Effect of Palladium Form on Tetraphenylborate Decomposition Rate

by

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WSRC-TR-98-00073, Rev. 0

**Keywords: In-Tank Process, Benzene
Retention: Permanent**

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Publication Date: April 13, 1998

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Tetraphenylborate Solids Stability Tests

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EFFECT OF PALLADIUM FORM ON TETRAPHENYLBORATE DECOMPOSITION RATE

By D. D. WALKER

SUMMARY

Palladium catalyzes the decomposition of tetraphenylborate in alkaline solutions. Researchers postulate several decomposition mechanisms that differ in the form of the palladium catalyst (see Appendix A). Potential forms include solid and soluble, different soluble species (such as aqueous or organic soluble), and different oxidation states (i.e., 0, II, and IV). Initial tests measured the reactivity and distribution of four Pd forms in tetraphenylborate slurries. The four forms are aqueous-soluble Pd(II) nitrate, solid Pd⁰ supported on barium sulfate powder, solid Pd⁰ powder suspended in mercury, and solid Pd(II) oxide hydrate. The following points summarize the test results.

- Addition of aqueous soluble Pd(II) produced the most rapid decomposition reaction.
 - Relative reactivities of the four Pd forms tested were:
$$\text{Pd(II) nitrate} > \text{Pd(BaSO}_4) \sim \text{Pd(Hg)} > \text{PdO} \cdot \text{H}_2\text{O}$$
 - Soluble Pd(II) nitrate used in previous simulant tests proved the most reactive of the palladium forms tested.
- The reactive form of palladium appears to be Pd⁰.
 - In reacting slurries, only a small fraction of the total palladium resides in the aqueous phase.
 - In reacting and non-reacting systems, the palladium did not extract with benzene.
 - In reacting systems, the majority of the palladium associates with the sludge and KTPB solids.
- Due to limitations in the extraction and separation methods, a Pd catalyst at the benzene-aqueous interface cannot be excluded. Similarly, a highly reactive soluble species that is a minor component in all of the palladium forms tested cannot be excluded.

INTRODUCTION

Previous studies indicated that palladium is a catalytically active component of rapidly decomposing alkaline tetraphenylborate slurries.¹⁻⁵ Although statistical regression shows total palladium concentration as a significant factor in correlations of rate constants, the

resulting expressions provide relatively poor fit to the data.⁶ The mechanisms proposed to explain the experimental results differ in the form and location of the palladium catalyst (see Appendix A). The variability in results and the potential existence of different forms of palladium suggest that a variable fraction of the total palladium activates or that different forms of palladium exhibit widely varying reactivities. Improved understanding of the catalytic mechanism requires identification of the forms and distribution of palladium within the multiphase slurry system in addition to determining the relative reactivities of the different forms.

Tests described in this report represent an initial attempt to identify the chemical form and location of palladium in a reacting system. Information gained from these experiments could potentially explain the variability in previous testing, suggesting better measurements and variables to correlate the results.

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 complies 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.

TEST DESIGN AND RESULTS

Tests investigated (1) the effect of the form of palladium on the reaction rate, (2) the amount of soluble palladium in each form, and (3) the effect of removal of sludge and palladium solids on the reaction rate. The palladium form test compared the reactivity of soluble Pd(II) nitrate, solid Pd⁰ on barium sulfate particles, amalgamated Pd⁰, and Pd(II) oxide hydrate by measuring tetraphenylborate decomposition rates and palladium concentrations. The purpose of this test was to gain insight into the chemical form of the active catalyst. To help interpret the palladium form test, the fraction of the total palladium that was soluble in the simulant salt solution was measured for each of the four palladium forms. The differences in soluble palladium suggest an explanation for differences in the reactivities. The sludge removal test investigated the effect of removing insoluble sludge and palladium from the reaction mixture. This tests probes the source of the active palladium catalyst (i.e., soluble or insoluble palladium). Appendix B describes experimental details of the tests.

Palladium Form Test

Test Design

This test sought insight into the chemical form of the active palladium catalyst. The test obtained information in two ways. First, palladium was introduced in different forms and the rate of decomposition measured. Thus, the observed differences in reactivity may reflect the differences in form. Second, as the decomposition reaction progressed,

TABLE I. Summary of Fixed Conditions and Variables in the Pd Form Test

Fixed conditions

Total palladium	11 mg/L
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
Vessels	glass

Palladium forms

<u>Test</u>	<u>Form</u>
1	Pd(II) nitrate (40.0 wt % Pd), dissolved in 0.1 M HNO ₃ .
2	Pd, 5 wt % on BaSO ₄ powder, reduced
3	Pd black (~5 wt % oxygen), surface area ~20 m ² /g, suspended in Hg ⁰
4	Palladium(II) oxide hydrate, PdO·H ₂ O, 78 wt % Pd, dark brown, finely divided powder

* ECC = Enhanced Comprehensive Catalyst. See Appendix B and Reference 5 for composition.

aliquots of slurry were extracted with benzene and separated into different phases (aqueous, KTPB solids, and sludge solids) to determine the location of the palladium.

Table I lists controlled test conditions and the forms of palladium examined. Table II lists chemical features of the different forms. The selection of forms provides a representative, but not exhaustive list of species possibly present for the various postulated mechanisms.

Reaction Rates**Rate of Loss of TPB⁻**

Figure 1 shows the loss of tetraphenylborate during the 41-day test period. In all cases, decomposition occurred and different forms of palladium reacted at different rates. The order of reactivity was:

Table III lists quantitative estimates of the rates obtained from the initial slopes of the curves shown in Figure 1. Although the rates fall into three distinctly different ranges, the differences do not conclusively point to a particular form as the catalytic species. This could indicate that all four palladium forms will catalyze the reaction (but at different

TABLE II. Characteristics of Palladium Forms**Pd(II) nitrate**

Oxidation state:	+2
Solubility:	Soluble under aerobic conditions
Other:	Same form used in previous testing

Pd(BaSO₄)

Oxidation state:	0
	Possibly minor amounts of PdO present
Solubility:	Insoluble in simulant
Dispersion:	Distributed on BaSO ₄ particles, finely divided powder, surface area and particle size unknown
Other:	Selected for insolubility in aqueous system

Pd(Hg)

Oxidation state:	0 and +2
	62 wt % Pd ⁰ and 38 wt % PdO
Solubility:	Insoluble in simulant
Dispersion:	Fine particles of Pd ⁰ , PdO and PdHg ₄ suspended in dispersed mercury droplets
Other:	Preparation method used 10-fold molar excess of Hg over Pd; Pd is sparingly soluble in Hg (0.005 atom % at 25 °C),* Pd forms PdHg ₄ in excess Hg; Hg/Pd atomic ratio in this test was approx. 2.5X normal ECC ratio

PdO hydrate

Oxidation state:	+2
Solubility:	Insoluble in simulant
Dispersion:	Very fine powder, particle size unknown

*See Reference 8.

rates), that the catalytically active form is an impurity in the inactive forms, or that inactive forms convert to the catalytic form under the test conditions (forming different amounts of active catalyst). Table II lists some of the potential impurity forms. An example of conversion is the slow change from PdO hydrate to Pd⁰ under anoxic conditions.⁷

Rate of Appearance of K⁺

The tests with Pd(II) nitrate and Pd(BaSO₄) consumed all of the initial TPB⁻ and decomposed measurable amounts of KTPB before the test ended. Figure 1 shows the changes in potassium concentration and Table III lists the rates. Unexpectedly, the solids reaction with Pd(II) nitrate slowed and stopped after approximately 25 days with only 2.4% of the KTPB decomposed. In previous testing, solids reactions continued until more than 50% of the solids decomposed.

FIGURE 1. Loss of TPB^- and Appearance of K^+ TABLE III. Rates of Loss of TPB^- and Increase in K^+

<u>Form</u>	<u>Rate (mM/d)</u>	
	<u>TPB⁻*</u>	<u>K⁺</u>
Pd(II) nitrate	0.6	0.2
Pd(BaSO ₄)	0.3	0.01
Pd(Hg)	0.2	**
PdO hydrate	0.02	**

*Based on initial slopes.

** No reaction during test duration.

Palladium Distribution

The recoveries of palladium from slurry samples were low and erratic, so conclusions from the results are tentative. Table IV lists the results for the distribution of palladium in the slurries. Recoveries average 63% and varied from 19 to 86%. Most of the recoveries exceeded 50%, but two were particularly low (19 and 29%). The low and erratic recoveries may reflect sampling error in obtaining a portion of the slurry from the reaction vessel. However, the author believes significant improvement could result from refining the extraction and separation techniques.

TABLE IV. Distribution of Palladium

<u>Form</u>	<u>Time</u> <u>(days)</u>	<u>Recovery*</u> <u>(%)</u>	<u>Distribution (% of recovered)</u>			
			<u>Aqueous</u>	<u>Benzene</u>	<u>KTPB</u>	<u>Sludge</u>
Pd(II) nitrate	0	72	49	1	44	6
	13	19	11	1	68	21
	34	73	5	0.1	84	11
Pd(BaSO ₄)	0	86	6	0.1	48	46
	13	52	4	0.2	42	54
	34	74	7	0.1	82	11
Pd(Hg)	0	81	2	0.1	57	41
	13	76	0.3	0.1	96	4
	34	29	12	0.3	66	21
PdO·H ₂ O	0	87	2	0	60	38
	13	50	4	0.2	76	20
	34	60	10	0.2	15	75

*The theoretical amount of palladium in each sample was 110 µg.

The recovered palladium resided primarily in the solid phases (50 to 100%), typically with more in the KTPB than in the sludge. Lesser portions (0.3 to 12%) of the palladium were found in the aqueous phase, except in the first sample from the Pd(II) nitrate test (49%). Subsequent aqueous samples from the Pd(II) nitrate tests decreased in soluble palladium. Researchers found this pattern (i.e., drop in aqueous soluble Pd during reaction) in previous studies.^{9,10} Very little of the palladium was found in the benzene extracts (0.1% to 1%). The distribution was similar in all four tests and did not differ notably between reactive and non-reactive slurries.

Soluble Palladium Test

The soluble fraction of the total palladium was measured for each of the four palladium forms used in the reactivity tests. In separate experiments, researchers placed each source material into a 2.8 M Na⁺, 0.8 M OH⁻ salt solution at ~23 °C. In each case, the total palladium added was 11 mg/L. All components of the ECC catalyst system were added except NaTPB, KTPB, 3PB, 2PB, 1PB, and benzene. The concentrations of palladium and several other metals were measured after 7 and 14 days. Table V lists the palladium concentrations. The results for other metals are listed in Appendix B, Table B-4. The concentrations listed in Table V should not be considered solubility limits since the tests were not run long enough to verify equilibrium was achieved. The soluble palladium

TABLE V. Comparison of Soluble Pd Concentrations and TPB⁻ Decomposition Rates

<u>Test</u>	<u>Pd Form</u>	<u>Soluble Pd (mg/L)*</u>		<u>TPB⁻ Rate** (mM/d)</u>
		<u>7 days</u>	<u>14 days</u>	
1	Pd(II) nitrate	10.2	9.3	0.6
2	Pd(BaSO ₄)	0.65	1.7	0.3
3	Pd(Hg)	0.022	0.042	0.2
4	PdO hydrate	0.085	0.18	0.02

* Measured in a non-reactive system without phenyl borate compounds present.

** From Table III, measured from reacting systems.

concentrations increased between the first and second week in three of the four forms. The most soluble form, Pd(II) nitrate, decreased slightly, although the two measurements may reflect analytical uncertainty more than a change in concentration. The soluble palladium concentration does not correlate well with the decomposition rate.

Solids Removal Test

The effect of removing insoluble sludge and palladium prior to precipitation of KTPB solids was examined as a potential method for removing part or all of the catalytic palladium. In this test, a salt solution was stirred for a week with the sludge and palladium. In this test, the palladium was originally added to the sludge as Pd(II) nitrate solution, but it had been in contact with the alkaline sludge slurry for almost four years, possibly allowing time for conversion of the soluble palladium to other forms. After stirring at ambient temperature (22 ± 3 °C), the soluble palladium concentration was 6.4 mg/L after 3 days and did not change significantly between 3 and 7 days. The salt solution was divided in half and the sludge removed from one of the halves by filtration. KTPB was precipitated in both the filtered and unfiltered portions of the salt solution, and the resulting slurries were incubated at 45 °C. The loss of NaTPB, increase in soluble K⁺, and palladium concentration were monitored periodically for 52 days. Figure 2 shows the results of these measurements. Removal of the sludge and palladium solids did not significantly effect the final rate of decomposition, although it appears to have delayed the onset of the reaction by about two weeks. The rates of increase in potassium ion for the two tests were: filtered, 0.69 mM K⁺/d; and unfiltered (with sludge) 0.66 mM/d. In both cases, the soluble palladium concentration dropped to less than 0.1 mg/L within the first 12 days following the precipitation of the KTPB. Figure 3 shows the loss of palladium in the filtered test in comparison to the rise in potassium. The unfiltered test with sludge and Pd solids present showed similar changes in soluble palladium (see Appendix, Table B-6). The drop in palladium concentration at time zero was due to

FIGURE 2. Appearance of K^+ in the Presence and Absence of Sludge Solids

FIGURE 3. Decrease in Soluble Pd and Increase in K^+ in Filtered Test

dilution caused by addition of NaTPB solution to precipitate KTPB. The decrease in soluble palladium was coincident with the decomposition of the soluble tetraphenylborate. The initial soluble Pd concentration in these tests (4.5 mg/L, see Appendix B, Table B-6) was significantly higher than the soluble Pd concentration in real waste tests (≤ 0.26 mg/L).¹¹

The near equivalence in rate between the filtered and unfiltered tests suggests that the source of the active catalyst is the soluble palladium. The relative activity can be estimated knowing (1) half of the palladium was insoluble and (2) the decomposition rates differed by less than 10%. Thus the insoluble palladium is less than 10% as active as the soluble form (or produces less than 10% of the amount of active catalyst as does the soluble Pd).

The rate of decomposition of solid KTPB was faster in both tests than in previous tests at comparable hydroxide ion concentration.^{9,10} Table VI lists the results of current and previous tests. The rate of decomposition of soluble TPB⁻ was not calculated due to insufficient data. Over the pH range of 10 to 14.5, the solids decomposition rate correlates with the pH. Previous studies showed the rate decreases as the pH (or hydroxide ion concentration) increases.⁹⁻¹⁰ However, the lack of correlation between pH and rate of appearance of K^+ in Table VI suggests the rate is affected by another variable.

TABLE VI. Comparison of Solid KTPB Decomposition Rates

<u>[OH⁻]</u> <u>(M)</u>	<u>[Na⁺]</u> <u>(M)</u>	<u>Other**</u>	Decomposition Rate		
			<u>K⁺</u> <u>(mM/d)</u>	<u>K⁺</u> <u>(mg/L/d)</u>	<u>Benzene*</u> <u>(mg/L/h)</u>
1.5	2.8	This report, filtered	0.66	25.8	8.6
1.5	2.8	This report, unfiltered	0.69	27.0	9.0
3.0	4.5	Ref. 10, Test 3	0.27	10.5	3.5
1.8	5.5	Ref. 10, Test 1	0.15	5.8	1.9
1.5	4.5	Ref. 10, Test 4	0.18	7.1	2.4
0.6	5.5	Ref. 10, Test 2	0.43	16.8	5.6
1.5	5.5	Ref. 9, Test 1	0.10	3.8	1.3

* Calculated from rate of increase in K⁺ assuming 4 moles of benzene are produced from each mole of K⁺.

** The solids removal test and the Ref. 9 results were obtained using palladium aged with alkaline sludge metals for approximately 3 years prior to use. The Ref. 10 results were obtained using palladium from an acidic palladium nitrate solution added at the start of the test. Total palladium concentrations were similar (10-13 mg Pd/L) in all tests.

The current tests differed from previous tests in the following ways: (1) the contact time between sludge, palladium, and salt solution was longer (one week in these tests compared to 2 hours in other simulant tests), (2) the sodium ion concentration during precipitation of KTPB was higher (3.5 molar initially versus 0.4 molar), and (3) the KTPB solids were precipitated in the presence of the sludge and palladium. The solids removal test conditions (e.g., higher salt concentration and presence of sludge solids during KTPB precipitation) were more representative of process operations than previous simulant tests.

Contact time with the highly alkaline salt solution and other sludge metals may affect the oxidation state, hydration state, or distribution of the palladium thus influencing the amount or activity of the palladium catalyst. High sodium ion concentration during KTPB precipitation may produce smaller crystals with different surface characteristics. Precipitation of KTPB in the presence of the sludge and palladium may either affect the crystal morphology (if sludge particles act as nucleating sites for KTPB) or the distribution of palladium on (or among) KTPB solids. The difference in contact time is likely not the reason for the high rates in the solids removal test. Aging of the palladium in the presence of alkaline sludge was suggested as a potential reason why the Reference 10 rates were more rapid than Reference 9 (Table VI). However, the other two differences could produce a more finely distributed catalyst (and thus a more active catalyst per gram of palladium) compared to previous tests.

DISCUSSION

Several pieces of evidence suggest that the active catalyst is a solid, low valent palladium species. This evidence includes the following observations.

- Less than 10% of the total palladium is found in the aqueous phase during rapid reaction.
- Solids decomposition rates do not correlate with soluble palladium concentrations.
- The majority of the palladium is associated with the sludge and KTPB solids.
- Reaction occurs with highly insoluble, low-valent forms of palladium (i.e., $\text{Pd}(\text{BaSO}_4)$ and $\text{Pd}(\text{Hg})$).
- Soluble palladium(II) converts to insoluble Pd^0 under alkaline, anoxic conditions.⁷
- When only soluble palladium is present, it converts to an insoluble form during the initial reaction phase.

The first two points above suggest that the active catalyst is not an aqueous soluble form: (1) most of the palladium is not aqueous soluble, and (2) the rate of reaction is not proportional to the soluble Pd concentration. Even though the fastest reaction occurred with the most soluble form of Pd (i.e., with Pd(II) nitrate where the initial soluble Pd concentration was 3.5 mg/L, 7 to 15 times higher than the others), the measured soluble Pd concentrations during the time period of rapid reaction (9-21 days) were comparable to the slower reactions (Table VII). The reaction rates varied by 30x whereas the soluble Pd differed by <2x. Table VIII lists pertinent data from previous *solids* stability tests.^{9,10} The table groups tests with similar sodium and hydroxide concentrations. Not only does there appear to be no correlation between decomposition rate and soluble palladium, but neither is there a correlation with initial palladium or change in soluble palladium. There is no palladium data available to correlate with reaction rates for *soluble* NaTPB.

The observation that addition of soluble Pd(II) nitrate produces the most rapid reaction appears contrary to the suggestion that the active catalyst is a solid, low valent palladium species. However, it is supported by the following arguments based on results from decomposition of solid tetraphenylborates.⁹⁻¹⁰ First, when palladium is added in the soluble form, most of it does not remain in solution. In many cases where the initial soluble palladium is high, the concentration decreases prior to rapid decomposition. In all cases, insoluble palladium was present initially or was produced from soluble palladium early in the test. Second, the most stable form of palladium in alkaline tetraphenylborate slurries is Pd^0 . The stable oxidation state is determined largely by the solution pH and Eh. Alkaline tetraphenylborate slurries have pH values between 12 and 14.7 and Eh values of approximately -600 mV (Figure 4).¹² Figure 5 shows the thermodynamically stable phases of palladium over a wide range of pH and Eh. The pH and Eh conditions in simulants indicate that Pd(II) would reduce to the most stable form, Pd^0 . In fact, the slurries are so strongly reducing that palladium hydride may be the most stable form, suggesting additional decomposition mechanisms.

TABLE VII. Soluble Palladium Concentrations During Rapid Reaction

<u>Form</u>	<u>Soluble Pd Concentration (mg/L)</u>		
	<u>9 days</u>	<u>13 days</u>	<u>20 days</u>
Pd(II) nitrate	0.55	0.22	0.10
Pd(BaSO ₄)	0.42	0.21	0.12
Pd(Hg)	0.42	0.23	0.11
PdO hydrate	0.42	0.24	0.18

TABLE VIII. Selected Decomposition Rates and Soluble Palladium Concentrations from KTPB Solids Stability Tests (45 °C)

<u>Pd (mg/L)</u>			<u>K⁺ Rate</u>		<u>pH</u>	<u>Na⁺ (M)</u>	<u>Ref.</u>
<u>Initial</u>	<u>Change</u>	<u>Final</u>	<u>mM/d</u>	<u>(mg/L/d)</u>			
4.9	-1.3	3.6	0.66	26	10.5	5.5	9
14.	-12.8	1.2	3.2	124	10.7	5.5	9
3.8	+2.8	6.6	0.56	22	10.2	2.8	9
3.4	-1.7	1.7	0.36	14	9.9	2.8	9
4.1	-3.9	0.2	0.49	19	10.5	2.8	9
5.7	+1.8	7.5	0.056	2.2	10.2	0.1	9
2.3	-1.6	0.6	0.59	23	10.3	0.1	9
0.1	-0.1	<0.1	0.43	17	10.4	0.1	9
3.1	+6.9	10.	0.074	2.9	14.5	5.5	9
7.4	-7.2	0.2	0.097	3.8	14.5	5.5	9
8.6	-8.4	0.2	0.15	5.8	14.3	5.5	10
1.8	-1.5	0.3	0.22	8.5	14.2	4.5	10
10.7	-10.6	0.1	0.26	10.1	14.5	4.5	10
5.5	-5.4	0.1	0.18	7.1	14.2	4.5	10

FIGURE 4. Eh of Alkaline Tetraphenylborate Slurry

Note: The standard calomel electrode (SCE) is -282 mV vs. the standard hydrogen electrode.

(from D. F Bickford, *et al*, Reference 12)

Figure 5. Stability Diagram for Palladium

FIG. 1. Potential-pH equilibrium diagram for the system palladium-water, at 25°C.

(from M. Pourbair, Reference 13)

By the arguments above, PdO hydrate should convert to Pd^0 and catalyze the reaction. However the rate of conversion of PdO hydrate to Pd^0 under anoxic conditions is slow and the conversion is incomplete after six months under anoxic conditions.⁷ Thus, the difference in reactivity between soluble Pd(II) and insoluble PdO hydrate may be due to their relative rates of conversion of Pd^0 .

Identification of the active catalyst as a low valent species is supported by the reactivity of the two zero-valent forms tested and the thermodynamic stability of Pd^0 under the test conditions. It is also supported by the observed distribution in which the majority of the total palladium is found with the tetraphenylborate and sludge solids.

The presence of large amounts of palladium with the tetraphenylborate solids and failure to remove palladium by benzene extraction suggests that the catalytic form is not a benzene soluble compound. This result must be considered tentative since other factors could have intervened to prevent extraction. The extraction procedure successfully removed mercury, presumably in the form of diphenylmercury. However, if the catalytic palladium compound is distributed differently or is more strongly adsorbed on tetraphenylborate solids, the extraction could have failed for a palladium compound. Tests on the distribution of benzene in KTPB slurries indicate that shaking by hand may not be sufficient to wet the KTPB particles with benzene within the time period used in the test.¹⁴ In addition, the extraction procedure introduces oxygen into the slurry sample and could have changed the oxidation state (and, thus, the distribution and extractability) of the palladium compound.

Although the observations suggest an insoluble palladium catalyst, they do not preclude a soluble form at the benzene-water interface. In the benzene extraction procedure, small amounts of benzene (including, presumably, the interface) remained with the solids. Thus, an interfacial palladium compound could have been left with the solids

Another interpretation of the results is that only a small fraction of the total palladium is catalytically active. In this interpretation, the experimental results are inconclusive since some palladium was found in each of the phases analyzed, including the benzene phase.

UNCERTAINTIES IN CURRENT WORK

The results of the experiments suggest that the palladium catalyst is an insoluble low-valent compound. If additional understanding of the catalyst system is needed, future testing should include the following areas of investigation.

- Determine the distribution and form of palladium in SRS radioactive wastes.

The rate of decomposition of tetraphenylborate and the methods suitable for removing palladium are sensitive to the amount and form of the palladium present. Before deciding on methods for palladium removal, the distribution of palladium in the SRS wastes should be explored.

- Determine the rate of conversion and final form of soluble Pd(II) nitrate under experimental conditions.

When Pd(II) nitrate is added to tetraphenylborate slurries, the majority converts to an insoluble form. XRD could be used to identify the final form and possibly further characterize the insoluble forms of palladium used in tests reported here.

- Measure the catalytic activity of other forms of palladium.

This is an extension of the work described in this report. Tests with additional forms might provide additional information on the identity of the active catalyst. Additional forms are available commercially, including palladium dispersed on activated carbon. This approach could be extended to include the synthesis of low-valent Pd compounds that are stable under the test conditions.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the helpful discussions and suggestions from John R. Fowler in the design and interpretation of the experiments described in this report.

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APPENDIX A

Postulated Mechanisms

The following eight decomposition mechanisms have been postulated.

Mechanism 1. Aqueous-Soluble Catalyst and Aqueous-Soluble Substrate

Decomposition occurs when the aqueous-soluble palladium catalyst reacts with soluble TPB^- ion. Solid tetraphenylborates must dissolve to react with catalyst. The rate will depend on the concentration of soluble palladium and TPB^- , but will be independent of solids.

Mechanism 2. Micellar Catalyst and Aqueous-soluble Substrate

The palladium catalyst is a polar molecule, presumably with a phenyl groups at one end and hydroxo groups opposite. The catalyst resides at the benzene aqueous interface. Soluble TPB^- approaches the catalyst from the aqueous side of the interface to react. The rate of reaction depends on the presence of benzene and solids (to disperse the benzene phase), the concentration of aqueous TPB^- , but is independent of aqueous soluble

Mechanism 3. Benzene-soluble Catalyst and Benzene-soluble Substrate

The palladium catalyst (possibly a phenylated, neutral species) is soluble in a benzene layer distributed over the slurry solids. The catalyst reacts with TPB^- ion (or ion pair) dissolved in the benzene phase. Benzene-soluble substrate could come from extraction of aqueous TPB^- ion or dissolution of tetraphenylborate solids.

Mechanism 4. Benzene-soluble Catalyst and Solid Substrate

The catalyst is dissolved in a benzene phase distributed over the surface of the tetraphenylborate solids. The catalyst reacts primarily at the solid surface. The reaction rate will depend on the presence of benzene and tetraphenylborate solids, but would be independent of soluble TPB^- or aqueous soluble palladium.

Mechanism 5. Solid Catalyst and Benzene-soluble Substrate

A solid palladium catalyst (insoluble in water or benzene) is coated with benzene and reacts with TPB^- dissolved in the benzene. The presence of the benzene phase promotes removal of 3PB^- from the activated complex as a phenyl anion remains with the palladium catalyst.

Mechanism 6. Solid Catalyst and Aqueous-soluble Substrate

Decomposition occurs when TPB^- in the aqueous phase encounters the solid phase palladium catalyst. During reaction, Pd might not be detectable in the aqueous phase, but the rate would depend very strongly on the soluble TPB^- concentration.

Mechanism 7. Aqueous-soluble Catalyst and Solid Substrate

The soluble catalyst reacts at the surface of the tetraphenylborate solids. In this mechanism, the reaction rate should be independent of the concentration of soluble TPB^- .

Mechanism 8. Solid catalyst and Solid Substrate

Both the palladium catalyst and tetraphenylborate solids react as solids. This is a very unlikely mechanism since the reaction rate would be exceedingly slow due to limited reaction zone where the two solids contact.

APPENDIX B

Experimental

Preparation of Slurries

Researchers prepared a simulated KTPB slurry (nominally 5 wt % KTPB solids) with the composition shown in Table B-1. Researchers added ~0.8 M NaTPB solution to a ~0.15 M KNO_3 solution to ensure complete and rapid precipitation of KTPB, followed by addition of soluble sodium salts to achieve 2.8 M Na^+ . All chemicals were reagent grade. NaTPB (99+% purity) came from Aldrich Chemical Company. Next, all of the components of the catalyst system (Table B-2) except palladium, benzene, diphenylmercury, and the alcohols were added to the slurry. The slurry was then split into four 175-mL portions. To each portion of slurry was added one of the palladium forms (Table B-3). Enough of the palladium form was added to achieve 11 mg Pd per liter of slurry. After stirring for one hour, approximately 130 mL of slurry were placed in 150-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 55 °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. Periodically, the vials were removed from the oven, shaken briefly by hand, and sampled by syringe.

The Pd(Hg) mixture was prepared as follows:

- (1) 1.9 mg of Pd black, 62 mg of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and 1 g water were weighed into a glass beaker. The mixture was stirred to dissolve the mercuric nitrate and suspend the palladium black.
- (2) 82 mg of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 1 mL water, then added to the Pd and mercury mixture to reduce the $\text{Hg}(\text{II})$ to Hg^0 .
- (3) The mixture was stirred overnight and the entire contents added to one portion of the slurry.

At all sampling times, a portion of slurry was filtered using disposable acrylic copolymer syringe filters (0.45 micron nominal pore size) (Gelman Sciences) and the filtrate analyzed for soluble metals, NaTPB, and decomposition products. Three times during the test, a second sample (~10 g) was taken and placed in a centrifuge tube. Benzene (15 mL) was added and the mixture shaken by hand for 5 minutes. The benzene was separated by centrifuging and decanting. The benzene extraction was repeated three more times using 10-mL aliquots of benzene. The benzene extracts (45 mL) were evaporated to dryness and the residue submitted for analysis. Due to the density of the salt solution, the sludge solids sank to the bottom of the centrifuge tube while the KTPB solids floated on the surface. The KTPB solids and salt solution were removed and filtered. Water (~5 mL) was used to facilitate removal of all the KTPB solids from the centrifuge tube and rinse the solids. The solids were dried at 45 °C and submitted for analysis. The sludge was removed from the centrifuge tube by suspending in water and transferring to a glass beaker. The sludge and water were dried at 45 °C and the residue analyzed.

Soluble Palladium Test

A test was run to determine the amount of palladium that dissolves from the four palladium forms under air in the absence of tetraphenylborate and intermediate decomposition products. Table B-1 lists the salt solution composition. It corresponds to the average composition of soluble waste at the Savannah River Site. The ECC catalyst system (Table B-2) was added at 1 wt %, including inactive organics (methanol, isopropanol, and phenol), but not benzene, tetraphenylborate, or decomposition intermediates (3PB, 2PB, and 1PB). Palladium was added from the same sources used in the reactivity tests (Table B-3). To 100 mL portions of the salt solution and ECC catalyst, enough of the Pd source was added to produce 11 mg Pd per liter. The solutions were stirred at room temperature and sampled after 7 and 14 days. The samples were filtered using 0.45 micron acrylic copolymer syringe filters (Gelman Sciences) and analyzed for selected metals by ICP-MS. The results are listed in Table B-4.

TABLE B-1 Composition of Simulated Waste Slurry (Excluding Catalyst Components)*

<u>Component</u>	<u>Concentration (molar)</u>
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
TPB ⁻	0.002
KTPB	60 g/L (~5 wt %)

*See Table B-2 for catalyst components.

TABLE B-2. 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
Rh	0.06	Zn	0.2
Cr	0.2	Zr	2.5

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	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		

TABLE B-3. Palladium Sources

<u>Form</u>	<u>Source</u>	<u>Vendor</u>
Pd(II) nitrate*	Pd(II) nitrate solution 15.27 wt % Pd	Colonial Metals, Inc.
Pd(BaSO ₄)	5 wt % reduced Pd on powdered BaSO ₄	Alfa Aesar
Pd(Hg)**	Pd black (~5 wt % oxygen)	Alfa Aesar
PdO hydrate	PdO·H ₂ O (76.9 wt % Pd)	Alfa Products

* Dissolved in 0.1 M HNO₃.** Suspended in Hg⁰.

TABLE B-4. Concentrations of Selected Metals in Solubility Test of Four Palladium Sources

<u>Metal</u>	<u>Elapsed Time (d)</u>	<u>Concentration (mg/L)</u>			
		<u>Pd(NO₃)₂*</u>	<u>Pd(BaSO₄)*</u>	<u>PdO*</u>	<u>Pd(Hg)*</u>
Pd	7	10.2	0.65	0.085	0.022
	14	9.3	1.70	0.180	0.042
Cu	7	0.117	0.129	0.130	0.139
	14	0.179	0.193	0.202	0.200
Hg	7	0.52	0.57	0.67	0.100
	14	0.54	0.69	0.73	0.125
Ag	7	0.036	0.060	0.032	<.020
	14	0.81	0.57	0.43	0.35
Ru	7	0.030	<.020	0.028	<.020
	14	0.036	0.033	0.036	0.036
Rh	7	0.042	0.031	0.042	0.020
	14	0.010	0.011	0.014	0.018

* See Table B-3 for description of palladium sources.

Solids Removal Test

Researchers prepared a salt solution containing 3.53 M Na⁺ with the same relative distribution of anions currently found in Tank 48H but without organic compounds (Table B-5). The components of the ECC catalyst system (Table B-2) were added (1 wt % catalyst) except for the organic components. The sludge contained 0.11 wt % palladium. The palladium was added to the sludge metals in January 1994 and the sludge was used for this experiment in October 1997. The total palladium concentration in the sludge and salt solution slurry was 13 mg/L. The slurry was stirred at ambient temperature (22±3 °C) for seven days. Samples were removed, filtered, and analyzed after 5 minutes, 1 day, 3 days, and 7 days. After seven days, the salt solution was divided into two parts and one part was filtered to remove the insoluble sludge components. Sodium tetraphenylborate (0.55 M) was added to each half to precipitate soluble potassium and produce 60 g KTPB per liter. Addition of the ECC catalyst components and the NaTPB solution diluted the total sodium concentration to 2.8 molar and the composition shown in Table B-1. The organic components of the catalytic system (see Table B-2) were added to both slurries and the resulting mixtures incubated at 45 °C for

TABLE B-5. Composition of Salt Solution for Solids Removal Test

<u>Component</u>	<u>Concentration (M)</u>	
	<u>Initial</u>	<u>After KTPB Precipitation</u>
Na ⁺	3.53	2.8
OH ⁻	1.93	1.5
NO ₃ ⁻	0.87	0.69
NO ₂ ⁻	0.32	0.25
AlO ₂ ⁻	0.13	0.10
CO ₃ ²⁻	0.064	0.051
SO ₄ ²⁻	0.060	0.048
Cl ⁻	0.010	0.008
F ⁻	0.006	0.005
PO ₄ ³⁻	0.004	0.003

52 days. Periodically, portions were removed, filtered, and analyzed for loss of NaTPB, increase in soluble K⁺, and concentrations of soluble heavy metals (Ag, Ru, Rh, and Pd).

Analytical Results

The samples were analyzed for potassium ion, organic compounds (NaTPB, 3PB, 2PB, 1PB, and phenol), and metals (Cu, Hg, Ag, Ru, Rh, and Pd). Table B-6 lists the analytical results from the palladium form test, Table III lists results from the solubility test, and Table B-7 lists results from the test on the effect of filtering to remove insoluble palladium and sludge.

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.

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 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 $\pm 10\%$ of the average.

Potassium ion concentrations on aqueous samples 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 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. The methods are described in Manual L16.1, Procedure #ADS-1509 and in Reference 15.

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.

Solid samples were digested completely and diluted to constant volume for analysis. The benzene extract samples were digested in nitric acid with microwave heating. KTPB and sludge solids were digested by sodium peroxide fusion followed by uptake in hydrochloric acid.

TABLE B-6. Analytical Results for Palladium Form Tests

Pd(II) nitrate													
Time (days)	Sample	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	Hg (mg/L)	K+	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Sample wt (g)
0	Aqueous	<.02	2.300	0.170	3.540	0.000	<2	856	1259	334	284	768	11.32
	Benzene	0.244	0.041	0.049	0.908	4.920	-	-	-	-	-	-	-
	KTPB	29	88	26	38.0	<1	-	-	-	-	-	-	0.8403
	Sludge	31	10.3	234	21.4	-	-	-	-	-	-	-	0.1688
2	Aqueous	<.02	3.95	0.450	1.78	0.000	-	451	936	614	-	-	-
6	Aqueous	<.02	3.92	0.714	0.576	-	<4	<10	170	763	-	-	-
9	Aqueous	<.02	4.71	1.140	0.551	<1	28	<10	<10	482	-	-	-
13	Aqueous	<.02	4.39	1.03	0.225	<1	69	<10	<10	262	-	-	10.6
	Benzene	0.360	0.100	<.4	0.238	960	-	-	-	-	-	-	-
	KTPB	542	2.63	1.98	22	202	-	-	-	-	-	-	0.6024
	Sludge	39	4.83	163	14	16	-	-	-	-	-	-	0.284
20	Aqueous	<.02	4.56	1.16	0.102	<1	121	<10	<10	149	-	-	-
27	Aqueous	<.02	4.86	1.53	0.296	<1	148	<10	<10	85	300	1352	-
34	Aqueous	<.02	4.22	1.42	0.416	<1	155	<10	<10	33	180	1457	-
	Benzene	0.629	0.08	0.04	0.101	1005	-	-	-	-	-	-	-
	KTPB	2182	0.37	5.12	80.5	477	-	-	-	-	-	-	0.7632
	Sludge	313	3.18	95.70	15.4	14	-	-	-	-	-	-	0.4924
41	Aqueous	0.068	3.75	1.25	0.154	<1	156	<10	<10	<10	104	1537	-
Pd on BaSO4													
Time (days)	Sample	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	Hg (mg/L)	K+	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Sample wt (g)
0	Aqueous	<.02	2.400	0.174	0.539	0.000	<1	852	1279	341	281	776	11.32
	Benzene	0.061	<.02	0.042	0.127	5.160	-	-	-	-	-	-	-
	KTPB	618	60	15	50.7	2,000	-	-	-	-	-	-	0.8171
	Sludge	31	22	251	233	-	-	-	-	-	-	-	0.1689
2	Aqueous	<.02	3.400	0.453	0.694	0.000	-	623	1055	453	-	-	-
6	Aqueous	<.02	4.980	0.829	0.327	-	<4	504	880	443	-	-	-
9	Aqueous	<.02	4.050	1.030	0.424	<1	<4	342	740	366	-	-	-
13	Aqueous	<.02	3.540	0.823	0.213	<1	<4	172	148	302	-	-	10.77
	Benzene	0.081	0.088	<.04	0.073	1086	-	-	-	-	-	-	-
	KTPB	1950	2.90	30	27	-	-	-	-	-	-	-	0.8019
	Sludge	42	5.73	134	181	141	-	-	-	-	-	-	0.152
20	Aqueous	<.02	3.770	0.979	0.118	<1	<4	56	292	260	-	-	-
27	Aqueous	<.02	4.140	1.350	0.341	<1	6.4	<10	119	186	241	1574	-
34	Aqueous	<.02	3.580	1.290	0.487	<1	8.5	<10	58	112	184	1653	-
	Benzene	1.320	0.073	0.037	0.069	1106	-	-	-	-	-	-	-
	KTPB	1803	0.457	6.82	31.8	109	-	-	-	-	-	-	0.8286
	Sludge	191	4.730	109	75.1	64	-	-	-	-	-	-	0.3919
41	Aqueous	<.02	3.150	1.100	0.022	<1	12.9	<10	35	77	121	1793	-
Pd(Hg)													
Time (days)	Sample	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	Hg (mg/L)	K+	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Sample wt (g)
0	Aqueous	<.02	2.500	0.198	0.239	0.000	<2	630	1151	541	286	767	11.3
	Benzene	0.092	<.02	0.044	0.087	7.5	-	-	-	-	-	-	-
	KTPB	688	61	17.4	49	105	-	-	-	-	-	-	0.9351
	Sludge	29	24	218	183	-	-	-	-	-	-	-	0.1802
2	Aqueous	<.02	3.480	0.457	0.450	0.000	-	469	952	614	-	-	-
6	Aqueous	<.02	3.330	0.762	0.296	-	<4	324	481	788	-	-	-
9	Aqueous	<.02	3.970	1.010	0.416	<1	<4	202	666	349	-	-	-
13	Aqueous	<.02	4.130	0.873	0.232	<1	<4	121	602	239	-	-	10.63
	Benzene	0.074	0.100	<.01	0.074	-	-	-	-	-	-	-	-
	KTPB	1210	2.99	33	86	-	-	-	-	-	-	-	0.8483
	Sludge	29	9.92	157	23	27	-	-	-	-	-	-	0.136
20	Aqueous	<.02	10.80	2.400	0.106	<1	<4	68	327	161	-	-	-
27	Aqueous	<.02	4.010	1.310	0.497	-	<4	40	330	111	174	1584	-
34	Aqueous	<.02	2.050	0.711	0.354	<1	<4	21	248	70	116	1637	-
	Benzene	1.660	0.085	0.027	0.046	3190	-	-	-	-	-	-	-
	KTPB	2626	1.59	23.6	23.6	16	-	-	-	-	-	-	0.7969
	Sludge	186	9.07	133.0	25.2	20	-	-	-	-	-	-	0.2576
41	Aqueous	<.02	3.400	1.220	0.036	<1	<4	<10	221	61	93	1782	-
PdO hydrate													
Time (days)	Sample	Ag (mg/L)	Ru (mg/L)	Rh (mg/L)	Pd (mg/L)	Hg (mg/L)	K+	NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Sample wt (g)
0	Aqueous	0.054	2.400	0.185	0.213	0.000	<2	876	1299	343	282	776	11.32
	Benzene	<.02	0.032	0.078	0.043	4.920	-	-	-	-	-	-	-
	KTPB	1408	7.4	16.2	54	1,000	-	-	-	-	-	-	0.9561
	Sludge	30	24	296	192	-	-	-	-	-	-	-	0.1714
2	Aqueous	0.058	4.320	0.487	0.398	0.000	-	781	1223	287	-	-	-
6	Aqueous	<.02	5.010	0.857	0.159	-	<4	815	1223	210	-	-	-
9	Aqueous	<.02	3.970	1.010	0.416	<1	<4	789	1230	179	-	-	-
13	Aqueous	<.02	5.730	1.020	0.243	<1	<4	835	1328	139	-	-	10.46
	Benzene	0.045	<.02	<.01	0.072	-	-	-	-	-	-	-	-
	KTPB	1700	2.60	29	59	-	-	-	-	-	-	-	0.6473
	Sludge	29	6.82	181	67	<20	-	-	-	-	-	-	0.153
20	Aqueous	<.02	6.530	1.230	0.176	<1	<4	732	1213	95	-	-	-
27	Aqueous	<.02	7.140	1.520	0.639	<1	<4	754	1256	86	-	-	-
34	Aqueous	<.02	6.920	1.500	0.597	<1	<4	610	1147	68	106	1206	-
	Benzene	0.062	<.02	0.034	0.048	1256	-	-	-	-	-	-	-
	KTPB	2511	0.613	14	11.5	425	-	-	-	-	-	-	0.8003
	Sludge	157	2.350	133	184	<1	-	-	-	-	-	-	0.2452
41	Aqueous	<.02	6.600	1.400	0.110	<1	<4	590	1191	63	114	1316	-

TABLE B-7. Analytical Results from Experiment on the Effect of Filtering Insoluble Sludge and Palladium

Metal concentrations in salt solution prior to KTPB precipitation (23 °C)										
Elapsed Time					Cu	Hg	Ag	Ru	Rh	Pd
					(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
5 min					0.13	0.044	0.07	0.37	0.04	3.2
1 day					0.082	0.059	0.09	0.70	0.08	5.9
3 days					0.081	0.043	0.07	0.66	0.11	6.4
7 days					0.072	0.16	<.05	0.50	0.13	6.4
Slurry from filtered salt solution (no insoluble sludge)										
Elapsed Time	K+	4PB	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)
0	<.2	425	834	201	244	276	<.05	0.31	0.10	4.5
5	3	24	566	611	303	307	<.05	0.26	0.08	0.240
12	<1	<10	178	834	368	347	<.02	0.29	0.03	0.039
19	51	<10	34	889	502	418	<.02	0.30	0.10	0.035
26	98	<10	<10	882	738	595	24.80	0.31	0.12	0.038
33	231	<10	<10	436	1027	878	0.12	0.30	0.11	0.064
39	367	<10	<10	203	1169	1188	<.02	0.29	0.14	0.083
52	720	<10	<10	61	1326	1885	<.02	0.25	<.01	0.063
Slurry with sludge solids present										
Elapsed Time	K+	4PB	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)
0	<.2	867	869	211	245	290	<.05	0.39	0.12	4.1
5	26	<10	13	283	939	338	<.05	1.41	0.29	0.02
12	60	<10	<10	95	935	383	<.02	1.46	0.43	0.03
19	93	<10	<10	61	797	473	<.02	1.64	0.47	0.02
26	157	<10	<10	75	740	617	<.02	1.59	0.56	0.026
33	249	<10	<10	63	600	732	0.046	1.46	0.56	0.038
39	291	<10	<10	62	452	832	<.02	1.54	0.56	0.061
52	623	<10	<10	100	645	1398	<.02	1.42	0.46	0.065

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