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SENSITIVITY ANALYSIS OF A TPB DEGRADATION RATE MODEL

Charles L. Crawford
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August 2006

Statistical Consulting Section
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Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

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EXECUTIVE SUMMARY

A tetraphenylborate (TPB) degradation model for use in aggregating Tank 48 material in Tank 50 is developed in this report. The influential factors for this model are listed as the headings in the table below. A sensitivity study of the predictions of the model over intervals of values for the influential factors affecting the model was conducted. These intervals bound the levels of these factors expected during Tank 50 aggregations. The results from the sensitivity analysis were used to identify settings for the influential factors that yielded the largest predicted TPB degradation rate. Thus, these factor settings are considered as those that yield the "worst-case" scenario for TPB degradation rate for Tank 50 aggregation, and, as such they would define the test conditions that should be studied in a waste qualification program whose dual purpose would be the investigation of the introduction of Tank 48 material for aggregation in Tank 50 and the bounding of TPB degradation rates for such aggregations.

The recommended conditions for testing the decomposition of Tank 48 waste slurries in a waste qualification program are:

Temperature (°C)	pH	Na+ (M)	wt% KTPB	Rad/ No Rad	Soluble TPB Present
45	14	6	0.1	Rad	No

For these settings of the influential factors, the model yields the highest expected TPB rate with a value of 2.04×10^{-6} mole KTPB/L/day. Since the rate used in the modeling is expressed as a natural logarithm (ln[rate]), the expected value of the model may be thought of as the average of the ln[rate]'s that would be generated by running a series of experiments – all at the conditions specified in the table above. The upper bound on this expected rate, at 95% confidence, is given by 4.95×10^{-6} mole KTPB/L/day.

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DSS	Decontaminated Salt Solution
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
JMP	Pronounced "jump." It's a statistical software package, a registered trademark of SAS Institute, Inc.
MCU	Modular Caustic Side Solvent Extraction Unit
MDL	Minimum Detection Limit
RMSE	Root Mean Square Error
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TPB	Tetraphenylborate

1.0 INTRODUCTION AND BACKGROUND

Options are currently under study for returning the H-area's Tank 48 to service by disposing of its current ~250,000 gallons of salt solution which contains 21,800 kg of potassium (K) and cesium (Cs) tetraphenylborate (TPB) [1]. One option that has been explored is the aggregation of the Tank 48 material in Tank 50 with Defense Waste Processing Facility (DWPF) recycle material and decontaminated salt solution (DSS) from the Modular Caustic Side Solvent Extraction Unit (MCU). The available data on decomposition rates for potassium tetraphenylborate (KTPB) solids have been fitted to statistical models in an effort to derive expressions of the solids decomposition rate as a function of a number of variables including sodium ion concentration, temperature, pH, wt % KTPB, etc. (see References [2] and [3] for background information of the data and model discussed in this paper). A model was initially developed to predict the TPB decomposition rate for conditions anticipated for the Tank 48 residual heel. After the model was developed it was also considered for predictions of TPB decomposition under conditions anticipated during the aggregation of Tank 48 material in Tank 50.

A waste qualification program is to be developed to validate that the degradation rates for the planned Tank 50 aggregation streams will be below levels of concern with high confidence before actual aggregation would be conducted. The waste qualification program is to be an experimental study, and for it to be successful it is necessary to define an appropriate experimental protocol to represent the planned aggregations. This includes establishing settings for the levels of the influential inputs to the degradation process as anticipated by the model described below.

This technical report is being prepared to document an important input to the planning of the waste qualification program. The purpose of the paper is to document the data used in model development, the fitted model to be used to predict TPB degradation rate, and a sensitivity study for the predictions of the model over intervals of values for its respective influential factors. The results from the sensitivity analysis are to be used to identify settings for the influential factors that are to be studied as part of the waste qualification program. To accomplish this, the predicted rates for TPB decomposition for the model are to be explored over a range of conditions of interest, the maximum predicted TPB decomposition rate for the model over a range of conditions of interest is to be determined, and the settings (i.e., the values of the influential factors) for the maximum rate are to be identified.

2.0 RESULTS

The data in Table A1 of Appendix A provide the set of experimental outcomes that was compiled from available studies to support this modeling effort. Reference [2] provides the details associated with the compilation of these data. As the data were evaluated during this process, an attempt was made to reconcile experimental outcomes which were below the measurement detection limit (MDL) of the analytical process. These situations are identified by an entry of "MDL" in the "Notes" column of Table A1. There are also some entries in this table that reflect experiments with outcomes that were above the upper limit of the analytical process. These are indicated in the table by the label "Pegged high." The model discussed in this paper, however, was based on all of the data of Table A1.

In Table A1, there are columns for the quantitative factors: "Temp" (temperature in ºC), pH, weight percent potassium TPB (wt% KTPB), and Na^+ concentration (in moles/Liter, or Molar (M)) and qualitative factors: Rad/No Rad (radioactive or non-radioactive experimental trials) and

TPB Present (yes or no for the presence of soluble TPB in the experiment trial). A "no" for this last variable indicates that the amount of soluble TPB present, if any is present, is below 10 mg/L, the nominal DL of High Pressure Liquid Chromatography (HPLC). The TPB rate is the response of interest in Table A1. The values are expressed in the units E-06 moles of KTPB/L/day. A column also identifies if the testing involved a simulant or an actual high level waste (HLW) tank sample. Table 2-1 provides the minimum (min) and maximum (max) values for the quantitative factors for different groupings of the experiments. These data show that 127 data points, or observations, were considered. The temperatures ranged from 25ºC to 75ºC, the pH's ranged from 7 to 14.5, the wt% KTPB ranged from 0.0034 wt% to 5 wt% and the sodium molarity ranged from 0.1 to 8.58 M.

Table 2-1. Minimum and Maximum Factor Levels

		No Rad	**No Rad**	**No Rad**	**Rad**	**Rad**	**Rad**	
Soluble TPB Present		No	Yes	Both	No	Yes	Both	**Overall**
Number of Observations		31	34	65	30	32	62	127
Temperature (ºC)	min	25	25	25	25	30	25	25
	max	60	70	70	75	64	75	75
pH	min	7	10.1	7	11	9.8	9.8	7
	max	14	14.5	14.5	14.5	14.5	14.5	14.5
wt% KTPB	min	0.2147	2.6	0.2147	0.0034	0.8	0.0034	0.0034
	max	2.32	5	5	2.06	5	5	5
Na^+ (M)	min	2	0.1	0.1	0.14	0.1	0.1	0.1
	max	5.6	5.5	5.6	8.58	5.5	8.58	8.58

Before moving on to the discussion of model development, there is a need to carefully frame how the model predictions are going to be used. Note that the response used in the models developed in this study is the natural logarithm of the TPB rates of Table A1. JMP Version 5.1.2 from SAS Institute, Inc. [4] was used to conduct the statistical modeling. Statistical science provides several different types of confidence intervals for a predictive model like the one developed in this report. For the purposes of this report, the bound of interest is an upper 95% confidence limit on the expected log TPB rate for a single set of aggregation conditions (the two-sided version of this interval is available as a JMP option).

Figure 2-1 provides the legend of symbols and colors used to represent the experimental results in the plots used for model fitting. The main scheme used is to separate the Rad versus No Rad and the TPB Present versus Not Present data. A designation between simulant versus HLW tests is also incorporated in the legend. In addition there is one data point in Table A1 with an estimated TPB rate of 14,821 (×E-06 moles of KTPB/L/day) that was identified as a questionable result. This value is represented by a unique symbol and color (it is a No Rad/No TPB Present experimental result) so that its location on the various plots can be readily seen.

	Type of System	Rad/No Rad	TPB Present	Estimate TPB Rate (xE-6 moles KPTB/L/day)	Notes
1	HLW	Rad	No	•	
2	HLW	Rad	Yes	•	
3	Simulant	No Rad	No	•	
4	Simulant	No Rad	No	14821	Questionable pt
5	Simulant	No Rad	Yes	•	
6	Simulant	Rad	No	•	
7	Simulant	Rad	Yes	•	

Figure 2-1. Legend of Symbols/Colors Used to Represent Experimental Results

Figure 2-2 provides a look at the (natural logarithm of the) TPB rate data generated by the set of experiments. In this exhibit, a box plot is superimposed on the data. The upper end of each box represents the 75th percentile while the lower end represents the 25th percentile. The solid line crossing each box is the 50th percentile, or median. The horizontal hash mark within the box represents the mean of the data. Each box has lines, sometimes called *whiskers*, that extend from each end. The whiskers extend from the ends of the box to the outermost data point that falls within the distances computed

upper quartile + 1.5*(interquartile range)

lower quartile - 1.5*(interquartile range).

where the interquartile range is equal to the difference between the 25th and 75th percentiles. Data outside of this range are the more extreme values. These box plots show the wide interval of TPB rates (since the y-axis for these plots is in log space) that are covered in the experimental outcomes recorded in Table A1.

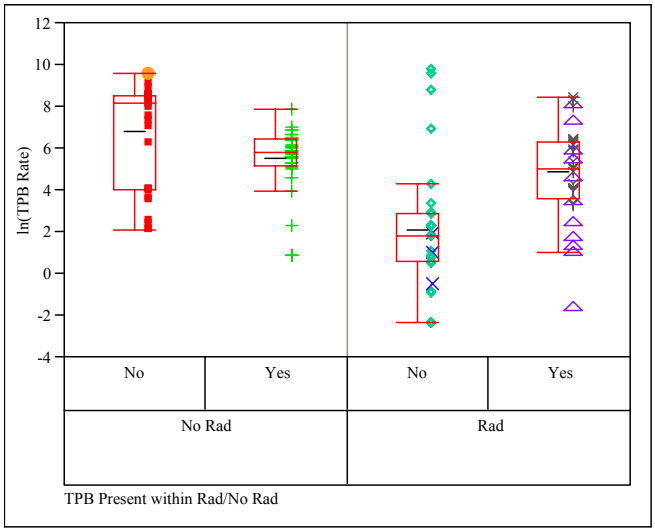


Figure 2-2. A Set of Box Plots Showing the ln(rate) Values Grouped by Rad vs Non-Rad and Soluble TPB Present vs Not Present

It is the sensitivities of the predicted degradation rates for the statistical model that are explored in this study. The prediction equation for the model is provided in Figure 2-3. The degradation rates for the model are predicted as natural logarithms in the units of 10^{-6} mole KTPB/L/day.

All of the data were used in the fitting of the TPB model discussed in this report. A full factorial model of degree 2 involving all of the factors defined the candidate terms that were submitted to JMP's Stepwise regression routine to select the "best subset" of terms for the model. Any interactive terms with p-values much greater than 5% were removed from the model as well. The JMP results including the p-values for the final model are given in Exhibit A1 in Appendix A. The R^2 value for the fitted model is 77.6% with a root mean square error (RMSE) of 1.462 in log units. There is no indication of a significant lack of fit (at the 5% significance level) for this model.

Figure 2-3 provides the JMP formula for the model's expected value of the natural logarithm of the TPB rate. Note that the TPB decomposition rate in the units of E-06 moles of KTPB/L/day is determined by taking the exponential of the model's predicted value. The formula for the predicted log value involves different calculations depending on the values of the qualitative factors (i.e., Rad or Non-rad experiments and TPB Present or Not Present). The options for the calculations are indicated and handled by JMP's "Match" function. Further details of the development of the JMP formula for the model's expected value of the natural logarithm of the TPB rate can be found in Ref. [2].

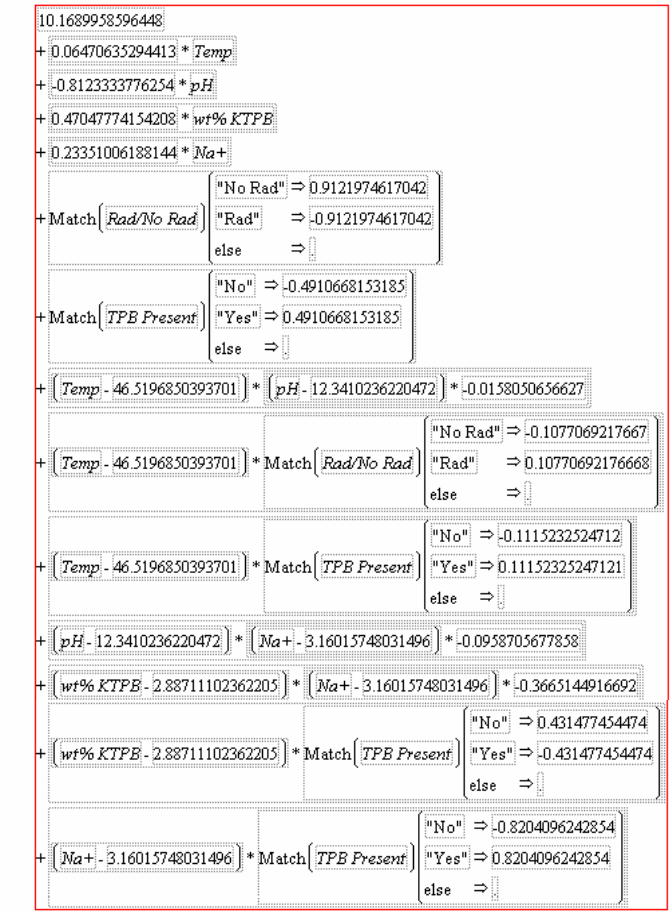


Figure 2-3 ln(rate) Prediction Formula for TPB Model

During the development of the aggregation flowsheet in 2005, the intervals of values for temperature, sodium ion concentration (Na^+), weight percent (wt%) KTPB solids, and pH for radioactive conditions without any soluble TPB being present at concentrations above 10 mg/L were evaluated. The intervals, which were derived from this process, include the maximum values from individual streams. The intervals are presented in Table 2-2, and these intervals were used as the initial inputs to the sensitivity analysis for the TPB model.

Table 2-2. Initial Intervals for Sensitivity Study of the TPB Model

Factor	Interval of Interest	Unit of Measure	Grid Values
Na^+	$1 \le Na^+ \le 7$	M	1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7
Temperature	$25 \le$ temperature ≤ 50	°C	25, 30, 35, 30, 45, 50
pH	$14 \le pH \le 14.5$	-	14, 14.1, 14.2, 14.3, 14.4, 14.5
wt% KTPB	$0.001 \le$ wt% KTPB ≤ 0.9	wt%	0.001, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9
Rad/No Rad	Rad		
Soluble TPB Present Yes/No	No		

The statistical package, JMP® Version 5.1.2 [4] was used to create a grid of points covering the intervals outlined in Table 2-2. Specifically, the grid was created with every possible combination of the values in the right-most column of Table 2-2; thus, a total of 13×6×6×12 = 5,616 points defined the grid. Figure 2-4 provides a scatterplot matrix of pairwise plots of the levels in Table 2-2 outlining the grid. The grid points are shown using the symbol, ○, while the symbol □ is used to represent the factor levels for Tank 50 Batches 2, 10, 20, 30, 40, 48, and 60 as derived from the aggregation flowsheet [1].

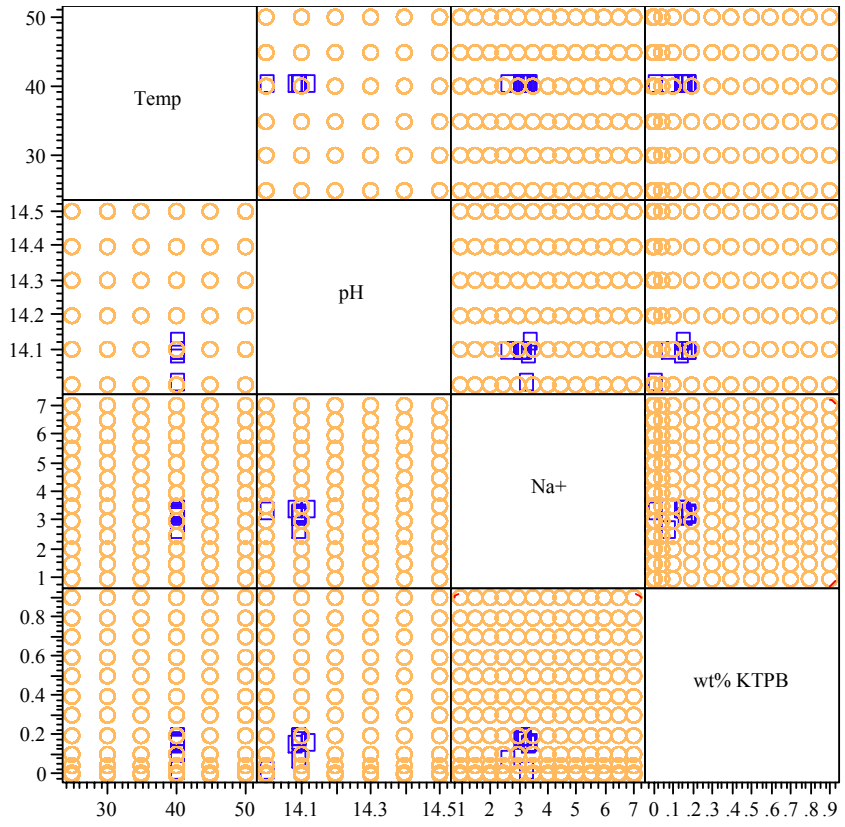


Figure 2-4 Scatterplot Matrix for Grid Outlined in Table 2-2

Using this grid covering the factor space of interest, the TPB model was used to predict the corresponding degradation rates. Figure 2-5 provides a plot of the predicted rates versus the factor levels for each of the four factors: temperature (Temp in °C), pH, wt% KTPB, and sodium ion concentration (Na^+ moles/Liter).

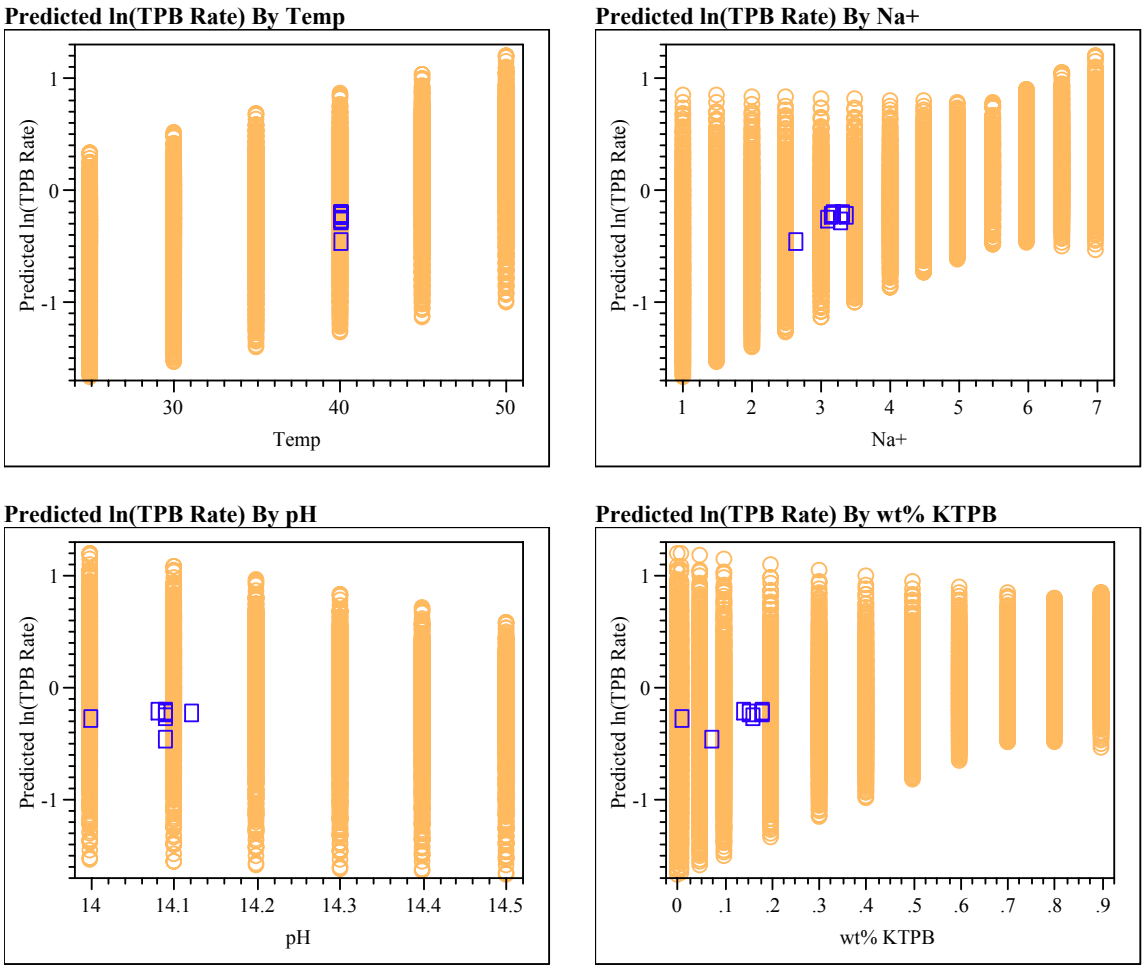


Figure 2-5 TPB Model Predictions by Factor for Grid Outlined in Table 2-2

The review of the model predictions over this grid of points also led to refinements in the flowsheet [1] that yielded the intervals actually used to conduct the sensitivity analysis for TPB model. These actual intervals for the model factors are outlined in Table 2-3.

Table 2-3 Actual Intervals for Sensitivity Study of the TPB Model

Factor	Interval of Interest	Unit of Measure	Grid Values
Na^+	$1 \le Na^+ \le 6$	M	1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6
Temperature	$25 \le$ temperature ≤ 45	°C	25, 30, 35, 30, 45
pH	$14 \le pH \le 14.5$	M	14, 14.1, 14.2, 14.3, 14.4, 14.5
wt% KTPB	$0.001 \le$ wt% KTPB ≤ 0.4	wt%	0.001, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4
Rad/No Rad	Rad		
TPB Present/No	No		

JMP® was used to create a grid of 11×5×6×7 = 2310 points covering the intervals outlined in Table 2-3, and the TPB model was used to predict the degradation rates over this grid of points. Figure 2-6 provides a scatterplot matrix of pairwise plots of the levels in Table 2-3 outlining the grid. As in the earlier plots, the grid points are shown using the symbol, ○, while the symbol □ is used to represent the factor levels for Tank 50 Batches 2, 10, 20, 30, 40, 48, and 60.

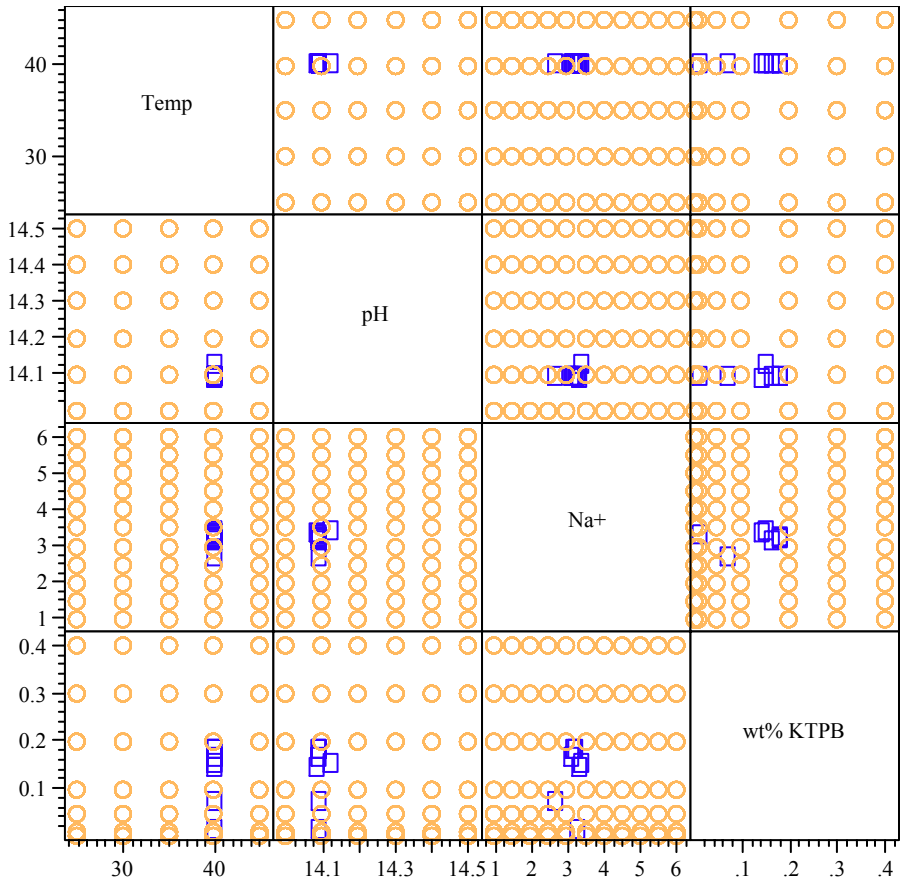


Figure 2-6 Scatterplot Matrix for Grid Outlined in Table 2-3

Using this grid covering the factor space of interest, the TPB model was used to predict the corresponding degradation rates. Figure 2-7 provides a plot of the predicted rates versus the factor levels for each of the four factors: temperature (Temp in °C), pH, wt% KTPB, and sodium ion concentration (Na^+ in moles/Liter).

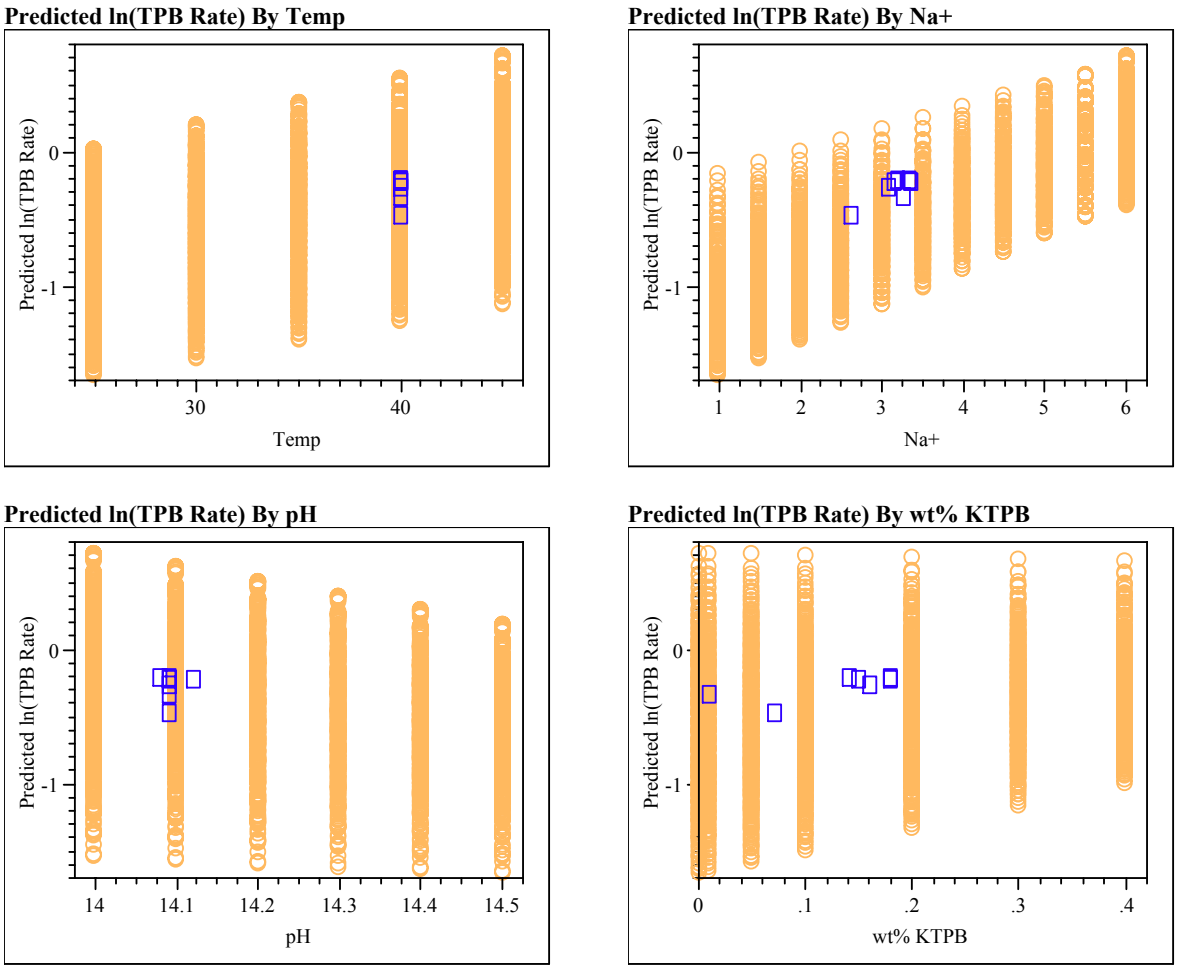


Figure 2-7 TPB Model Predictions by Factor for Grid Outlined in Table 2-3

It is interesting to note that the span of the 2,310 predicted TPB decomposition rates shown in the Figure 2-7 plots covers a range of about 10X. The highest predicted rate is ln(TPB predicted rate) = 0.729, or 2.07 E-06 mole KTPB/L/day, whereas the lowest predicted rate is ln(TPB predicted rate) = -1.656, or 0.19 E-06 mole KTPB/L/day. To help in the identification of a bounding rate over the factor space from Table 2-3 and Figure 2-7, the highest 100 predicted rates for the TPB model were determined. Table 2-4 provides the listing of the highest rates for the model along with the values of the factors that correspond to the prediction and the values providing an upper 95% bound on the average ln(rate). The highest 100 predicted rates range from ln(TPB predicted rate) = 0.729, or 2.07E-06 mole KTPB/L/day to ln(TPB predicted rate) = 0.327, or 1.39E-06 mole KTPB/L/day. It can be seen from the ~ 20 highest rates shown in Table 2-4 that conditions of highest temperature (45ºC), lowest pH (14 – 14.1), highest sodium molarity (6 to 5.5M) result in the highest rates. Within these parameters, the range of wt% KTPB from 0.001 to 0.4 wt% has limited influence. For instance, the highest 7 rates (lines 1-7 at top of Table 2-4) under conditions of 45ºC, pH=14 and 6M Na+ are in the range of 0.674 to 0.729 predicted ln(TPB Rate), or in the range of 1.96E-6 mole KTPB/L/day to 2.07E-6 mole KTBP/L/day.

Table 2-4 Highest 100 Predicted ln(rates) for TPB Model and the Factor Levels That Produced Them

Rank	Temp	pH	Na+	wt% KTPB	Rad/No Rad	Soluble TPB Present	Predicted ln(TPB Rate)	Upper 95% Limit for Mean ln(rate)
1	45	14	6	0.001	Rad	No	0.729	1.640
2	45	14	6	0.01	Rad	No	0.728	1.636
3	45	14	6	0.05	Rad	No	0.722	1.619
4	45	14	6	0.1	Rad	No	0.715	1.599
5	45	14	6	0.2	Rad	No	0.702	1.563
6	45	14	6	0.3	Rad	No	0.688	1.534
7	45	14	6	0.4	Rad	No	0.674	1.510
8	45	14.1	6	0.001	Rad	No	0.623	1.544
9	45	14.1	6	0.01	Rad	No	0.622	1.540
10	45	14.1	6	0.05	Rad	No	0.616	1.523
11	45	14.1	6	0.1	Rad	No	0.609	1.504
12	45	14.1	6	0.2	Rad	No	0.596	1.469
13	45	14	5.5	0.4	Rad	No	0.591	1.338
14	45	14	5.5	0.3	Rad	No	0.587	1.345
15	45	14	5.5	0.2	Rad	No	0.582	1.357
16	45	14.1	6	0.3	Rad	No	0.582	1.440
17	45	14	5.5	0.1	Rad	No	0.578	1.375
18	45	14	5.5	0.05	Rad	No	0.575	1.386
19	45	14	5.5	0.01	Rad	No	0.574	1.395
20	45	14	5.5	0.001	Rad	No	0.573	1.397
21	45	14.1	6	0.4	Rad	No	0.568	1.417
22	40	14	6	0.001	Rad	No	0.556	1.457
23	40	14	6	0.01	Rad	No	0.555	1.453
24	40	14	6	0.05	Rad	No	0.549	1.437
25	40	14	6	0.1	Rad	No	0.542	1.419
26	40	14	6	0.2	Rad	No	0.528	1.387
27	45	14.2	6	0.001	Rad	No	0.517	1.449
28	45	14.2	6	0.01	Rad	No	0.516	1.445
29	40	14	6	0.3	Rad	No	0.514	1.360
30	45	14.2	6	0.05	Rad	No	0.510	1.429
31	45	14	5	0.4	Rad	No	0.508	1.175
32	45	14.2	6	0.1	Rad	No	0.503	1.410
33	40	14	6	0.4	Rad	No	0.500	1.340
34	45	14.1	5.5	0.4	Rad	No	0.490	1.248
35	45	14.2	6	0.2	Rad	No	0.489	1.376
36	45	14	5	0.3	Rad	No	0.485	1.165
37	45	14.1	5.5	0.3	Rad	No	0.485	1.254
38	45	14.1	5.5	0.2	Rad	No	0.481	1.266
39	45	14.1	5.5	0.1	Rad	No	0.476	1.283
40	45	14.2	6	0.3	Rad	No	0.476	1.347
41	45	14.1	5.5	0.05	Rad	No	0.474	1.293
42	45	14.1	5.5	0.01	Rad	No	0.472	1.302
43	45	14.1	5.5	0.001	Rad	No	0.472	1.304
44	45	14	5	0.2	Rad	No	0.463	1.161
45	45	14.2	6	0.4	Rad	No	0.462	1.325
46	40	14.1	6	0.001	Rad	No	0.458	1.366
47	40	14.1	6	0.01	Rad	No	0.456	1.363
48	40	14.1	6	0.05	Rad	No	0.451	1.348
49	40	14.1	6	0.1	Rad	No	0.444	1.330
50	45	14	5	0.1	Rad	No	0.440	1.161
51	40	14.1	6	0.2	Rad	No	0.430	1.298
52	45	14	5	0.05	Rad	No	0.429	1.162
53	45	14	4.5	0.4	Rad	No	0.425	1.025

Table 2-4 Highest 100 Predicted ln(rates) for TPB Model and the Factor Levels That Produced Them *(continued)*

Rank	Temp	pH	Na+	wt% KTPB	Rad/No Rad	TPB Present	Predicted ln(TPB Rate)	Upper 95% Limit for Mean ln(rate)
54	45	14	5	0.01	Rad	No	0.419	1.164
55	40	14	5.5	0.4	Rad	No	0.418	1.170
56	45	14	5	0.001	Rad	No	0.417	1.165
57	40	14.1	6	0.3	Rad	No	0.416	1.273
58	40	14	5.5	0.3	Rad	No	0.413	1.173
59	45	14.1	5	0.4	Rad	No	0.412	1.087
60	45	14.3	6	0.001	Rad	No	0.411	1.354
61	45	14.3	6	0.01	Rad	No	0.410	1.350
62	40	14	5.5	0.2	Rad	No	0.409	1.182
63	40	14	5.5	0.1	Rad	No	0.404	1.196
64	45	14.3	6	0.05	Rad	No	0.404	1.334
65	40	14.1	6	0.4	Rad	No	0.402	1.253
66	40	14	5.5	0.05	Rad	No	0.402	1.205
67	40	14	5.5	0.01	Rad	No	0.400	1.213
68	40	14	5.5	0.001	Rad	No	0.400	1.215
69	45	14.3	6	0.1	Rad	No	0.397	1.316
70	45	14.1	5	0.3	Rad	No	0.389	1.077
71	45	14.2	5.5	0.4	Rad	No	0.388	1.158
72	45	14	4.5	0.3	Rad	No	0.384	0.999
73	45	14.2	5.5	0.3	Rad	No	0.384	1.164
74	45	14.3	6	0.2	Rad	No	0.383	1.283
75	35	14	6	0.001	Rad	No	0.383	1.303
76	35	14	6	0.01	Rad	No	0.381	1.300
77	45	14.2	5.5	0.2	Rad	No	0.380	1.175
78	35	14	6	0.05	Rad	No	0.376	1.286
79	45	14.2	5.5	0.1	Rad	No	0.375	1.191
80	45	14.2	5.5	0.05	Rad	No	0.373	1.201
81	45	14.2	5.5	0.01	Rad	No	0.371	1.209
82	45	14.2	5.5	0.001	Rad	No	0.371	1.211
83	45	14.3	6	0.3	Rad	No	0.370	1.255
84	35	14	6	0.1	Rad	No	0.369	1.270
85	45	14.1	5	0.2	Rad	No	0.366	1.072
86	40	14.2	6	0.001	Rad	No	0.360	1.277
87	40	14.2	6	0.01	Rad	No	0.358	1.273
88	45	14.3	6	0.4	Rad	No	0.356	1.234
89	35	14	6	0.2	Rad	No	0.355	1.241
90	40	14.2	6	0.05	Rad	No	0.353	1.259
91	40	14.2	6	0.1	Rad	No	0.346	1.241
92	45	14.1	5	0.1	Rad	No	0.343	1.071
93	45	14	4.5	0.2	Rad	No	0.343	0.978
94	45	14	4	0.4	Rad	No	0.343	0.893
95	35	14	6	0.3	Rad	No	0.341	1.219
96	40	14	5	0.4	Rad	No	0.335	1.008
97	45	14.1	4.5	0.4	Rad	No	0.334	0.940
98	45	14.1	5	0.05	Rad	No	0.332	1.072
99	40	14.2	6	0.2	Rad	No	0.332	1.211
100	35	14	6	0.4	Rad	No	0.327	1.203

3.0 RECOMMENDED SETTINGS

As discussed in Section 2.0 and seen in Table 2-4, wt% KTPB values within the interval studied (although statistically significant in the model) have minimal influence on the predicted TPB degradation rates. In selecting the conditions from Table 2-4 to be tested in the waste qualification program, a value of 0.1 wt% KTPB (the mid-point of the grid of values studied) was chosen. The complete set of conditions for testing by the waste qualification program (with corresponding model prediction and upper 95% confidence limit on the expected model prediction) is given by:

Temp (°C)	pH	Na+ (M)	wt% KTPB	Rad/ No Rad	TPB Present	Predicted ln(TPB Rate)	Upper 95% Limit for Mean ln(rate)
45	14	6	0.1	Rad	No	0.715	1.599

For these settings of the influential factors, the model yields the highest expected TPB rate with a value of 2.04×10^{-6} mole KTPB/L/day (this is the antilog of the corresponding 0.715 value in log-space for the fitted model's expected value at the selected conditions). Since the rate used in the model is expressed as a natural logarithm (ln[rate]), the expected value of the model may be thought of as the average of the ln[rate]'s that would be generated by running a series of experiments – all at the conditions specified in the table above. The upper bound on this expected rate, at 95% confidence, is given by 4.95×10^{-6} mole KTPB/L/day (this is the antilog of the confidence limit of 1.599 in log-space for the fitted model's expected value at the selected conditions).

4.0 CONCLUSIONS

A TPB degradation model for use in the aggregation of Tank 48 material in Tank 50 was developed. A sensitivity study of the predictions of the model over intervals of values for the influential factors was conducted. The results from the sensitivity analysis were used to identify settings for the influential factors that can be used as the test conditions for the waste qualification program.

5.0 REFERENCES

[1] Maxwell, D, "Tank 48 Disposition Project Flowsheet for Aggregation Strategy 0.2 Ci/gal Cesium Max Feed," CBU-PIT-2004-0012, Revision 2, April 2006.

[2] Edwards, TB, CL Crawford, DD Walker, "TPB Decomposition Rate Models for a Compiled Set of Experimental Results (U)," SRNL-SCS-2005-00032, Revision 1, September 9, 2005.

[3] Wilmarth, WR, CL Crawford, TB Edwards, RE Eibling, DD Walker, "Potassium Tetraphenylborate Decomposition Rate Analysis," WSRC-TR-2005-00318, September 2, 2005.

[4] SAS Institute, Inc., **JMP Statistics and Graphics Guide**, SAS Institute, Inc., Cary, NC, 2002.

Appendix A.

Table A1. Compilation of SRNL Research Data Available for TPB Degradation Rate Modeling

Rad/No Rad	TPB Present	Simulant /HLW	Temp (°C)	pH	wt% KTPB	Na+ (M)	Estimate TPB Rate (xE-6 moles KTPB/L/day)	Notes
Rad	Yes	HLW	39	14.3	3.2	3.7	102	
Rad	Yes	HLW	52	14.3	3.2	3.5	12	
Rad	Yes	HLW	30	14.2	2.3	3.6	0.2	
Rad	Yes	HLW	40	14.2	0.8	2.7	3.8	
Rad	Yes	HLW	40	14.2	4.7	2.7	2.8	
Rad	Yes	HLW	50	14.2	0.8	2.7	5.6	
Rad	Yes	HLW	50	14.2	4.7	2.7	33	
Rad	Yes	HLW	64	13.3	4.1	0.4	1500	
Rad	Yes	HLW	64	13.6	4.8	0.9	3300	
No Rad	Yes	Simulant	40	14.2	4	3	2.5	MDL
No Rad	Yes	Simulant	40	14.2	4	3	2.5	MDL
No Rad	Yes	Simulant	49	14.2	4	3	51	
No Rad	Yes	Simulant	70	14.2	4	3	1000	
No Rad	Yes	Simulant	45	14.5	5	5.5	97.1867008	
Rad	Yes	Simulant	45	14.5	5	5.5	74.1687979	
Rad	Yes	Simulant	45	10.4	5	5.5	660	
Rad	Yes	Simulant	45	10.3	5	5.5	580	
Rad	Yes	Simulant	45	10.2	5	5.5	510	
Rad	Yes	Simulant	45	10.46	5	5.5	3200	
Rad	Yes	Simulant	45	10.45	5	5.5	4600	
Rad	Yes	Simulant	45	10.35	5	5.5	4100	
Rad	Yes	Simulant	45	12.2	5	2.8	150	
Rad	Yes	Simulant	45	12.2	5	2.8	160	
Rad	Yes	Simulant	45	12	5	2.8	220	
Rad	Yes	Simulant	45	11.8	5	2.8	28.1329923	
Rad	Yes	Simulant	45	13.7	5	0.65	130	
Rad	Yes	Simulant	45	13.7	5	0.65	30.6905371	
No Rad	Yes	Simulant	45	10.3	5	0.1	660	
No Rad	Yes	Simulant	45	10.1	5	0.1	960	
No Rad	Yes	Simulant	45	10.2	5	0.1	810	
No Rad	Yes	Simulant	45	10.4	5	0.1	440	
Rad	Yes	Simulant	45	10.2	5	0.1	56.2659847	
Rad	Yes	Simulant	45	9.8	5	0.1	61	
Rad	Yes	Simulant	45	9.8	5	0.1	61	
Rad	Yes	Simulant	45	10.1	2.5	0.1	51.1508951	
Rad	Yes	Simulant	45	10.2	5	2.8	380	
Rad	Yes	Simulant	45	9.9	5	2.8	360	
Rad	Yes	Simulant	45	10.5	5	2.8	490	
Rad	Yes	Simulant	45	10.2	2.5	2.8	560	
Rad	Yes	HLW	45	14.3	0.9	5	230	
Rad	Yes	HLW	45	14.4	0.9	5	370	
No Rad	Yes	Simulant	45	14.3	5	5.5	150	
No Rad	Yes	Simulant	45	13.8	5	5.5	429.667519	
No Rad	Yes	Simulant	45	14.5	5	4.5	270	
No Rad	Yes	Simulant	45	14.2	5	4.5	180	
No Rad	Yes	Simulant	45	13.7	5	4.5	250	
No Rad	Yes	Simulant	45	13.7	5	4.5	270	
No Rad	Yes	Simulant	45	14	5	3.2	320	
No Rad	Yes	Simulant	45	14	5	3.15	160	
No Rad	Yes	Simulant	45	14.3	5	2.8	320	
No Rad	Yes	Simulant	45	14.3	5	2.8	180	
No Rad	Yes	Simulant	45	13.5	5	2.8	590	
No Rad	Yes	Simulant	45	13.5	5	2.8	360	
No Rad	Yes	Simulant	45	13.8	5	1.8	620	
No Rad	Yes	Simulant	45	13.8	5	1.8	210	
No Rad	Yes	Simulant	45	13	5	1	640	
No Rad	Yes	Simulant	45	13	5	1	490	
No Rad	Yes	Simulant	45	13.5	5	0.4	440	

Table A1. Compilation of SRNL Research Data Available for TPB Degradation Rate Modeling

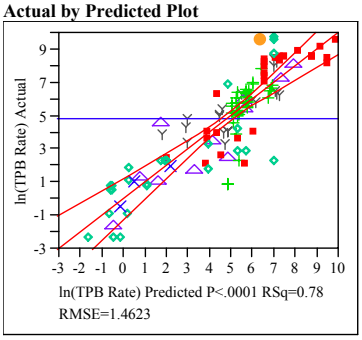
Rad/No Rad	TPB Present	Simulant /HLW	Temp (ºC)	pH	wt% KTPB	Na+ (M)	Estimate TPB Rate (xE-6 moles KTPB/L/day)	Notes
No Rad	Yes	Simulant	45	13.5	5	0.4	330	
No Rad	Yes	Simulant	45	12.3	5	0.2	700	
No Rad	Yes	Simulant	45	12.3	5	0.2	350	
No Rad	Yes	Simulant	45	13.9	5	2.8	200	
No Rad	Yes	Simulant	45	13.9	5	2.8	10	
No Rad	Yes	Simulant	25	14.43	2.6	4.7	769	
No Rad	Yes	Simulant	35	14.43	2.6	4.7	1150	
No Rad	Yes	Simulant	45	14.43	2.6	4.7	2690	
Rad	No	HLW	50	13.4	0.0034	0.3	1.7	
Rad	No	HLW	50	13.7	0.0034	0.8	2.2	
Rad	No	HLW	50	14	0.0092	1	0.43	
Rad	No	HLW	25	13.4	0.0034	0.3	0.1	MDL
Rad	No	HLW	50	14.5	0.0034	5.6	0.41	
Rad	No	HLW	25	14.5	0.0034	5.6	0.1	MDL
Rad	No	HLW	25	14	0.0034	5.6	0.1	MDL
No Rad	No	Simulant	25	9	0.4065	5.6	13749	
No Rad	No	Simulant	25	10	0.4065	5.6	8880	MDL
No Rad	No	Simulant	25	11.5	0.4065	5.6	7260	
No Rad	No	Simulant	25	13	0.4065	5.6	4514	
No Rad	No	Simulant	25	14	0.4065	5.6	14821	Questionable pt
Rad	No	HLW	25	14.2	0.0369	4.5	1.8	
Rad	No	HLW	25	14.2	0.0369	4.5	2.2	
Rad	No	HLW	50	14.2	0.0369	4.5	6.7	
Rad	No	HLW	50	14.2	0.0369	4.5	3.1	
No Rad	No	Simulant	45	11	2.32	2.6	1924	
No Rad	No	Simulant	45	11	2.32	2.6	3536	
No Rad	No	Simulant	45	7	2.32	2.6	3380	
No Rad	No	Simulant	45	7	2.32	2.6	4576	
No Rad	No	Simulant	45	11	2.32	2.6	1144	
No Rad	No	Simulant	45	11	2.32	2.6	1560	
No Rad	No	Simulant	45	8	2.32	2.6	5148	
No Rad	No	Simulant	45	10	2.32	2.6	3900	
No Rad	No	Simulant	45	11	2.32	2.6	2912	
No Rad	No	Simulant	45	14	2.32	2.6	520	
No Rad	No	Simulant	45	8	2.32	2.6	5148	Pegged high
No Rad	No	Simulant	60	8	2.32	2.6	5148	Pegged high
No Rad	No	Simulant	45	8	2.32	2.6	5148	Pegged high
No Rad	No	Simulant	45	10	2.32	2.6	5148	Pegged high
No Rad	No	Simulant	45	11	2.32	2.6	4368	
No Rad	No	Simulant	45	14	2.32	2.6	52	MDL
No Rad	No	Simulant	45	8	2.32	2.6	5148	Pegged high
No Rad	No	Simulant	60	8	2.32	2.6	5148	Pegged high
Rad	No	HLW	30	13.9	1.84	2.9	2.4	
No Rad	No	Simulant	35	14	1.87	2.7	8	MDL
No Rad	No	Simulant	45	14	1.87	2.7	8	MDL
No Rad	No	Simulant	55	14	1.87	2.7	11	MDL
No Rad	No	Simulant	45	13	1.87	2.7	13	MDL
No Rad	No	Simulant	45	12	1.87	2.7	36	MDL
No Rad	No	Simulant	45	11	1.87	2.7	56.6666667	
No Rad	No	Simulant	45	11	0.2147	2	35	
No Rad	No	Simulant	45	11	0.2147	2	55	
Rad	No	Simulant	55	14	2.06	2.9	6.6	MDL
Rad	No	Simulant	45	13.5	0.61	1.06	2.7	MDL
Rad	No	Simulant	45	12.5	0.1	0.14	0.6	MDL
Rad	No	HLW	75	11	0.82	8.58	18000	
Rad	No	HLW	75	11	0.82	8.58	15000	
Rad	No	HLW	75	11	0.82	8.58	10	MDL
Rad	No	HLW	75	14	1.69	4.27	10	MDL

Table A1. Compilation of SRNL Research Data Available for TPB Degradation Rate Modeling

Rad/No Rad	TPB Present	Simulant /HLW	Temp (ºC)	pH	wt% KTPB	Na+ (M)	Estimate TPB Rate (xE-6 moles KTPB/L/day)	Notes
Rad	No	HLW	75	14	1.69	4.27	10	MDL
Rad	No	HLW	75	11	0.811	2.9	73	MDL
Rad	No	HLW	75	11	0.836	1.38	1050	
Rad	No	HLW	75	11	0.832	8.58	6600	
Rad	No	HLW	75	11	0.816	4.27	18	MDL
Rad	No	HLW	65	11	0.852	5.69	19	
Rad	No	HLW	65	12	0.909	5.79	29	
Rad	No	HLW	55	14	1.69	2.95	10	MDL
Rad	No	HLW	55	14	1.88	2.96	10	MDL
Rad	No	HLW	55	11	0.828	3.9	6	MDL
Rad	No	HLW	30	14.06	1.94	2.99	2.3	

Exhibit A1. Model Fit

Response ln(TPB Rate)
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.775502
RSquare Adj	0.749675
Root Mean Square Error	1.462343
Mean of Response	4.869122
Observations (or Sum Wgts)	127

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	13	834.7327	64.2102	30.0266
Error	113	241.6445	2.1384	Prob > F
C. Total	126	1076.3772		<.0001

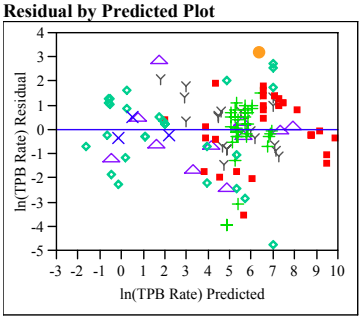
Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	83	193.87619	2.33586	1.4670
Pure Error	30	47.76827	1.59228	Prob > F
Total Error	113	241.64446		0.1192
				Max RSq
				0.9556

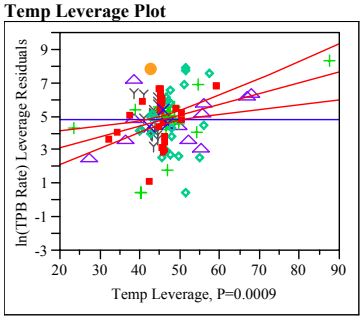
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	10.168996	1.366669	7.44	<.0001
Temp	0.0647064	0.018905	3.42	0.0009
pH	-0.812333	0.074335	-10.93	<.0001
wt% KTPB	0.4704777	0.167002	2.82	0.0057
Na+	0.2335101	0.085164	2.74	0.0071
Rad/No Rad[No Rad]	0.9121975	0.164833	5.53	<.0001
TPB Present[No]	-0.491067	0.305064	-1.61	0.1102
(Temp-46.5197)*(pH-12.341)	-0.015805	0.00818	-1.93	0.0558
(Temp-46.5197)*Rad/No Rad[No Rad]	-0.107707	0.017923	-6.01	<.0001
(Temp-46.5197)*TPB Present[No]	-0.111523	0.020173	-5.53	<.0001
(pH-12.341)*(Na+-3.16016)	-0.095871	0.046134	-2.08	0.0400
(wt% KTPB-2.88711)*(Na+-3.16016)	-0.366514	0.107676	-3.40	0.0009
(wt% KTPB-2.88711)*TPB Present[No]	0.4314775	0.150467	2.87	0.0049
(Na+-3.16016)*TPB Present[No]	-0.82041	0.237653	-3.45	0.0008

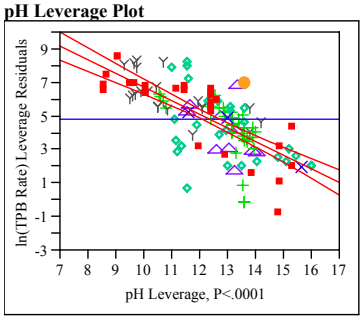
Residual by Predicted Plot



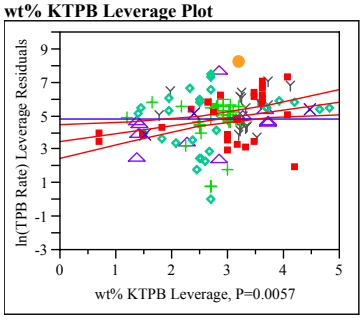
Temp Leverage Plot



pH Leverage Plot



wt% KTPB Leverage Plot



Na+ Leverage Plot

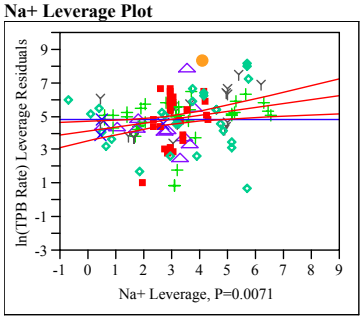
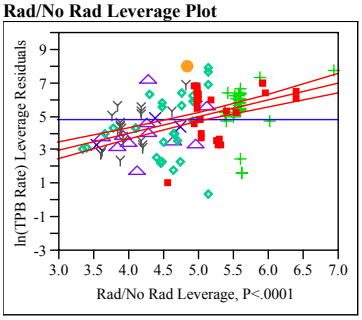


Exhibit A1. Model Fit

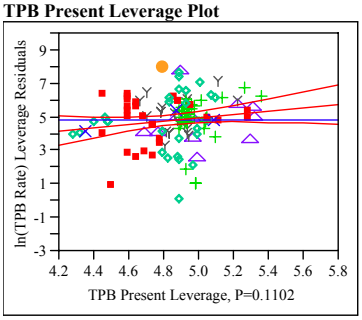
Rad/No Rad Leverage Plot



Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
No Rad	6.1625371	0.29606650	6.14676
Rad	4.3381422	0.34525563	3.52967

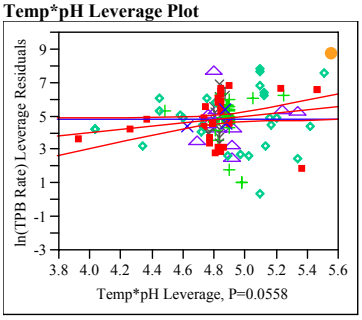
TPB Present Leverage Plot



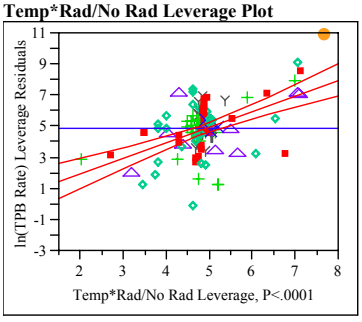
Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
No	4.7592728	0.47746690	4.49671
Yes	5.7414065	0.33267098	5.21333

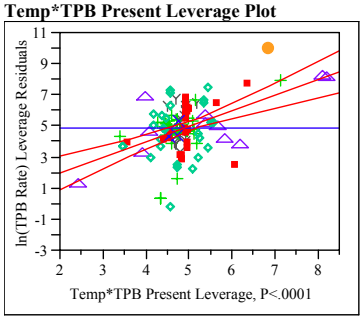
Temp*pH Leverage Plot



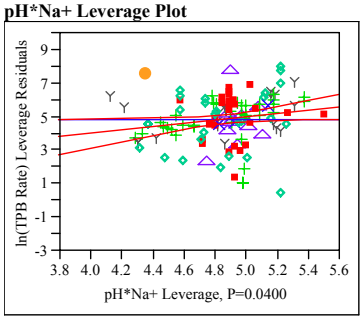
Temp*Rad/No Rad Leverage Plot



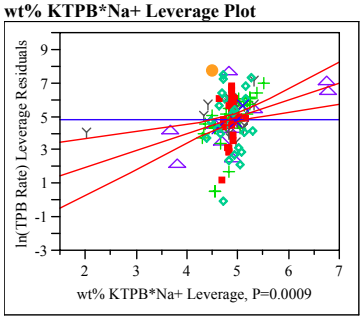
Temp*TPB Present Leverage Plot



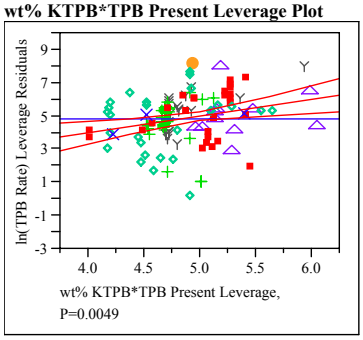
pH*Na+ Leverage Plot



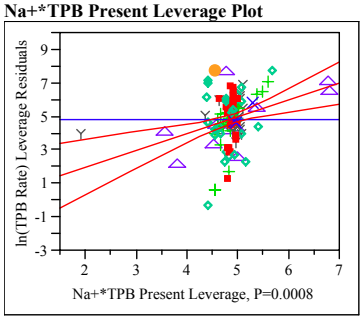
wt% KTPB*Na+ Leverage Plot



wt% KTPB*TPB Present Leverage Plot



Na+*TPB Present Leverage Plot



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Distribution:

D. T. Conrad, 766-H
R. E. Edwards, SRNL
T. B. Edwards, 773-42A
R. E. Eibling, 999-W
J. C. Griffin, SRNL
S. P. Harris, 773-42A
D. Maxwell, 766-H
C. L. Crawford, 773-41A
D. D. Walker, SRNL
R. H. Spires, 766-H
R. C. Tuckfield, 773-42A
W. R. Wilmarth, 773-42A