ITP Solids Stability Operating Window Tests

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ITP SOLIDS STABILITY OPERATING WINDOW TESTS

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ITP Solids Stability Operating Window Tests

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ITP SOLIDS STABILITY OPERATING WINDOW TESTS

By D. D. WALKER

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. Recent tests investigated the stability of the potassium tetraphenylborate (KTPB) solids under process conditions, during both precipitation and washing. In addition, the tests measured the relative stabilities of the sodium, potassium and cesium tetraphenylborate (NaTPB, KTPB, and CsTPB, respectively). Additional tests examined the similarity of the catalytic system in the reaction of soluble and insoluble tetraphenylborates. The following points summarize the test results.

- Maintaining the pH of the slurry above 12 does not ensure benzene generation rates less than 7 mg/L/h.
    - The rates of increase in soluble potassium vary from 5.8 to 27.1 mg/L/day at 45 °C, corresponding to benzene generation rates of 2-9 mg/L/h.
- Reaction rates in the simulants containing 13 mg Pd per liter nearly equaled those for radioactive waste tests by Hobbs, et al.[5] containing only 0.15 mg Pd per liter. The differences in reactivity relative to the total mass of palladium may reflect
    - presence of palladium in a catalytically inactive form (e.g., PdO),
    - synergistic effect between Pd and other metals in the mixture (e.g., Cu, Mo, Ce, or Hg), or
    - the presence of an additional catalytic metal in radioactive waste (e.g., Pt, Tc, V, W, Re, Os, or Ir).
- The experimental method for preparing dilute salt solutions affects the rate of decomposition.
    - The dilution method most closely resembling tank operations produces slower decomposition rates, varying from 5.8 to 19.3 mg K^+/L/d (or 2-6.4 mg benzene/L/h).
- Statistically significant correlations of the K^+ rate with hydroxide ion or sodium ion concentration (i.e., the variables in the test matrix) were not found.
    - This suggests an uncontrolled variable affects the rates in the simulant tests.

- Solid tetraphenylborate compounds show the following relative reactivity:

  $$\text{Rate}_{\text{NaTPB}} = 24\cdot\text{Rate}_{\text{KTPB}} = 73\cdot\text{Rate}_{\text{CsTPB}}$$

  - The Tank 48H observation that excess NaTPB reacted much faster than KTPB is consistent with expectations from the drop in tank temperature and this order of reactivity.

- Increasing the initial concentrations of triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB) from 250 mg/L to 2000 mg/L of each did not significantly increase the rate of decomposition of KTPB solids.

- The catalytic system for decomposition of solids is similar to the catalytic system for decomposition of soluble tetraphenylborate.

INTRODUCTION

Previous measurements of the rate of increase in soluble potassium and cesium from the decomposition of KTPB slurries suggested hydroxide ion concentration and temperature as major controlling factors.[1-2] Based on data at 45-70°C, temperature was judged an insufficient control to maintain solids reaction rates below 21 mg K^+/L/d (corresponding to a benzene generation rate of 7 mg/L/h).[2] However, the previous results suggested that maintaining the pH above 12 would produce potassium rates in the range 1-10 mg/L/d. In this study, additional simulant tests over a range of waste compositions above pH 12 were carried out at 45 °C to define an operating window for Tank 48H. Other tests measured the relative rates of decomposition of NaTPB, KTPB, and CsTPB solids. The purpose of these tests was to establish an explanation for an observation during radioactive operations in Tank 48H in 1995. In Tank 48H, the excess NaTPB reacted rapidly and completely within a few weeks, but KTPB and CsTPB solids reacted very slowly during the following year. This test also examined the effect of intermediates on the reactivity of the solids. The design and results of these tests are described in this report.

The results of these tests are summarized as 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 phenol 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.

$$\left(\frac{1\ \text{mg K}^+}{\text{L-day}}\right)\text{x}\left(\frac{1\ \text{mmol K}^+}{39.1\ \text{mg K}^+}\right)\text{x}\left(\frac{4\ \text{mmol benzene}}{1\ \text{mmol K}^+}\right)\text{x}\left(\frac{78.12\ \text{mg benzene}}{1\ \text{mmol benzene}}\right)\text{x}\left(\frac{1\ \text{day}}{24\ \text{h}}\right) = 0.333\ \frac{\text{mg benzene}}{\text{L-h}}$$

This work fulfills a request from P. L. Rutland, "TPB Solids Stability," Technical Task Request #HLE-TTR-98039, Rev.0, March 11, 1998. The work was performed in accordance with the following plan: D. D. Walker, "Technical Task Plan for Solids Stability Studies of Tetraphenylborate Slurries - Additional Studies," WSRC-RP-98-00055, Rev.0, March 4, 1998.

DISCUSSION

Operating Window Test Design

The purpose of the operating window test was to determine the rate of KTPB solids decomposition at conditions within the expected operating range in Tank 48H. The major variables in the test were total salt concentration and hydroxide ion concentration (pH). The test also examined the dependence of the reaction rate on the method of reducing the salt concentration (i.e., the influence of the washing process on reaction rate). The test matrix included 20 experiments with simulated waste slurries. Table I summarizes the variables and fixed conditions.

The concentrations of sodium ion (0.2 to 5.5 M) and hydroxide ion concentrations (0.022 to 3.0 M) varied within the expected ITP operating range. Figure 1 shows the distribution of the test compositions. The range included dilute solutions arising from precipitate washing ($pH > 12$), but did not include low pH slurries ($pH < 12$) that might arise during long term storage of washed precipitates in Tank 49H.

In preparing the slurries for the test, the following two preparation sequences were used.

A. Prepare KTPB slurry at the target salt solution concentration, add catalyst, and incubate.

B. Prepare KTPB slurry in concentrated salt solution, add catalyst, incubate for 1 week to initiate decomposition of excess NaTPB, dilute to required [Na^+](potentially affecting catalyst concentration), add NaTPB and intermediates, and incubate.

Methods A and B differ in two potentially important ways. In Method A, palladium is added after dilution to the desired sodium concentration whereas in Method B dilution occurs after palladium addition. Thus, a portion of the palladium could be removed by Method B. In this respect, Method B more closely resembles proposed operations than does Method A. The second difference relates to the conditions under which the catalyst is activated. Method A activates the catalyst under the final dilution conditions. Method B activates the catalyst at high salt concentrations. Both methods were tested on all salt compositions that correspond to partially or fully washed slurries. However, both methods employ shorter contact times between catalyst and salt solution compared to proposed operations. Slow changes in the form of palladium could affect the final decomposition rate.

TABLE I. Solids Stability Operating Window Test Design

Fixed conditions

Temperature	45 °C
KTPB solids concentration	60 g/L (~5 wt %)
Sludge/ECC catalyst*	12 g/L (~1 wt %)
Atmosphere	sealed under air
Mixing	no mixing

Salt solution compositions

Test	Na^+(M)	OH^-(M)	Dilution Sequence**
1	5.5	1.8	A
2	5.5	0.6	A
3	4.5	3.0	A
4	4.5	1.5	A
5	4.5	0.5	A & B
6	3.15	1.05	A & B
7	2.8	1.9	A & B
8	2.8	0.3	A & B
9	1.8	0.6	A & B
10	1.0	0.11	A & B
11	0.4	0.3	A & B
12	0.2	0.022	A & B

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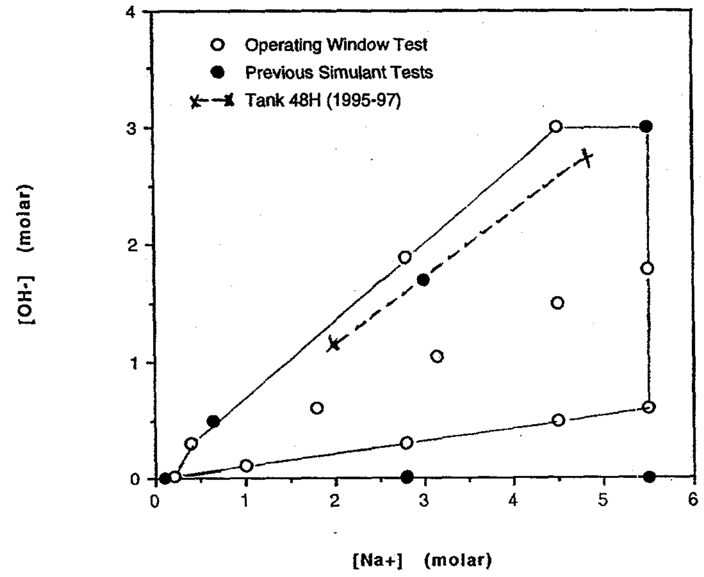
*ECC = Enhanced Comprehensive Catalyst. See Reference 3 for composition.

**Dilution sequences include: A, prepare concentrated solution, add catalyst, and incubate; and B, prepare concentrated solution, add catalyst, incubate for 1 week, dilute to required [Na^+], add NaTPB and intermediates, and incubate.

Figure 1. Distribution of Salt Solution Compositions



Operating Window Test Results

K^+ Rates

The appearance of soluble potassium ion was used as a measure of the loss of tetraphenylborate solids (KTPB and CsTPB). In all cases the concentration of K^+ ion increased linearly with time after the initial excess NaTPB decomposed. Table II summarizes the test conditions and the observed rates of increase in soluble potassium. All data and details of the experiments are listed in Appendix A with graphs showing the linear increase in potassium.

The rates of increase in soluble potassium varied from 5.8 to 27.1 mg/L/day at 45 °C. As expected, these rates fall within the range of 1 to 178 mg/L/day measured in previous testing over a broader pH range (pH 10 to pH 14.5). However, this range is higher than expected for the restricted pH range (pH 12 to 14.5). Previous testing showed no rates greater than 10 mg K^+/L/day when the pH was greater than 12. Table III lists selected data from earlier tests[2] for comparison to results listed in Table II. For example, the first two entries in Table III (rates = 3.8 and 2.9 mg/L/day) provide the nearest matches in composition to Tests 1 and 3 in Table II (rates = 5.8 and 10.5 mg/L/day). Although the Table II rates are faster, they compare favorably when one considers the differences in sodium and hydroxide concentrations. Previous testing found that decreasing the hydroxide concentration or increasing the sodium concentration increased the reaction rate. However, comparing the third and fourth entries in Table III (rates = 5.9 and 6.3 mg K^+/L/d) to tests #7 and 8 in Table II (rates = 7.2 to 23.0 mg/L), the recent results are much faster despite the much higher hydroxide concentrations. Also, comparing the last two entries in Table III (rates = 5.0 and 1.2 mg/L/d) to Test #11 in Table II (13.0 to 17.4 mg K^+/L/d), the recent results are again much faster despite similar hydroxide concentration.

Although suppression of the previous rates is due in part to radiation effects, the higher range in the current data set may be due to a change in the experimental method of adding palladium. In previous solids stability tests, only one source of sludge and palladium was used. This sludge batch was prepared in 1994 when acidic palladium(II) nitrate solution was added to the alkaline sludge. The mixture was subsequently aged for 2-3 years prior to use in earlier tetraphenylborate decomposition tests. In the ITP solids stability operating window tests, a new sludge batch was used and the acidic palladium(II) nitrate solution was added to the alkaline tetraphenylborate slurry at the start of the decomposition test. Aging in alkaline solution may provide time for soluble palladium to convert to insoluble forms. Pd(II) slowly changes to less soluble Pd^0 under anoxic, high pH conditions.[4] Since the slurry was aged under aerobic, high pH conditions, conversion to Pd^0 is unlikely. However, it may have slowly precipitated as the less reactive PdO hydrate.[6] Thus, tests using freshly added Pd(II) will have higher initial soluble palladium concentrations which may more easily become active catalyst, thereby yielding higher reaction rates.

The difference in soluble palladium was confirmed by comparing the two sources in the absence of tetraphenylborate solids but with monosodium titanate and other sludge metals

TABLE II. Rates of Increase in Soluble K$^+$ from Operating Window Test*

Test	Na$^+$(M)	OH$^-$(M)	Dilution Method†	K$^+$ Rate (mg/L/day)	K$^+$ Rate (mM/day)	Benzene** (mg/L/h)
1	5.5	1.8	A	5.8	0.15	1.9
2	5.5	0.6	A	16.8	0.43	5.6
3	4.5	3.0	A	10.5	0.27	3.5
4	4.5	1.5	A	7.1	0.18	2.4
5	4.5	0.5	A	9.9	0.25	3.3
			B	10.6	0.27	3.5
6	3.2	1.0	A	12.4	0.32	4.1
			B	6.1	0.16	2.0
7	2.8	1.9	A	12.4	0.32	4.1
			B	7.2	0.18	2.4
8	2.8	0.3	A	23.0	0.59	7.7
			B	13.9	0.36	4.6
9	1.8	0.6	A	24.1	0.62	8.0
			B	8.3	0.21	2.8
10	1.0	0.11	A	25.0	0.64	8.3
			B	19.3	0.49	6.4
11	0.4	0.3	A	17.4	0.44	5.8
			B	13.0	0.33	4.3
12	0.2	0.022	A	27.1	0.69	9.0
			B	13.6	0.35	4.5

---

* Fixed conditions: Temperature, 45 °C; KTPB solids concentration, 60 g/L (~5 wt %); Sludge/ECC catalyst concentration, 12 g/L (~1 wt %); atmosphere, sealed under air; and no mixing. ECC = Enhanced Comprehensive Catalyst (see Reference 3).

**See Introduction for method of calculation.

† Dilution sequences are: A, prepare concentrated solution, add catalyst, and incubate; and B, prepare concentrated solution, add catalyst, incubate for 1 week, dilute to required [Na$^+$], add NaTPB and intermediates, and incubate.

TABLE III. Selected K$^+$ Rates From Previous Tests*

Na$^+$(M)	OH$^-$(M)	Radiation Pre-test** (Mrad)	Radiation During*** (rad/h)	K$^+$ Rate (mg/L/day)
5.5	3.0	0	0	3.8
5.5	3.0	30	2.8E4	2.9
2.8	0.015	15	1.5E4	5.9
2.8	0.015	15	1.5E4	6.3
0.65	0.50	0	2.8E4	5.0
0.65	0.50	30	0	1.2

---

*See Reference 2.

** Co-60 gamma dose applied to slurry prior to adding catalyst and incubating.

*** Gamma dose rate applied after adding catalyst and during incubation.

present. The two sources were stirred in salt solution for two weeks at 45 °C, filtered, and analyzed for soluble palladium. The new method (addition of fresh, acidic Pd(II) solution to the salt solution containing sludge solids) yielded higher soluble Pd than the older method (addition of aged, alkaline sludge solids containing palladium), even though the total palladium was the same.

Source	Soluble Pd (mg/L)
New method (acidic Pd(II) added at start of test)	9.3
Previous method (Pd(II) aged 3 yr in alkaline sludge)	4.8

These results are based on single analyses and the reproducibility was not measured. However, these and the results of solubility tests showing slow changes in the form of palladium[4] suggest that slurry preparation and catalyst addition methods may affect the form of the palladium and thus the rate of decomposition. The effects of different slurry preparation methods, catalyst addition methods, and aging of simulants is unknown.

Comparison to Radioactive Waste Tests

The rates of solids decomposition in radioactive waste tests[5] overlap the range of rates found in the Operating Window Tests at similar sodium and hydroxide concentrations. Table IV summarizes results of the radioactive waste and simulant tests. However, the concentration of palladium, which is the most significant catalytic metal, differ by two orders of magnitude. There are three potential reasons for the difference. First, another metal (besides Pd) or synergism between metals in the radioactive waste may increase the reaction rate when palladium is present in low concentrations. Hobbs[5] found that radioactive waste contains measurable quantities of several metals (i.e., Tc, W, Re, Os, Ir, and Pt) not included in the ECC catalyst system. In addition, other metals (such as Cu and Ce) are present in radioactive waste at much higher concentrations than in the ECC catalyst. Second, the palladium in the radioactive waste may be more reactive because it is in a more active form. Recent tests with different forms of palladium suggest that different chemical forms catalyze the reaction at different rates.[6] However, the most reactive of the forms tested is used in the simulants, suggesting that this is a less likely explanation. Third, there may be a larger fraction of active palladium in radioactive waste tests compared to simulants. If this is true, then less than 1 % of the palladium in the simulant tests is active.

Effect of Washing Sequence

The washing sequence appears to affect the decomposition rate. Method B (dilution after adding catalyst) yielded slower rates in all but one test (Table V). The average drop in rate was 35%. Less than 4% of the total palladium was removed by washing and the change in rate did not correlate with the amount removed. Thus, it seems unlikely that the loss of palladium was the cause of the rate reduction, unless washing selectively removes the active catalyst. It seems more likely that stopping the reaction (i.e., cooling and washing) has a general deactivating effect on the insoluble catalyst.

TABLE IV. Comparison of Radioactive Waste and Simulant Tests[a]

Test	Na^+ (M)	OH^- (M)	Total Pd (mg/L)	K^+ rate (range) (mg/L/d)
Radioactive[b]				
3A	4.8	2.1	0.15	4.8 - 10.2
3C	4.9	2.2	0.16	10.5 - 13.5
4A	5.0	2.1	0.09	3.3 - 7.5
Simulant[c]				
1	5.5	1.8	13	5.8
2	5.5	0.6	13	16.8
3	4.5	3.0	13	10.5
4	4.5	1.5	13	7.1

---

[a] Temperature = 45 °C.
[b] See Reference 5.
[c] See Table II.

TABLE V. Effect of Dilution Method on K^+ Rate

Test	K^+ Rate (mg/L/day) Dilution Method A	B	Rate Change (A-B)	Rate Ratio (A/B)	Dilution Factor*	Pd Removed (mg)**
5	9.9	10.6	-0.7	0.93	1.2	0.005
6	12.4	6.1	6.3	2.0	1.4	0.005
7	12.4	7.2	5.2	1.7	1.6	0.005
8	23.0	13.9	9.1	1.7	2.0	0.018
9	24.1	8.3	15.8	2.9	2.5	0.021
10	25.0	19.3	5.7	1.3	5.5	0.11
11	17.4	13.0	4.4	1.3	22.5	0.35
12	27.1	13.6	13.5	2.0	27.5	0.30

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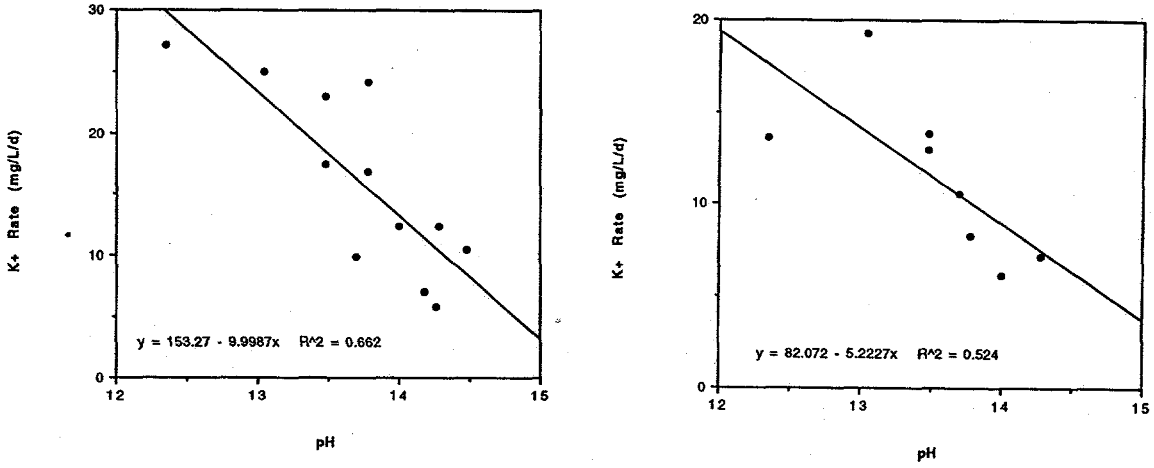
*Dilution factor = Initial $[Na^+]$/Final $[Na^+]$
** The total Pd was approximately 10 mg.

FIGURE 2. Correlation Between K$^+$ Rate and pH


Dilution Method A

Dilution Method B

Statistical correlations with [OH$^-$] and [Na$^+$]

Statistically significant correlations of the K$^+$ rate with hydroxide ion or sodium ion concentrations were not found when data from both washing sequences were combined. When the data from the two washing sequences were separated, statistically significant correlations were obtained. For Method A data, the rate of appearance of potassium correlated with the hydroxide ion concentration in molar units. For Method B data, the rate correlated with pH, in agreement with previous results.[2] Figure 2 shows these correlations for the two data sets. Including sodium ion concentration in the correlation did not improve the correlation coefficients shown in Figure 2. The low correlation coefficients (0.66 and 0.52) indicate additional factors are affecting the rate.

Implication to Reaction Mechanism

The absence of a correlation between changes in rate and the amount of soluble palladium removed by washing suggests that the active catalyst is not a soluble palladium species. This is further supported by the observation that the rate tends to decrease with increasing pH. The solubility of palladium increases with pH,[4] so the rate of decomposition should also increase if the catalyst is a soluble Pd(II) aquo or hydroxo complex.

B Rates

The rates of increase in soluble potassium are paralleled by similar rates of increase in the soluble boron. Since soluble TPB$^-$ disappeared during the tests, this result confirms that

KTPB decomposed. The decomposition rates calculated from the changes in boron concentrations were slightly higher than the potassium rates. This is attributed to leaching of boron from the borosilicate glass containers used in the tests. The magnitude of the difference was confirmed by leaching a glass vessel in the absence of phenyl borate compounds (see Appendix A).

Comparative Reactivity of Solids

Test Design

The relative rates of decomposition were measured for NaTPB, KTPB, CsTPB, and mixtures of NaTPB and KTPB solids. Table VI lists the fixed conditions and variables for these tests. The elevated temperature (55 °C) compared to other tests decreased the duration of the test. The initial sodium ion concentration was 5.0 M to depress the solubility of sodium tetraphenylborate. The rates of reaction were determined from increases in soluble boron and, where feasible, from increases in soluble K^+ or Cs^+. The rate of decomposition of NaTPB solids cannot be reliably determined from changes in sodium concentration in concentrated salt solutions, so in this case the rate was calculated from the soluble boron analyses.

TABLE VI. Test Design to Compare Reactivity of Na, K, Cs, and Na/K mixtures of Tetraphenylborate Solids

Fixed Conditions

Temperature	55 °C
TPB Solids concentration	60 g/L (~5 wt %)
Sludge/ECC catalyst*	12 g/L (~1 wt %)
Atmosphere	sealed under air
Mixing	no mixing

Tetraphenylborate solids

Test	Solids	Initial Intermediates (mg/L of each)**
1	NaTPB	250
2	NaTPB	2000
3	KTPB	250
4	KTPB	2000
5	CsTPB	250
6	NaTPB/KTPB	250

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* ECC = Enhanced Comprehensive Catalyst. See Reference 3 for composition.

**Intermediates = triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB).

A second objective of these tests was to determine the effect of high concentrations of intermediate phenyl borate compounds on the decomposition rates of the solids NaTPB and KTPB solids. The initial concentrations of the intermediates were 2000 mg/L (of each intermediate) compared to 250 mg/L in other tests.

Three tests were repeated. Table VI, Test 3 using KTPB was repeated as a control to measure the reproducibility. Table VI, Test 5 using CsTPB was repeated because Cs^+ was not completely precipitated at the start of the experiment. As the first attempt at this test progressed, the Cs^+ decreased, then increased, limiting the accuracy of the measurement of the decomposition rate. Table VI, Test 6 using the mixture of NaTPB and KTPB was repeated to test the effect of the order of precipitation on the rate of decomposition. In the original test, KTPB was precipitated first, followed by precipitation of NaTPB. In the repeat test, KTPB and NaTPB were precipitated simultaneously.

Reaction Rates for NaTPB, KTPB, CsTPB, and Mixtures

Table VII lists the rates for the tests summarized in Table VI. Figure 3 shows graphically the difference in reactivity between the different compounds. The relative reaction rates and solubilities under the test conditions are listed in Table VIII. The calculated reaction rates are based on changes in B, K, and Cs for NaTPB, KTPB, and CsTPB respectively. The K and Cs reaction rates were confirmed by measurements of soluble boron (corrected for boron leaching from the glass vials). The NaTPB reaction rate was not corrected for boron leaching since the correction factor was negligible (<1.2%). The relative order of reactivity of the three compounds is:

$$\text{NaTPB} > \text{KTPB} > \text{CsTPB}.$$

The reactivity increases with solubility, but the differences in reactivity are smaller than the differences in the solubilities of the compounds.

The lower reactivity of KTPB and CsTPB solids relative to NaTPB solids agrees with observations from Tank 48H.[7] During the initial radioactive operations in 1995, rapid decomposition of the excess NaTPB (largely present as solids) was followed by slow decomposition of the KTPB and CsTPB. The NaTPB reaction rate was approximately 4 mM/day (based on loss of 35,600 moles of NaTPB in 161,000 gallons of slurry over a 2 week period).[7] The Tank 48H temperature during the two weeks ranged from 50 to 35 °C. Following the loss of NaTPB, the KTPB reacted at a rate of 0.001 mM/day in agreement with expected radiolytic decomposition. The turndown in Tank 48H ($\text{rate}_{\text{NaTPB}}/\text{rate}_{\text{KTPB}} = 4000$) was clearly much larger than in the laboratory tests (24). The larger turndown in Tank 48H was likely due to lowering the temperature of the tank (which eventually dropped to less than 30 °C).

FIGURE 3. Comparison of Reactivity of NaTPB, KTPB, CsTPB, and a Mixture of NaTPB and KTPB

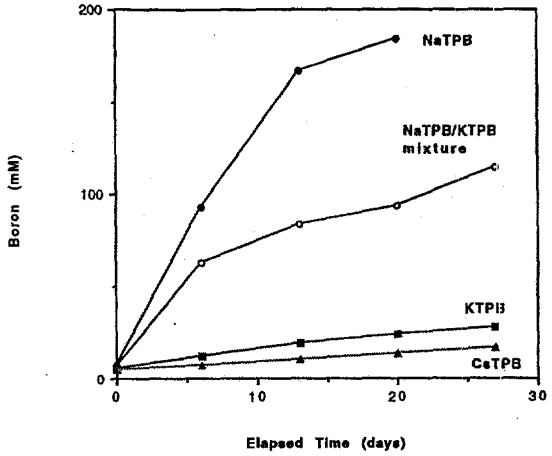

TABLE VII. Reaction Rates for Tetraphenylborate Solids

Test*	Solid Form	Rate (mM/d)
1	NaTPB (low intermediates)	12.2
2	NaTPB (high intermediates)	12.6
3	KTPB (low intermediates)	0.6
	KTPB repeat	0.44
4	KTPB (high intermediates)	0.50
5	CsTPB (low intermediates)	0.11
	CsTPB repeat	0.23
6	NaTPB/KTPB (precipitated separately)	9.4
	NaTPB/KTPB (precipitated simultaneously)	4.7

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* See Table VI.

TABLE VIII. Reaction Rates and Solubilities of Tetraphenylborates.

Compound	K_{sp}*		Decomposition Rate	
	(M^2)	Ratio	(mM/d)	Ratio
NaTPB	1.05	2.6×10^9	12.4	73
KTPB	2.5×10^{-7}	610	0.5	3
CsTPB	4.1×10^{-10}	1	0.17	1

---

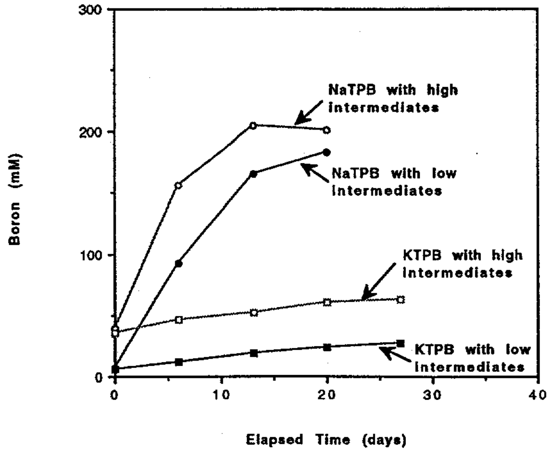
*At 55°C and 5.0 M Na^+. See Reference 8.

Mixed slurries containing 2.5 wt % NaTPB and 2.5 wt % KTPB were prepared by two methods. In one case, KTPB was precipitated first followed by NaTPB. In another case, the two compounds were precipitated simultaneously. When precipitated separately, the mixture initially decomposed rapidly at a rate similar to slurries in which only NaTPB was present (Figure 3). After the amount of decomposition equaled the amount of NaTPB initially present, the rate slowed to the rate of KTPB decomposition in a slurry containing only KTPB. When the two compounds were precipitated simultaneously, the initial reaction rate was slower and intermediate between the rates of NaTPB and KTPB. This result *suggests* mixed crystals are formed when the two compounds are precipitated simultaneously, thus showing reactivity intermediate between the two pure solid phases. However, reproducibility of the simultaneously-precipitated experiment was not determined except by similarity to the pure phase KTPB and NaTPB reactions. The standard deviations within these two sets of experiments were: KTPB, ±16%; and NaTPB, ±15%. Thus, the 50% slower rate observed for simultaneously precipitated NaTPB and KTPB (compared to separately precipitated) appears to differ more than expected from the variability within the two sets of pure phase experiments. Similar reasoning suggests that the difference in initial conditions for the two tests with CsTPB affected the decomposition rate.

Effect of Phenyl Borate Concentrations on Reaction Rate

No significant impact on the decomposition rate of tetraphenylborate was detected when the initial concentrations of the intermediate compounds (3PB, 2PB, and 1PB) were increased to 2000 mg/L (10 to 20 mM of each). Figure 4 shows the results for NaTPB and KTPB solids.

FIGURE 4. Effect of Intermediates on Decomposition Rate



Catalyst Identification Tests

Test Design

The catalyst identification tests investigated the effect of removing individual catalytic components (i.e., Pd, Hg, or intermediates) or all non-catalytic metals (i.e., include only Pd, Hg, intermediates, and benzene). The purpose of the tests was to determine if the catalytic system in the solids stability tests was similar to the catalytic system in *soluble* NaTPB decomposition tests. Five components of the simulated slurries have been identified as necessary for the rapid decomposition reaction of *soluble* tetraphenylborate: (1) palladium,[9] (2) mercury,[9] (3) intermediate compounds,[9] (4) tetraphenylborate solids,[10] and (5) benzene.[9] In the present study, five tests investigated the effect of removing catalytic components on the *solids* decomposition rate (Table IX).

The major difference between the soluble tetraphenylborate decomposition tests and solids decomposition tests is the initial soluble TPB^- concentration. Soluble TPB^- testing usually contains high initial amounts of TPB^- (15-30 mM) compared to the solids tests which contain low initial TPB^- (0.6 mM). In addition, soluble TPB^- tests usually terminate following the loss of the TPB^- (and before K^+ ion increases measurably). Solids tests normally ignore loss of the initial TPB^- but follow the subsequent increase in K^+ ion.

Catalyst Identification Test Results

The results of these tests indicate that the catalytic system for decomposition of solids is similar to the catalytic system for decomposition of soluble tetraphenylborate. That is, in those slurries in which soluble sodium tetraphenylborate decomposes, the reaction continues into the solid phase, decomposing KTPB and releasing K^+ ion.

Figure 5 shows the loss of tetraphenylborate and increase in potassium in the five tests. The major response features in each test are summarized below.

- Control: containing all of the ECC components
    - TPB^- decomposed within the first week.
    - K^+ increased at an average rate of 9 mg/L/d.
- Intermediate compounds removed (3PB, 2PB, and 1PB)
    - TPB^- decomposed slowly at first but became rapid after two weeks
    - K^+ increased at an average rate of 8 mg/L/d
- Sludge removed (contained only catalytic components)
    - TPB^- decomposed over 7 weeks
    - K^+ increased at >4 mg/L/d
- Mercury removed
    - TPB^- decomposed slowly, 40% loss in 67 days
    - No increase in K^+
- Pd removed
    - No loss of TPB^-
    - No increase in K^+

TABLE IX. Catalyst Identification Test Matrix

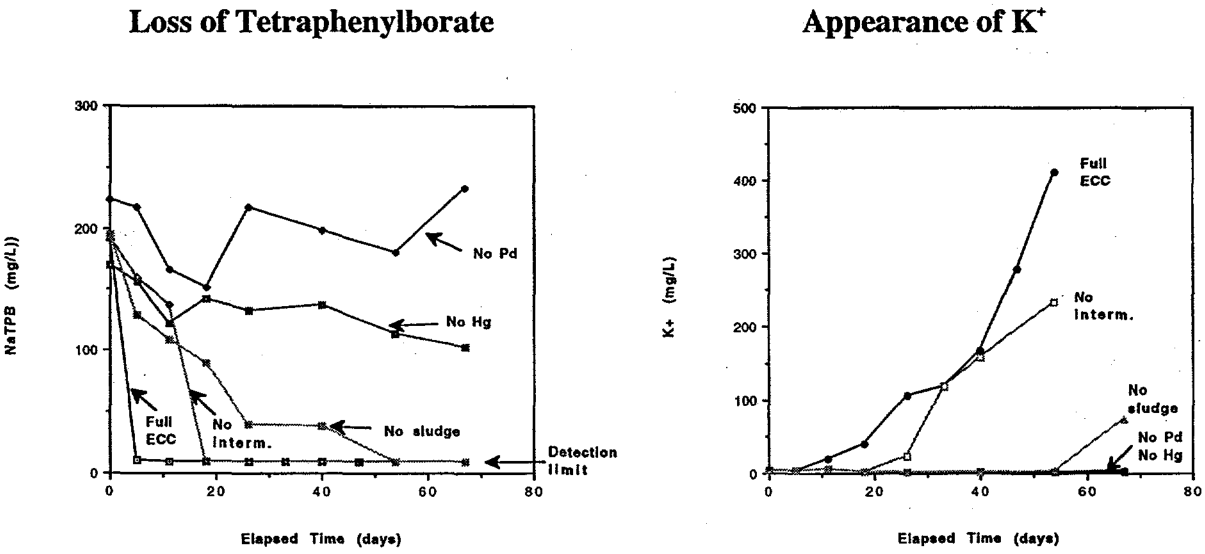
Fixed conditions:	Temperature:	45 °C
	Na^+ concentration	4.5 M
	OH- concentration	2.6 M
	KTPB concentration	60 g/L (~5 wt %)
	Container	glass, sealed under air
	Mixing	not mixed except when sampling

Test Matrix*

Test	Sludge	Pd	Hg	Interm.
1	+	+	+	+
2	+	-	+	+
3	+	+	-	+
4	+	+	+	-
5	-	+	+	+

A "+" indicates component was added at start of test. A "-" indicates component was omitted from test. When components were present, their concentration corresponded to 12 g sludge and catalyst per liter, or ~1 wt %.

Figure 5. Reactivity in Catalyst Identification Tests



The response of the control (9 mg/L/d) is intermediate between results from the operating window tests at similar sodium and hydroxide concentrations (Table II, Tests 3 and 4, 7.1 and 16.8 mg/L/d). The lack of reaction when palladium or mercury are removed and the delayed reaction when intermediates are initially absent mimic previous work by Barnes.[8] The apparently slow loss of soluble TPB^- when sludge was absent (i.e., only the catalytically active components - Pd, Hg, intermediates, and benzene - were added) may have been due to dissolution of more NaTPB solids compared to tests with sludge. The same amount of NaTPB was added to each test, but potassium in the sludge converted some of the excess NaTPB to KTPB in those cases where sludge was added. Thus, the test without sludge contained a larger amount of excess NaTPB (present as solid NaTPB). The excess NaTPB solids dissolved as soluble TPB^- decomposed. The larger excess in the absence of sludge maintained a higher soluble TPB^- concentration for a longer duration even though the reaction rates were similar. This was confirmed by a larger increase in boron in the test where sludge was not added.

The observation that solids decomposition follows loss of soluble TPB^- can be explained by two fundamentally different mechanisms. In one mechanism, the catalyst acts upon the soluble TPB^- first because it is more reactive than solids (due either to kinetic or thermodynamic differences). After the soluble TPB^- is consumed the catalyst reacts with the solids. In the second mechanism, the catalyst reacts only with solids. As KTPB decomposes, the released K^+ precipitates soluble TPB^- causing an apparent loss of soluble TPB^-. The first mechanism is supported by the apparent first order decay in TPB^- ion concentration observed in many tests. The second mechanism is suggested by Barnes' finding that the loss of soluble TPB^- is very slow in the absence of KTPB solids, although other explanations are possible.[10]

UNCERTAINTIES IN CURRENT WORK

The decomposition rate of solid tetraphenylborate generally increases if the temperature or palladium concentration is increased, or if pH is lowered. However, correlations between the reaction rate and these three parameters do not account for all of the variability in the data. The additional variability is likely due to an unidentified and uncontrolled variable. Testing employed a complicated simulant recipe with the intention of including all components that individually or synergistically affect the reaction rate. Since composition (in the sense of amounts and identity of elements added) is controlled, the uncontrolled variable may be the physical or chemical form of the components. Palladium is a likely candidate, but others such as particle size of the KTPB solids cannot be excluded. Since total palladium is controlled, different rates may arise due to differences in amounts of active palladium or differences in reactivity of different forms of palladium.

If additional understanding or more accurate predictions of reaction rates are needed, future testing should probe the identity of the active catalyst and the mechanism of activation. To answer these questions may require a fundamentally different experimental approach. To minimize the source of variables, the simulant should be simplified as much as possible. The following lines of investigation are suggested.

- Determine the catalytically active form of palladium.

  Use a simplified waste simulant to improve the usefulness of available analytical methods. Begin by examining the reaction of soluble TPB^- and soluble Pd(II). Extend this study to include other palladium forms, such as Pd metal of quantified surface area. Look for changes in the form of the palladium as the reaction proceeds. Once the active catalyst form is identified, previous experiments should be reviewed to determine how slurry preparation and catalyst addition methods may have affected the reaction rates.

- Determine the effect of redox state on the reactivity of the catalyst.

  Previous results suggest the oxidation state of the palladium is an important aspect of the active catalyst. Using a simplified waste simulant, study the effect of oxygen, Eh, radiation, organic compounds, and redox active metals (e.g., Cu, Hg) on the oxidation state of palladium and the reaction rate of palladium and TPB^-.

- Determine the effect of additional metals and test for synergism between metals.

  The difference in reaction rates between radioactive waste and simulants suggest additional metals (e.g., Pt, Tc, V, W, Re, Os, or Ir) are catalytic or synergism between metals (e.g., Cu, Mo, Ce, or Hg) is important at low palladium concentrations.

ACKNOWLEDGEMENTS

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APPENDIX A
Experimental

Preparation of Slurries

Researchers prepared simulated KTPB slurries (nominally 5 wt % KTPB solids) with the compositions shown in Table A-1. The operating window tests used Slurries A through C or dilutions of them as shown in Table A-2. The tests comparing the reactivity of NaTPB, KTPB, CsTPB and mixtures (comparative reactivity tests) used Slurry D. The catalyst identification tests used Slurry E. Slurries were prepared by the following general procedure unless otherwise noted. Researchers precipitated the KTPB (or CsTPB) in the presence of a low sodium ion concentration with the soluble sodium salts added after precipitation. For the NaTPB slurry required for the comparative reactivity test, the concentrated salt solution was prepared first followed by addition of 0.55 molar NaTPB solution. All chemicals were reagent grade. NaTPB (99+% purity) was obtained from Aldrich Chemical Company. On the day the tests began, 100 mL portions of slurry were placed in Erlenmeyer flasks and the components of the catalyst system (except benzene, diphenylmercury, and the alcohols) were added (Table A-3). The slurries and catalyst were stirred at room temperature for one hour. Approximately 65 mL of slurry were placed in 70-mL glass serum bottles, the benzene, diphenylmercury, and alcohols were added, the vials were capped with Teflon-lined serum caps and placed in an oven at 45 °C (±3 °C). The remaining slurry in the Erlenmeyer flask was used for the initial (zero time) sample. The vials were maintained at temperature, sealed, and unstirred for the duration of the test. Once a week, the vials were removed from the oven, shaken briefly by hand, and sampled by syringe. The samples were filtered using disposable nitrocellulose filters or copolymer syringe filters (0.45 micron nominal pore size).

In the operating window test, dilutions of the three high- sodium slurries (i.e., slurries B, C, and D in table A-1) were prepared by the following two methods.

Direct dilution without reaction.

(1) The original slurry was divided into portions (100-200 mL) prior to addition of the catalyst components.
(2) The required volume of dilution water was added and the slurry was mixed briefly by hand.
(3) The slurry was filtered, the filtered solids returned to the slurry, and the volume adjusted with filtrate to return to the starting volume (i.e., the slurry volume prior to dilution).
(4) The catalyst components were added.
(5) The slurries were placed in sealed vials and incubated at 45 °C.

Reaction followed by dilution.

(1) Catalyst was added to the original high sodium slurries.
(2) The slurries were placed in sealed containers and incubated at 45 °C for seven days.

TABLE A-1. Simulant Slurry Compositions

	Slurry				
Component	A	B	C	D	E
KTPB (g/L)	60	60	60	60	62
(~wt %)	5	5	5	5	5
	Concentration (molar)				
Na^+	4.5	5.5	5.5	5.5	4.5
OH^-	3.0	1.8	0.6	1.6	2.6
NO_3^-	0.84	2.0	2.7	2.1	0.64
NO_2^-	0.25	0.62	0.84	0.77	0.69
AlO_2^-	0.13	0.33	0.44	0.33	0.17
CO_3^{2-}	0.07	0.17	0.23	0.16	0.17
SO_4^{2-}	0.06	0.15	0.20	0.15	0.009
Cl^-	0.010	0.010	0.031	0.025	0.013
F^-	0.007	0.007	0.021	0.016	0.007
PO_4^{3-}	0.004	0.004	0.012	0.010	0.006

TABLE A-2. Diluted Slurries for Operating Window Tests

Initial slurry*	**A**	**A**	**B**	**B**	**B**
Dilution factor	**1.61**	**16.8**	**1.22**	**1.75**	**3.05**
	Final Concentration (molar)				
Na^+	2.8	0.40**	4.5	3.15	1.8
OH^-	1.9	0.30**	1.6	1.05	0.60
NO_3^-	0.52	0.05	1.6	1.15	0.65
NO_2^-	0.16	0.015	0.51	0.36	0.20
AlO_2^-	0.08	0.008	0.27	0.19	0.11
CO_3^{2-}	0.04	0.004	0.14	0.10	0.06
SO_4^{2-}	0.04	0.004	0.12	0.09	0.05
Cl^-	0.006	0.0006	0.008	0.006	0.003
F^-	0.004	0.0004	0.006	0.004	0.002
PO_4^{3-}	0.002	0.0002	0.003	0.002	0.001

Initial slurry*	**C**	**C**	**C**	**C**
Dilution factor	**1.22**	**1.96**	**5.5**	**27.5**
	Final Concentration (molar)			
Na^+	4.5	2.8	1.0	0.20
OH^-	0.5	0.3	0.11	0.022
NO_3^-	2.2	1.4	0.49	0.10
NO_2^-	0.69	0.43	0.15	0.031
AlO_2^-	0.36	0.22	0.08	0.16
CO_3^{2-}	0.19	0.12	0.040	0.008
SO_4^{2-}	0.16	0.10	0.036	0.007
Cl^-	0.025	0.016	0.006	0.0011
F^-	0.017	0.011	0.004	0.0008
PO_4^{3-}	0.010	0.006	0.002	0.0004

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*See Table A-1.

**Additional NaOH added after dilution.

TABLE A-3. Catalyst Components in Simulant Slurries

Insoluble Components

12 g/L (~1 wt %) sludge
12 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)	1.0

Organic Additives (mg/L)

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

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(3) The slurries were divided into portions, diluted with water, and filtered to concentrate to the original volume again.
(4) NaTPB, intermediates and benzene were added.
(5) The slurries were sealed and incubated at 45 °C.

Boron Leach Test

A salt solution (see Table A-1, without KTPB or other organic compounds) was placed into a previously used 70-mL glass serum vial, sealed, and incubated at 55 °C (±3°C) for 13 days. A portion of the solution was removed and analyzed after 0, 2, 6, and 13 days. The boron concentrations (mg/L) were 1.03, 2.34, 6.82, and 21.5 respectively. The average dissolution rate was 1.7 mg/L/day or 0.16 mM/day.

Soluble Palladium Test

This test measured the amount of soluble palladium derived from the two methods of palladium addition used in the current and previous tests. The test matrix included monosodium titanate and sludge components, but did not include potassium tetraphenylborate. Table A-4 lists the salt solution composition. The ECC catalyst system (Table A-3) was added at 1 wt %, including inactive organics (methanol, isopropanol, and phenol), but not benzene, tetraphenylborate, or decomposition intermediates (3PB, 2PB, and 1PB). Palladium (11 mg/L) was added either as a component in the sludge metals or as an acidic aqueous solution (2606 mg Pd/L in 0.1 M HNO_3). The salt solution and sludge slurries were stirred at room temperature and sampled after 14 days. The samples were filtered using 0.45 micron acrylic copolymer syringe filters (Gelman Sciences).

Analytical Results

The filtered samples were analyzed for potassium ion, cesium ion, soluble boron, organic compounds (NaTPB, 3PB, 2PB, 1PB, and phenol), and metals (Cu, Ag, Ru, Rh, and Pd). The analytical results are listed in Tables A-5 through A-7. The changes in potassium and boron concentrations are shown in Figure A-1. The graphs show the approximately linear increase in the two soluble products.

Analytical Methods

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. Tetraphenylborate, triphenylboron (3PB), and diphenylborinic acid (2PB) were measured on the same model instrument and column using a 0.1 % ammonium phosphate buffered acetonitrile-methanol-water eluent (La-mar-ka, Inc, Baton Rouge, LA). The HPLC instrument methods are described in Manual L16.1, Procedure #ADS-2655. The methodology

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TABLE A-4 Salt Solution Composition For Soluble Palladium Test

Component	Concentration (molar)
Na^+	2.8
OH^-	0.84
NO_3^-	1.06
NO_2^-	0.39
AlO_2^-	0.17
CO_3^{2-}	0.08
SO_4^{2-}	0.07
Cl^-	0.013
F^-	0.008
PO_4^{3-}	0.005

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 and cesium 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 11.

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.

TABLE A-5. Analytical Results for Operating Window Tests

Note: All results are soluble concentrations in filtered samples.

Conditions:	4.5 M Na+, 3.0 M OH-, no pre-reaction										
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<1	60	82	288	194	412	428	<.02	7.9	0.45	10.7
4	<6	66	<10	98	30	-	-	-	-	-	-
11	169	104	<10	<10	<10	-	-	-	-	-	-
18	166	133	<10	<10	<10	-	-	<.02	10.8	2.6	0.48
25	220	186	<10	<10	<10	-	-	-	-	-	-
32	351	250	-	-	-	-	-	-	-	-	-
39	406	279	-	-	-	-	-	-	-	-	-
46	482	326	<10	<10	<10	71	970	<.02	10.8	2.4	0.11
Conditions:	5.5 M Na+, 1.8 M OH-, no pre-reaction										
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	8	59	<10	374	376	324	423	0.38	7.7	1.34	8.6
4	<5	59	<10	50	33	-	-	-	-	-	-
11	24	71	<10	<10	<10	-	-	-	-	-	-
18	59	87	<10	<10	<10	-	-	<.02	9.4	4.2	0.29
25	89	123	<10	<10	<10	-	-	-	-	-	-
32	177	172	-	-	-	-	-	-	-	-	-
39	215	195	-	-	-	-	-	-	-	-	-
46	253	220	<10	<10	<10	28	1083	<.02	9	3.8	0.26
Conditions:	4.5 M Na+, 1.5 M OH-, no pre-reaction										
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<1	57	44	414	346	286	410	<.02	7.57	1.75	5.5
4	<6	66	<10	122	84	-	-	-	-	-	-
11	30	74	<10	<10	27	-	-	-	-	-	-
18	73	93	<10	<10	<10	-	-	<.02	8.8	3.3	0.21
25	111	127	<10	<10	<10	-	-	-	-	-	-
32	208	174	-	-	-	-	-	-	-	-	-
39	256	201	-	-	-	-	-	-	-	-	-
46	313	228	<10	<10	<10	67	1043	<.02	9.4	3.1	0.148
Conditions:	5.5 M Na+, 0.6 M OH-, no pre-reaction										
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<1	68	147	431	382	389	398	<.02	6.8	0.80	8.2
4	<5	57	<10	179	116	-	-	-	-	-	-
11	141	96	<10	<10	39	-	-	-	-	-	-
18	251	126	<10	<10	36	-	-	<.02	6.7	4.0	0.12
25	309	171	<10	<10	<10	-	-	-	-	-	-
32	566	244	-	-	-	-	-	-	-	-	-
39	634	275	-	-	-	-	-	-	-	-	-
46	716	290	<10	<10	<10	180	357	-	-	-	-
Conditions:	2.8 M Na+, 1.9 M OH-, no pre-reaction				(d=1.132)						
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<6	71	538	330	297	28	38	0.072	5.7	0.18	9.3
6	51	90	<10	12	122	-	-	-	-	-	-
13	158	122	<10	<10	37	-	-	-	-	-	-
20	204	170	<10	<10	27	-	-	<.02	10.7	1.13	0.065
27	341	221	-	-	-	-	-	-	-	-	-
34	402	255	-	-	-	-	-	-	-	-	-
41	448	258	-	-	-	-	-	-	-	-	-
48	626	365	<10	<10	34	171	1013	<.02	9.58	1.35	0.058
Conditions:	0.4 M Na+, 0.3 M OH-, no pre-reaction				(d=1.010)						
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<7	69	298	204	330	424	455	<.02	1.7	0.19	13.8
6	135	109	<10	<10	190	-	-	-	-	-	-
13	266	144	<10	<10	75	-	-	-	-	-	-
20	369	196	<10	<10	84	-	-	<.02	3.5	0.088	0.076
27	534	242	-	-	-	-	-	-	-	-	-
34	643	279	-	-	-	-	-	-	-	-	-
41	692	306	-	-	-	-	-	-	-	-	-
48	868	366	<10	<10	93	547	675	<.02	3.5	0.148	<.02
Conditions:	3.15 M Na+, 1.05 M OH-, no pre-reaction				(d=1.167)						
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<7	66	385	434	357	285	388	<.02	7.3	0.47	6.9
6	<8	69	<10	96	384	-	-	-	-	-	-
13	80	94	<10	<10	56	-	-	-	-	-	-
20	145	134	<10	<10	42	-	-	<.02	9.6	1.98	0.113
27	267	179	-	-	-	-	-	-	-	-	-
34	337	206	-	-	-	-	-	-	-	-	-
41	445	249	-	-	-	-	-	-	-	-	-
48	590	311	<10	<10	50	183	1163	<.02	7.82	2.08	<.02

TABLE A-5. Analytical Results for Operating Window Tests (continued)

Note: All results are soluble concentrations in filtered samples.

Conditions:	3.15 M Na+, 1.05 M OH-, w/ pre-reaction				(d=1.160)						
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<6	149	429	431	292	385	864	<.02	5.9	1.86	0.125
6	35	147	<10	<10	195	-	-	-	-	-	-
13	80	192	<10	<10	70	-	-	<.02	6.0	0.168	0.033
20	133	230	-	-	-	-	-	<.02	5.2	1.44	0.053
27	166	251	-	-	-	-	-	-	-	-	-
34	190	262	-	-	-	-	-	-	-	-	-
41	255	281	-	-	-	-	-	-	-	-	-
48	300	307	<10	<10	57	141	1205	<.02	5.89	2.21	0.13
Conditions:	1.8 M Na+, 0.6 M OH-, w/ pre-reaction				(d=1.094)						
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<6	116	323	470	335	346	690	<.02	3.2	0.84	0.143
6	54	121	<10	20	284	-	-	-	-	-	-
13	109	161	<10	13	111	-	-	<.02	3.0	0.68	0.021
20	177	195	-	-	-	-	-	<.02	2.7	0.61	<.02
27	242	196	-	-	-	-	-	-	-	-	-
34	273	238	-	-	-	-	-	-	-	-	-
41	349	254	-	-	-	-	-	-	-	-	-
48	406	276	<10	<10	97	284	968	<.02	2.97	1.11	0.076
Conditions:	4.5 M Na+, 0.49 M OH-, w/ pre-reaction				(d=1.226)						
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	<6	143	114	521	400	546	844	<.02	4.8	2.6	0.274
6	92	159	<10	<10	116	-	-	-	-	-	-
13	156	193	<10	<10	60	-	-	<.02	4.9	2.5	0.028
20	285	268	-	-	-	-	-	<.02	5.1	2.3	0.022
27	337	278	-	-	-	-	-	-	-	-	-
34	374	300	-	-	-	-	-	-	-	-	-
41	454	312	-	-	-	-	-	-	-	-	-
48	526	342	<10	<10	28	244	1143	<.02	5.15	3.15	0.067
Conditions:	*2.8 M Na+, 0.3 M OH-, w/ pre-reaction*										
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	14	129	293	532	383	451	689	<.02	2.8	1.48	0.183
6	119	150	<10	<10	197	-	-	-	-	-	-
13	198	199	<10	<10	109	-	-	<.02	2.9	1.28	<.02
20	324	247	<10	<10	75	-	-	<.02	2.7	1.17	<.02
27	404	262	-	-	-	-	-	-	-	-	-
34	469	305	-	-	-	-	-	-	-	-	-
41	589	328	-	-	-	-	-	-	-	-	-
48	706	362	<10	<10	49	471	1026	<.02	3.2	2.02	0.073
Conditions:	*1.0 M Na+, 0.11 M OH-, w/ pre-reaction*				*(d=1.053)*						
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	12	87	73	470	434	354	528	<.02	0.88	0.28	0.24
6	186	133	<10	23	231	-	-	-	-	-	-
13	268	178	<10	20	143	-	-	<.02	0.84	0.32	<.02
20	397	217	<10	<10	111	-	-	<.02	0.75	0.32	<.02
27	492	230	<10	<10	125	-	-	-	-	-	-
34	573	278	<10	<10	91	761	699	-	-	-	-
41	790	330	<10	<10	116	870	823	-	-	-	-
48	1035	403	<10	<10	157	1002	965	<.02	0.81	0.73	0.038
Conditions:	0.2 M Na+, 0.022 M OH-, w/ pre-reaction				(d=1.009)						
Elapsed Time (days)	K+ (mg/L)	B (mg/L)	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)
0	27	71	64	413	436	321	428	<.02	0.132	<.01	0.3
6	161	113	<10	41	437	-	-	-	-	-	-
13	261	162	<10	33	251	-	-	<.02	0.152	0.110	<.02
20	404	207	<10	<10	182	-	-	-	-	-	-
27	423	200	<10	<10	169	-	-	-	-	-	-
34	479	450	<10	<10	109	948	670	-	-	-	-
41	910	262	<10	<10	109	885	813	-	-	-	-
48	727	305	<10	<10	161	821	1050	<.02	0.178	0.295	0.03

TABLE A-5. Analytical Results for Operating Window Tests (continued)

Note: All results are soluble concentrations in filtered samples.

Conditions:	1.8 M Na+, 0.6 M OH-, no pre-reaction				(d=1.099)						
Elapsed Time	K+	B	NaTPB	3PB	2PB	1PB	Phenol	Ag	Ru	Rh	Pd
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<6	67	360	428	356	293	403	<.02	4.4	0.28	8.9
6	71	71	120	336	317	-	-	-	-	-	-
13	36	85	<10	25	225	-	-	-	-	-	-
20	216	152	<10	<10	126	-	-	<.02	5.5	0.68	0.20
27	421	226	<10	<10	66	-	-	-	-	-	-
34	535	251	-	-	-	-	-	-	-	-	-
41	720	322	-	-	-	-	-	-	-	-	-
48	893	380	<10	<10	93	339	1091	<.02	6.02	1.13	0.052
Conditions:	4.5 M Na+, 0.49 M OH-, no pre-reaction				(d=1.235)						
Elapsed Time	K+	B	NaTPB	3PB	2PB	1PB	Phenol	Ag	Ru	Rh	Pd
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<5	54	189	407	342	304	400	<.02	5.1	0.85	3.5
6	32	74	<10	<10	33	-	-	-	-	-	-
13	93	93	<10	<10	<10	-	-	-	-	-	-
20	146	124	<10	<10	<10	-	-	<.02	6.5	2.3	0.126
27	241	165	-	-	-	-	-	-	-	-	-
34	307	188	-	-	-	-	-	-	-	-	-
41	357	211	-	-	-	-	-	-	-	-	-
48	488	256	<10	<10	16	192	776	<.02	5.62	2.25	<.02
Conditions:	2.8 M Na+, 0.3 M OH-, no pre-reaction				(d=1.152)						
Elapsed Time	K+	B	NaTPB	3PB	2PB	1PB	Phenol	Ag	Ru	Rh	Pd
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<6	64	456	427	339	293	382	<.02	6.3	0.49	6.4
6	140	101	<10	15	270	-	-	-	-	-	-
13	275	135	<10	<10	46	-	-	-	-	-	-
20	343	188	<10	<10	30	-	-	<.02	6.0	1.25	0.113
27	558	252	-	-	-	-	-	-	-	-	-
34	762	306	-	-	-	-	-	-	-	-	-
41	936	362	-	-	-	-	-	-	-	-	-
48	1106	419	<10	<10	25	293	885	<.02	4.92	1.35	<.02
Conditions:	1.0 M Na+, 0.11 M OH-, no pre-reaction				(d=1.056)						
Elapsed Time	K+	B	NaTPB	3PB	2PB	1PB	Phenol	Ag	Ru	Rh	Pd
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<6	68	379	428	340	310	399	<.02	3.3	0.36	12
6	216	125	<10	<10	333	-	-	-	-	-	-
13	356	165	<10	<10	66	-	-	-	-	-	-
20	546	239	<10	<10	48	-	-	<.02	3.4	0.43	0.065
27	723	285	-	-	-	-	-	-	-	-	-
34	896	335	-	-	-	-	-	-	-	-	-
41	1050	402	-	-	-	-	-	-	-	-	-
48	1229	484	<10	<10	53	528	943	<.02	2.68	0.653	0.09
Conditions:	0.2 M Na+, 0.022 M OH-, no pre-reaction				(d=1.007)						
Elapsed Time	K+	B	NaTPB	3PB	2PB	1PB	Phenol	Ag	Ru	Rh	Pd
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<7	67	301	426	364	307	390	<.02	1.9	0.24	12.9
6	263	148	<10	<10	149	-	-	-	-	-	-
13	470	214	<10	<10	70	-	-	-	-	-	-
20	635	272	<10	<10	55	-	-	<.02	2.3	0.26	0.041
27	870	338	-	-	-	-	-	-	-	-	-
34	1042	382	-	-	-	-	-	-	-	-	-
41	1096	430	-	-	-	-	-	-	-	-	-
48	1390	503	<10	<10	57	442	891	<.02	2.02	0.377	<.02
Conditions:	2.8 M Na+, 1.9 M OH-, w/ pre-reaction				(d=1.132)						
Elapsed Time	K+	B	NaTPB	3PB	2PB	1PB	Phenol	Ag	Ru	Rh	Pd
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<6	155	323	434	326	451	819	<.02	6.85	1.25	0.091
6	24	151	<10	45	192	-	-	-	-	-	-
13	60	190	<10	<10	85	-	-	<.02	6.7	1.14	0.024
20	107	232	<10	<10	56	-	-	-	-	-	-
27	158	263	-	-	-	-	-	-	-	-	-
34	204	307	-	-	-	-	-	-	-	-	-
41	291	337	-	-	-	-	-	-	-	-	-
48	342	373	<10	<10	58	161	1281	<.02	6.09	1.5	0.099
Conditions:	0.4 M Na+, 0.3 M OH-, w/ pre-reaction				(d=1.010)						
Elapsed Time	K+	B	NaTPB	3PB	2PB	1PB	Phenol	Ag	Ru	Rh	Pd
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	12	72	81	433	393	333	468	<.02	0.48	<.01	0.162
6	115	106	<10	19	433	-	-	-	-	-	-
13	171	147	<10	17	197	-	-	<.02	0.57	0.152	0.013
20	236	164	<10	<10	163	-	-	<.02	0.5	0.148	<.02
27	329	204	<10	<10	220	-	-	-	-	-	-
34	402	227	<10	<10	249	950	664	-	-	-	-
41	532	278	<10	<10	304	969	777	-	-	-	-
48	682	323	<10	<10	407	1030	918	<.02	0.645	0.355	0.042

TABLE A-6. Analytical Results for Reactivity Comparison Tests

Note: All results are soluble concentrations in filtered samples.

Conditions:	5% NaTPB							
Elapsed Time	K+	Cs+	B	NaTPB	3PB	2PB	1PB	Phenol
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	-	-	74	216	573	301	316	177
6	-	-	1005	437	6386	5905	3187	898
13	-	-	1800	239	4338	4789	3024	785
20	-	-	1990	<10	923	3364	2299	810
Conditions:	5% KTPB							
Elapsed Time	K+	Cs+	B	NaTPB	3PB	2PB	1PB	Phenol
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	152	-	61	<10	359	309	258	171
6	287	-	132	<10	<10	54	176	599
13	473	-	204	<10	<10	45	453	627
20	338	-	256	<10	<10	25	332	664
27	388	-	302	<10	<10	23	293	661
Conditions:	*5% CsTPB*							
Elapsed Time	K+	Cs+	B	NaTPB	3PB	2PB	1PB	Phenol
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	-	2199	52	<10	193	307	270	175
6	-	1402	78	<10	<10	<10	62	482
13	-	920	110	<10	<10	<10	<10	575
20	-	963	143	<10	<10	<10	21	689
27	-	1026	179	<10	<10	<10	20	708
Conditions:	2.5% NaTPB/2.5% KTPB							
Elapsed Time	K+	Cs+	B	NaTPB	3PB	2PB	1PB	Phenol
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<4	-	70	211	293	293	275	171
6	<4	-	679	189	2593	5212	2237	425
13	58	-	906	<10	1033	3039	3138	450
20	30	-	1037	<10	20	513	1776	427
27	58	-	1012	<10	<10	131	1072	426
Conditions:	5% NaTPB, High intermediates							
Elapsed Time	*K+*	*Cs+*	B	*NaTPB*	3PB	2PB	*1PB*	*Phenol*
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	-	-	420	335	2041	2420	2239	294
6	-	-	1695	427	6716	8091	6222	1043
13	-	-	2214	135	3338	7554	9870	1226
20	-	-	2166	148	34	2557	10251	1133
Conditions:	5% KTPB, High intermediates							
Elapsed Time	K+	Cs+	B	NaTPB	3PB	2PB	1PB	Phenol
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	132	-	383	27	1780	2402	2254	279
6	457	-	506	<10	<10	75	1598	719
13	632	-	575	<10	<10	48	1379	828
20	592	-	654	<10	<10	38	942	711
27	734	-	685	<10	<10	<10	811	744
Conditions:	*5% KTPB repeat*							
Elapsed Time	K+	Cs+	B	NaTPB	3PB	2PB	1PB	Phenol
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<4	-	59	118	424	258	234	153
6	189	-	130	<10	<10	74	382	515
13	295	-	213	<10	<10	34	274	554
21	380	-		<10	<10	<10	150	551
Conditions:	5% CsTPB repeat							
Elapsed Time	K+	Cs+	B	NaTPB	3PB	2PB	1PB	Phenol
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	-	<2	60	207	457	216	240	154
6	-	218	118	<10	<10	<10	120	491
13	-	484	161	<10	<10	<10	89	525
21	-	628		<10	<10	<10	46	512
Conditions:	*2.5% NaKTPB/2.5% KTPB mix repeat*							
Elapsed Time	K+	Cs+	B	NaTPB	3PB	2PB	1PB	Phenol
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	1079	-	56	<10	286	266	271	198
2	<4	-	286	171	1961	2725	847	912
6	<4	-	441	133	2673	2323	1279	333
9	<4	-	561	112	2486	2069	1519	674
13	<4	-	764	34	1827	1716	1540	378
21	24	-		<10	168	481	605	330

TABLE A-7. Analytical Results for Catalyst Identification Tests

Note: All results are soluble concentrations in filtered samples

Conditions:	4.5 M Na+	1.0 wt % sludge, 1.0 wt % MST, full ECC catalyst										
Elapsed Time	K+	4PB	3PB	2PB	1PB	Phenol	Pd	Cu	Ag	Ru	Rh	B
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<3	192	395	211	215	268	1.8	0.35	<.05	0.74	0.27	-
5	<3	11	169	1659	-	-	0.056	-	<.05	2.8	0.79	-
11	19	<10	<10	423	-	-	0.083	-	<.05	2.9	0.90	-
18	39	<10	<10	63	-	-	0.087	-	<.05	2.9	1.0	-
26	106	<10	<10	20	-	-	0.041	-	<.05	2.9	1.1	-
33	117	<10	<10	19	-	-	0.09	-	<.05	2.7	1.03	-
40	167	<10	<10	16	44	888	0.27	-	<.02	2.8	1.12	-
47	279	<10	<10	39	-	-	0.15	-	<.02	3.3	1.3	-
54	412	<10	<10	62	241	1448	0.29	1.32	<.02	3.32	1.41	-
Conditions:	4.5 M Na+	1.0 wt % sludge, 1.0 wt % MST, Full ECC except w/o Pd (contains Ru, Rh)										
Elapsed Time	K+	4PB	3PB	2PB	1PB	Phenol	Pd	Cu	Ag	Ru	Rh	B
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<3	224	398	218	218	274	0.82	0.39	0.78	9.6	3.6	-
5	<3	217	417	113	-	-	0.03	-	<.05	15.0	4.4	-
11	6	166	376	45	-	-	0.06	-	<.05	15.4	4.7	-
18	<1	142	353	23	-	-	0.07	-	<.05	15.0	4.5	-
26	2	217	<10	<10	-	-	0.02	-	0.07	16.1	4.7	-
40	<1	199	303	<10	55	1078	0.035	-	0.09	14.5	3.2	-
54	<1	180	296	<10	<10	677	0.093	-	0.052	15	4.8	-
67	3	233	<10	<10	<10	705	0.028	0.7	0.31	10.8	3.3	-
Conditions:	4.5 M Na+	1.0 wt % sludge, 1.0 wt % MST, Full ECC except w/o Hg										
Elapsed Time	K+	4PB	3PB	2PB	1PB	Phenol	Pd	Cu	Ag	Ru	Rh	B
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<3	170	415	219	232	283	1.7	0.38	<.05	0.79	0.23	-
5	<3	156	349	79	-	-	1.5	-	<.05	2.9	0.65	-
11	6	122	418	34	-	-	1.01	-	<.05	2.7	0.78	-
18	<1	90	683	49	-	-	0.60	-	<.05	2.8	0.93	-
26	<1	133	796	47	-	-	1.06	-	<.05	2.7	0.93	-
40	<1	138	680	48	<10	<10	1.47	-	0.02	2.0	0.53	-
54	<1	113	595	47	41	1436	0.8	-	<.02	2.1	0.84	-
67	<1	103	441	31	35	1559	0.53	0.37	0.027	2.7	1.15	-
Conditions:	4.5 M Na+	1.0 wt % sludge, 1.0 wt % MST, Full ECC except w/o intermediates										
Elapsed Time	K+	4PB	3PB	2PB	1PB	Phenol	Pd	Cu	Ag	Ru	Rh	B
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<3	193	<10	<10	<20	259	2.7	0.3	<.05	0.5	0.24	6
5	<3	160	33	<10	<10	254	7.3	-	<.05	1.0	0.81	-
11	6	138	55	20	<10	265	6.1	-	<.05	0.92	1.01	-
18	<1	<10	229	843	742	758	0.28	-	<.05	1.3	0.93	-
26	23	<10	<10	48	1154	739	0.18	-	<.05	1.4	0.98	-
40	117	<10	<10	19	653	818	0.1	-	<.02	1.4	0.75	-
47	157	<10	<10	<10	369	808	0.059	-	<.02	1.5	1.05	-
54	233	<10	<10	28	269	914	0.2	1.39	<.02	1.61	1.22	431
Conditions:	4.5 M Na+	0 wt % sludge, 1.0 wt % MST, contains only Interm., bz, Hg, and Pd										
Elapsed Time	K+	4PB	3PB	2PB	1PB	Phenol	Pd	Cu	Ag	Ru	Rh	B
(days)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0	<3	195	402	232	275	46	11.5	0.08	<.05	<.02	0.075	43
5	<3	129	932	559	319	77	0.41	-	<.05	<.02	<.01	-
11	6	109	750	586	403	104	0.39	-	<.05	<.02	0.018	-
18	<1	152	759	811	565	135	0.11	-	<.05	0.022	0.051	-
26	<1	40	684	892	660	168	0.06	-	<.05	<.02	0.022	-
40	<1	38	258	1108	1123	294	0.03	-	<.02	<.02	<.01	-
54	3	<10	87	1580	1397	421	0.094	-	<.02	0.066	0.061	-
67	73	<10	<10	693	1827	536	0.2	<.07	<.02	<.02	0.061	525

FIGURE A-1. Changes in Potassium and Boron Concentrations in Operating Window Tests

Note: The vertical scales on these graphs differ. Use care when comparing different experiments.

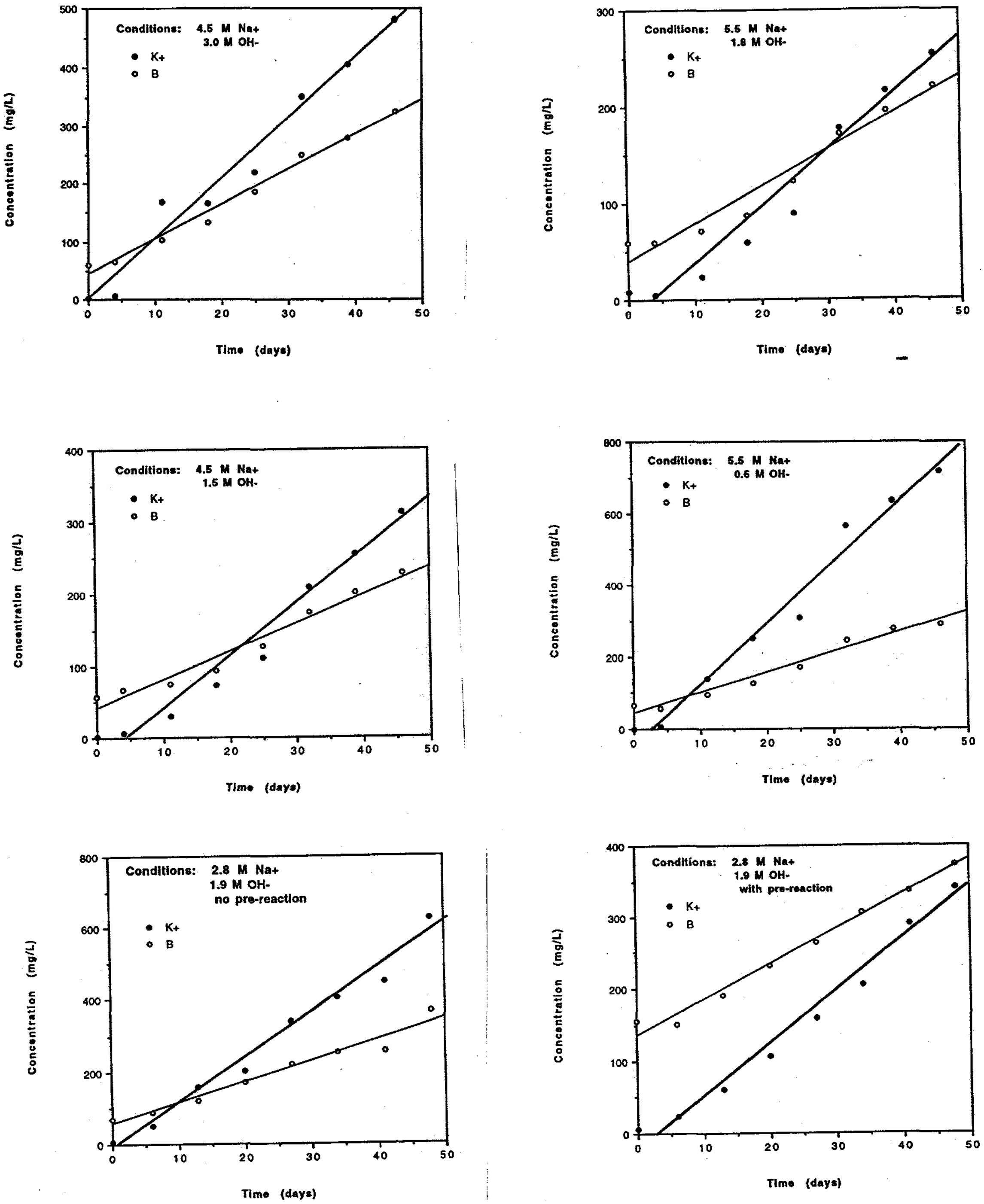


FIGURE A-1. Changes in Potassium and Boron Concentrations in Operating Window Tests (continued)

Note: The vertical scales on these graphs differ. Use care when comparing different experiments.

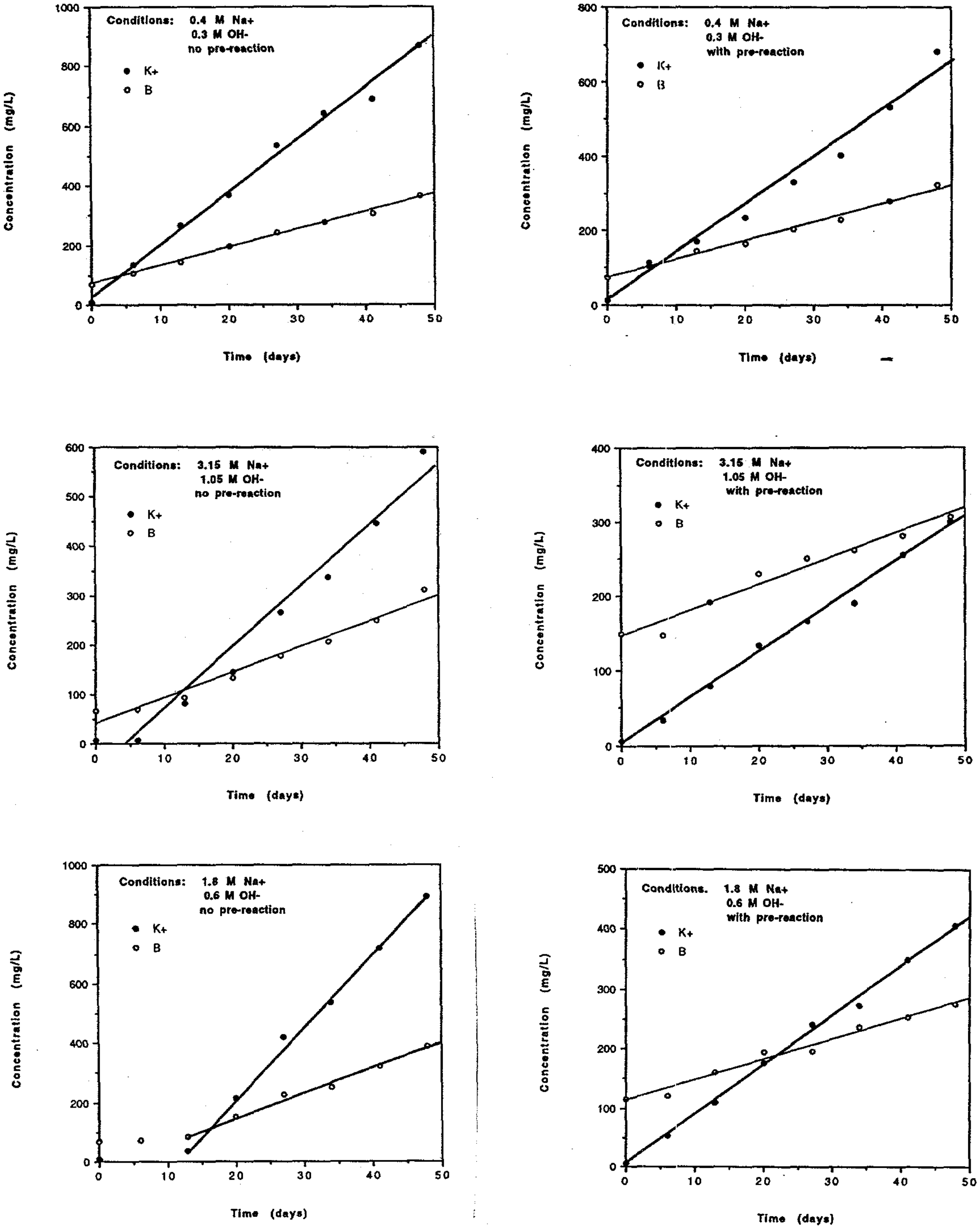


FIGURE A-1. Changes in Potassium and Boron Concentrations in Operating Window Tests (continued)

Note: The vertical scales on these graphs differ. Use care when comparing different experiments.

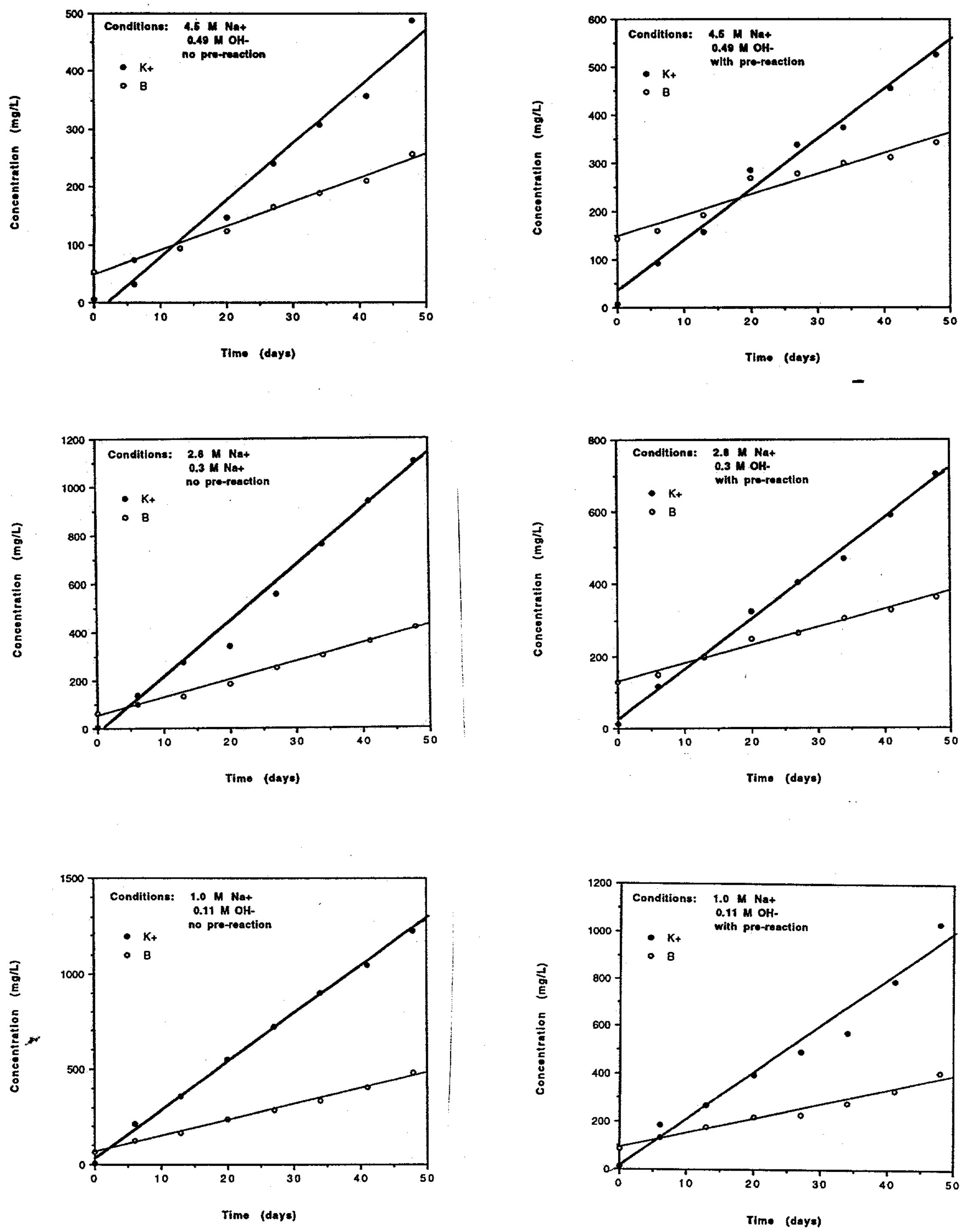
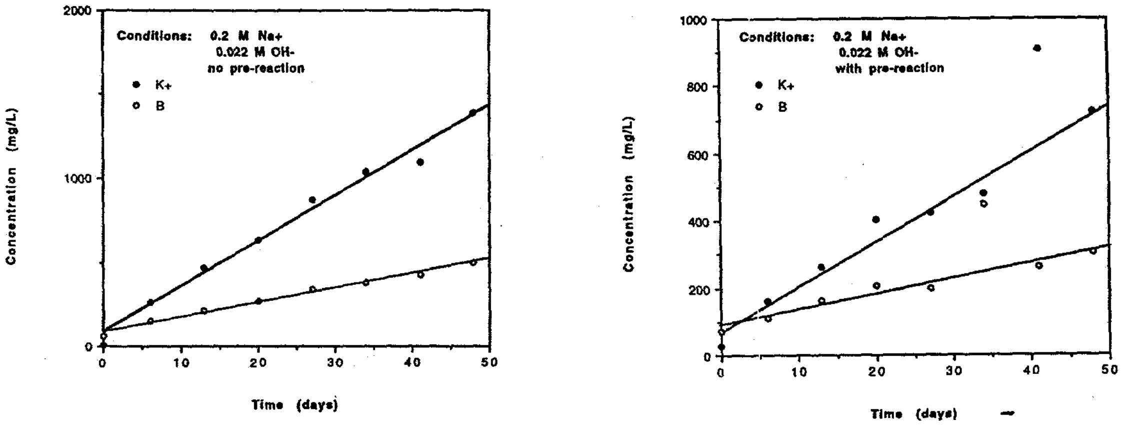


FIGURE A-1. Changes in Potassium and Boron Concentrations in Operating Window Tests (continued)

Note: The vertical scales on these graphs differ. Use care when comparing different experiments.



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