 *	0.112	-0.00184 *	$1/OH^-$	0.00964 *	
						$(1/OH^-)^2$	-5.352e-7 *	0.557

Model	Table 1 Data	Intercept Term	Na+	Pre-irrad	Dose Rate	Effect of pH Term	Estimate	R^2
8	init	9.4 *	0.973	-0.072	-0.00032 *	$1/OH^-$	0.00324 *	
						$(1/OH^-)^2$	-1.783e-7 *	0.557
	accel	1.2	10.953 *	0.100	-0.00184 *	$1/OH^-$	0.00984 *	
						$(1/OH^-)^2$	-5.508e-7 *	0.556

An * after a value indicates that the estimate was statistically significant at the 10%; init and accel represent the use of the data in Table 1 as indicated above; and f(Na) is used to represent $\exp\left(\sqrt{Na^+_{molar}}\right)$.

A Comparison of pH Adjustments Using HNO_3 Versus CO_2

The set of repeated experiments (flasks 15-22) used different mechanisms to adjust the pH (as indicated in Table 1): nitric acid (HNO_3) and carbon dioxide (CO_2). This provides an opportunity to test for an effect in the response due to this difference. The appropriate test (for the init and accel data) is in the form of a paired-t test which is provided in the following figures.

Figure B-1. Paired Comparison of K+ Rates (Initial and Accelerated)
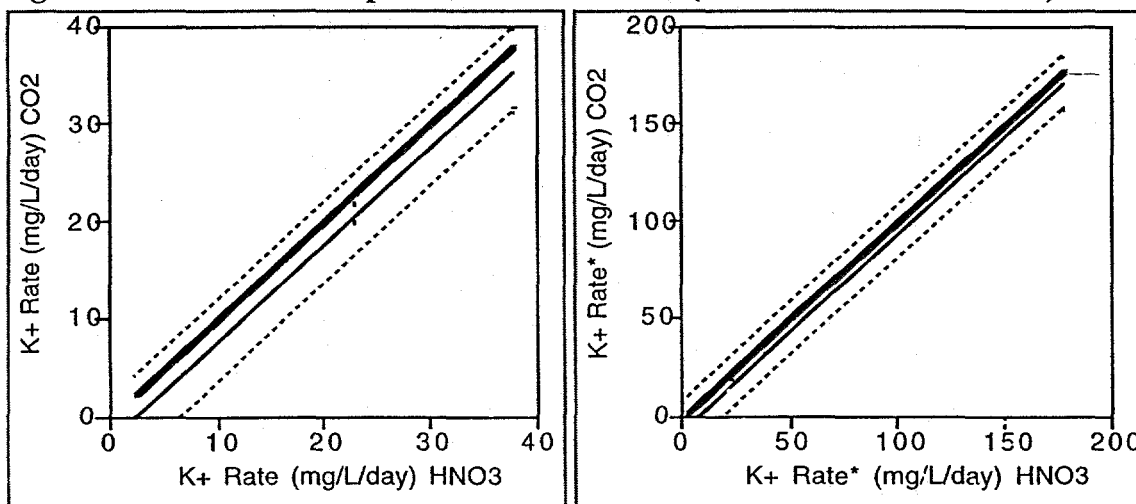
These are plots of the decomposition rates for the carbon dioxide experimental runs versus the nitric acid. The solid bold line on the diagonal shows where the points would fall if there was no effect on the response

due to the different pH adjustment mechanisms. The second solid line indicates the estimated effect from these data with the dotted lines being 95% confidence limits for this estimated effect. The responses for the nitric acid adjustments are somewhat higher than their corresponding carbon dioxide experiments. However, since the bold line is within the confidence limits, there is no indication of a statistical difference between the HNO_3 and CO_2 adjustments at the 5% significance level. The statistical details of these results are given in the following exhibits (a Prob > |t| value less than 0.05 would indicate a significant difference):

Paired t-Test for "init" Data

K+ Rate (mg/L/day) HNO3 - K+ Rate (mg/L/day) CO2

Mean Difference	2.5	Prob > |t|	0.1552
Std Error	1.322876	Prob > t	0.0776
t-Ratio	1.889822	Prob < t	0.9224
DF	3		

Paired t-Test for "accel" Data

K+ Rate* (mg/L/day) HNO3 - K+ Rate* (mg/L/day) CO2

Mean Difference	7	Prob > |t|	0.1929
Std Error	4.1833	Prob > t	0.0964
t-Ratio	1.67332	Prob < t	0.9036
DF	3		

Additional data from other paired HNO_3 and CO_2 experiments would allow for a more sensitive statistical test for a difference in the responses.

Concluding Comments

Based upon the results presented in Tables 2 and 3, several models indicate that the factors studied in these experiments have statistically significant effects on KTPB decomposition. The low R^2 values, however, indicate that the models explain only a small portion of the variability seen in these responses. Introducing additional factors in future experimentation and, possibly, exploring more complicated statistical models may be helpful in improving the understanding of the significant effects.

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