Hydrolysis of Late-Washed, Irradiated Tetraphenylborate Slurry Simulants I: Phenylboric Acid Hydrolysis Kinetics

by

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Department Defense Waste Processing Technology

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I hereby delegate signature authority to L. F. Landon

for the period from August 7, 1996 to September 3, 1996

for the reason of Business Travel

Signed E W Holtzscheiter

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Hydrolysis of Late-Washed, Irradiated Tetraphenylborate Slurry Simulants I: Phenylboric Acid Hydrolysis Kinetics (U)

The attached report details the kinetics of phenylboric acid (PBA) reactions at 90 °C during precipitate hydrolysis processing of late-washed, irradiated tetraphenylborate slurry simulants. Hydrolysis rate constants and initial phenylboric acid concentrations are reported with 95% confidence limits. Projected rates of benzene generation from residual phenylboric acid present in the precipitate reactor immediately after the precipitate transfer is stopped are also reported. The study covers a wide range of feed properties, including gamma irradiation doses of from 190 to 510 Mrads, mercury concentrations of 0 and 3150 mg/L, nitrite concentrations of from <14 to > 900 mg/L, and layup irradiation doses of 0 and 46 Mrads. Hydrolysis operating conditions covered a range of from 0.2 to 0.36 M acidity, copper catalyst concentrations of from 400 to 1200 ppm, and precipitate feedrates of 32 - 51 gpm (scaled to a 3600 gallon batch). The copper and acidity ranges extend considerably beyond the recommended process operating parameters (0.25 ± 0.05 M acidity and 950 ± 100 ppm copper) for the DWPF Salt Processing Cell.

Please refer any questions to J. C. Marek (7-7659).

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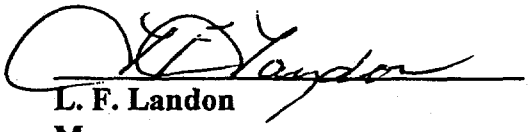

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HYDROLYSIS OF LATE-WASHED, IRRADIATED TETRAPHENYLBORATE SLURRY SIMULANTS I: PHENYLBORIC ACID HYDROLYSIS KINETICS (U)

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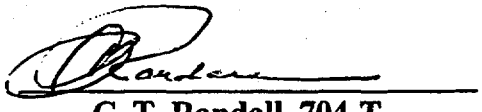

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Hydrolysis of Late-Washed, Irradiated Tetraphenylborate Slurry Simulants I: Phenylboric Acid Hydrolysis Kinetics (U)

Summary

Data from nineteen bench-scale precipitate hydrolysis experiments were analyzed to determine the kinetics of phenylboric acid (PBA) reactions at 90 °C during precipitate hydrolysis processing of late-washed, irradiated tetraphenylborate slurry simulants. The data for phenylboric acid disappearance were modeled as a first order, irreversible chemical reaction assuming batch reactor kinetics. Resultant rate constants and initial phenylboric acid concentrations are reported with 95% confidence limits. Projected rates of benzene generation immediately after the precipitate transfer are also reported. The results allow prediction of rates of benzene evolution from phenylboric acid hydrolysis. The results also provide conservative estimates of reaction times for complete conversion of phenylboric acid at 90 °C.

The late-washed, irradiated feeds used in this study cover a wide range of conditions, including gamma irradiation doses of 1.9 E+08 rads, 2.0 E+08 rads, 3.0 E+08 rads, and 5.1 E+08 rads, mercury concentrations of 0 and 3150 mg/L, nitrite concentrations of from < 14 mg/L to > 900 mg/L, and layup irradiation doses after the late washing operation of 0 and 4.6 E+07 rads. Hydrolysis operating conditions covered precipitate feedrates of 32 - 51 gpm (scaled to a 3,600 gallon batch), acidities ranging from 0.2 to 0.36 M, and copper catalyst concentrations ranging from 400 to 1200 ppm. The copper and acidity concentrations extend considerably beyond the recommended process operating parameters (0.25 ± 0.05 M acidity, 950 ± 100 ppm copper).

The maximum observed rate constant for phenylboric acid disappearance within the range of recommended process operating parameters was 2.52 ± 0.44 hr^{-1} at the 95% confidence level. The minimum observed rate constant for phenylboric acid disappearance within the range of recommended process operating parameters with feeds containing mercury was 1.26 ± 0.09 hr^{-1} at the 95% confidence level. Mercury increases the rate of phenylboric acid hydrolysis based on results from comparison runs with and without mercury. Assuming complete conversion of the phenylboric acid to benzene, the average benzene generation rate at 90 °C immediately after the precipitate transfer was 8.8 ± 0.9 g/hr•L at the 95% confidence level. The phenylboric acid

concentration in the Precipitate Hydrolysis Aqueous (PHA) product was less than 1 mg/L in eighteen of the nineteen experiments, including all the experiments that processed feeds containing mercury. The phenylboric acid concentration in the PHA product was 64 mg/L in run 92-18, which exceeds the TSR limit for DWPF. This run processed a feed containing no mercury and only 14 mg/l nitrite and used only 800 ppm copper catalyst. An experiment performed using the identical feed but with 950 ppm copper catalyst produced PHA containing less than one mg/L, successfully meeting the TSR limit for PHA in the DWPF. These data are valuable because there is a lack of any comparable data from operations in large scale experimental facilities, such as the Precipitate Hydrolysis Experimental Facility (PHEF) at TNX, for determining the kinetics of phenylboric acid hydrolysis during processing of late-washed, irradiated tetraphenylborate slurries containing mercury.

Introduction

Hydrolysis of the tetraphenylborate anion to boric acid and organic products (primarily benzene) proceeds through a sequential series reaction network that ultimately must convert phenylboric acid to boric acid, benzene, and other organic byproducts to achieve complete hydrolysis. Hydrolysis of phenylboric acid requires removal of the last phenyl group from the boron atom that was in tetrahedral coordination to four phenyl groups in the tetraphenylborate molecule. This is generally acknowledged to be the slowest step in the reaction network representing the complete hydrolysis of tetraphenylborate, requiring temperatures of about 150 °C in the absence of any catalyst[1]. Although many metals exhibit some catalytic effects on the rate of phenylboric acid hydrolysis, copper is by far the most active identified catalyst[2] and is used to achieve acceptable reaction rates and conversions of phenylboric acid at ambient pressures and temperatures of about 90 - 101°C[3].

Phenylboric acid hydrolysis kinetic data during acid hydrolysis of potassium tetraphenylborate precipitates were reported earlier by Bannochie et al[4, 5]. These studies were performed primarily with unirradiated tetraphenylborate precipitate feed slurry simulants characteristic of the feeds used in DWPF Cold Chemical runs and in the Precipitate Hydrolysis Experimental Facility (PHEF) at TNX. The low-nitrite feed simulants contained the expected levels of nitrite from the late washing operation, but these precipitate slurries were not actually washed and hence contained excess alkali. The feed simulants also omitted certain radiolysis products in addition to mercury, all of which are anticipated in the precipitate feed. A single data set was reported for hydrolysis of a tetraphenylborate precipitate feed simulant that contained mercury and was irradiated to 1.9 E+08 rads before late washing to $\leq$ 0.01 M nitrite[4, 5]. This work concluded that when diphenylmercury was present the hydrolysis of phenylboric acid was no longer first order in the phenylboric acid concentration and that only after hydrolysis of phenylboric acid was completed was the disappearance of diphenylmercury possible. Inspection of the original data, contained in Figure 2 of this report, indicates that even with diphenylmercury present the reaction was first order for about 1 - 1.5 hours, during which the majority (about 90%) of the phenylboric acid was hydrolyzed. Hence, the data were consistent with a reaction mechanism that starts out first order in phenylboric acid and changes order once a second reaction mechanism is initiated, perhaps involving diphenylmercury cleavage to generate phenylmercuric species.

Analysis of data from nineteen laboratory scale precipitate hydrolysis experiments was performed to determine nominal, maximum, and minimum phenylboric acid hydrolysis rates, assuming batch reaction kinetics first order in phenylboric acid. Seventeen of the experiments used precipitate feed simulants containing mercury, irradiated to doses of 2.0 E+08 or 5.1 E+08 rads, and late-washed in a cross-flow filter. The dose of 2.0 E+08 rads corresponds to storing washed precipitate containing 24 Ci/gal Cs-137 for two years in Tank 49, where 24 Ci/gal was the preliminary estimated average curie content of the precipitate for the first five years of ITP operation[6]. The dose of 5.1 E+08 rads corresponds to a conservative estimate of the maximum total dose to a precipitate slurry during storage in Tank 49, and is based on storing precipitate of the maximum permissible curie content in ITP (46 Ci/gal) at the maximum average storage time of 2.8 years[7]. Six experiments were performed with feed simulants that were re-irradiated to doses of 4.6 E+07 rads after the late-washing operation to simulate the effects of a ninety day layup on the precipitate feed. All but six experiments employed a re-precipitation step prior to the late washing operation. The six experiments with feeds prepared without the re-precipitation step were performed before the re-precipitation step became adopted in the technical baseline for late-washing.

The kinetic data are useful in several applications, including estimation of the rate of benzene generation during phenylboric acid hydrolysis, estimating the rate of benzene generation during interlock actions to stop the precipitate transfer to the PR, and calculating conservative estimates of the time required to reduce the phenylboric acid concentrations to the limits set in the DWPF TSRs.

Experimental

Apparatus

Figure 1 is a schematic diagram of the experimental apparatus. Two types of reactor vessels were used to perform the hydrolysis experiments. The first reactor was a Hastelloy® C-276 vessel (nominal volume 1 L) and the second reactor was a glass PYREX brand reaction kettle (nominal volume 4 L).

Hastelloy® C-276 Reaction Vessel

The metal vessel was used in runs 92-10, 11, 12, 13, 17, 18; 93-1, 2; and 94-3, 4, 5, 12, 13, 14. It was fabricated from 4 in. nominal schedule 10S Hastelloy® C-276 pipe (4.26 in. ID) and a pipe cap welded to form the bottom dish of the reactor vessel. The depth of the reactor was 5 3/4 inches from the lowest point of the bottom dish to the top flange. The reactor had four 3/8 inch wide, 1/8 inch thick Hastelloy® C-276 baffles spaced 90° apart. The reactor was fitted to a KIMAX (model 33720) glass lid with a ground glass flange. The lid was clamped to the reactor vessel flange to provide a gas-tight seal. The lid on the metal reactor provided four 24/40 standard taper access ports, one 14/20 standard taper access port, and two 1/4 in. threaded glass joints occupied by a cooling coil. The access ports were equipped as follows:

Port 1 (center 24/40): a dual impeller, stainless steel mechanical agitator shaft, 10 mm OD through a screw thread glass adapter joint with Teflon® trubore agitator bearing (Ace Glass Cat. No. 8066-20)

Port 2 (24/40): insulated glass vapor vent line, nominal 1 in. OD

Port 3 (24/40): tee connector to provide nozzle for purge gas inlet and platinum RTD temperature probe

Port 4 (24/40): tee connector to provide aqueous condensate return connection and glass sample tube

Port 5 (14/20): nominal 1/4 in. OD stainless steel feed tube (during precipitate transfer) or Type K thermocouple (during cooldown)

Ports 6&7: two 1/4 in. threaded glass joints for cooling coil inlet and outlet service

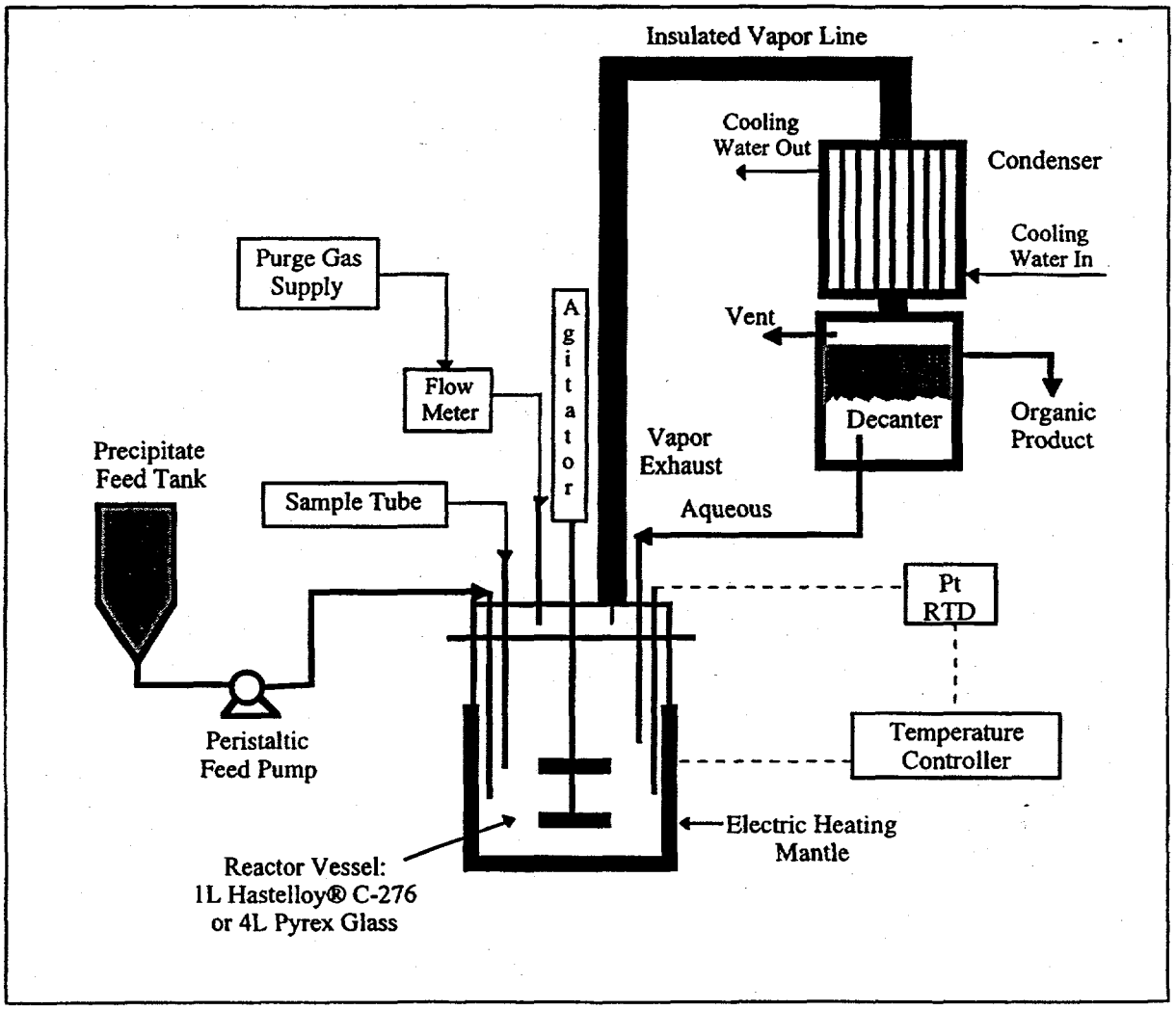

Figure 1. Schematic diagram of Precipitate Hydrolysis reaction system for studying phenylboric acid kinetics.

The 1 L metal reactor was heated with an aluminum housed electric heating mantle (Glas-Col, model TM 562) capable of supplying 300 W of power. The agitator shaft was fitted with two 1.875 in. diameter impellers spaced 2.25 inches apart (center hub to center hub). The top impeller was a 4-blade, 45° pitch blade and the bottom impeller was a 6-blade radial turbine located ≈ 1/4 inch above the reactor bottom dish. Carbon dioxide purge gas (CP grade, 99.8% min. purity) was metered into the gas inlet nozzle using a Brooks Sho-Rate flow controlling rotameter (Serial No. 81354, tube R-2-15-AA with spherical glass float) capable of providing from 6 - 108 cc/min carbon dioxide. Water flow to the cooling coil was also controlled with a Brooks Sho-Rate flow controlling rotameter (tube R-6-15-A with stainless steel 316 spherical float).

Glass Reaction Vessel

The glass reactor was used in runs 92-28, 29; 94-7, 17, 18. The vessel was a nominal 4 L PYREX reaction kettle (Corning Cat. No. 6946) fitted to a KIMAX (model 33720) glass lid with a ground glass flange. The lid was clamped to the reactor vessel flange to provide a gas-tight seal. The lid on the 4 L reactor provided three female 24/40 standard taper ground joint access ports arranged symmetrically about a central 34/45 female standard taper access port. The access ports were equipped as follows:

Port 1(center 34/45):	a dual impeller, stainless steel mechanical agitator shaft, 10 mm OD through a screw thread glass adapter joint with Teflon® trubore agitator bearing (Ace Glass Cat. No. 8066-32)
Port 2 (24/40):	insulated glass vapor vent line, nominal 1 in. OD.
Port 3 (24/40):	tee connector to provide nozzle for purge gas inlet and platinum RTD temperature probe
Port 4 (24/40):	tee connector to provide aqueous condensate return connection and a stainless steel feed tube during precipitate transfer or glass sample tube inserted post-precipitate transfer.

The 4 L glass reactor was heated with an aluminum housed electric heating mantle (Glas-Col, model 576) capable of supplying 470 W of power. The agitator shaft was fitted with two 3 in. diameter impellers spaced 4 inches apart (center hub to center hub). The top impeller was a 4-blade, 45° pitch impeller and the bottom impeller was a 6-blade radial turbine located ≈ 1/2 inch above the reactor bottom dish.

Purge gases provided for the glass reactor included ultra high purity nitrogen (< 1 ppm O_2, <1 ppm H_2O, < 0.5 ppm hydrocarbons) in run 94-7 and CP grade carbon dioxide (99.8% min. purity) in runs 92-28, 29; 94-17, 18. Purge gas was metered into the gas inlet nozzle using a flow controlling mass flowmeter (MKS model 1259B-01000SCVC) connected to a multigas flow controller (MKS model 1478-4). The outlet purge gas flowrate from the glass decanter vent was similarly measured with a mass flowmeter (MKS model 0258C-01000SV) connected to the mass flow computer. The exit flow was also routed to a wet test meter, (Precision Scientific, Cat. No. 63126, Serial No. SN10AY-12) which recorded the time for each 3 liter increment of gas vented from the system.

Associated Equipment

The following equipment was used on the reactor system during the hydrolysis run:

1) A peristaltic pump (Cole-Parmer Instruments, Masterflex, model 7550-90 with model 7518-12 pump head and size 15 silicone tubing) was used to transfer precipitate slurry from the feed tank to the reactor and to pump out aqueous product after cooldown.
2) A feed tank made from a 1.5 L glass vessel with a conical bottom drain and stopcock valve. An electric agitator drive motor (Talboys Engineering Co., T-Line model 104, 1/18 HP, 750 rpm max.) and stirrer in the feed tank provided suspension of the precipitate solids.
3) A temperature controller (Cole-Parmer Instruments, Dyna-Sense Electronic Temperature Controller model 2155) accepted input from the platinum RTD sensor and provided power to the electric heating mantle.
4) A water-cooled, countercurrent glass condenser (three tubes, vapor in downflow, water in upflow) connected to the reactor vapor vent line,
5) A glass decanter to separate the organic and aqueous phases produced by the hydrolysis reactions and return the aqueous phase to the reactor by gravity overflow
6) An electric agitator drive motor (Talboys Engineering Co., T-Line model 104, 1/18 HP, 750 rpm max.) connected to the reactor agitator shaft via a flexible coupling agitator drive shaft (Ace Glass Cat. No.8081-32).

Late-Washed Irradiated Tetraphenylborate Precipitate Feed Simulants

Seven different late-washed irradiated precipitate simulants were processed in the hydrolysis experiments, identified as LWRDPW3, IR-8, LWRDPW13, PF-113PW, PF-143PW, PF-143A200-46, and PF-143A510-46. The preparation of the precipitate feed simulants for irradiation are documented in research laboratory notebook WSRC-NB-89-123.

All metal salts used in the preparation of the precipitate feeds were reagent grade. All solutions were prepared using ASTM Type I distilled and deionized water. The sodium tetraphenylborate solutions were received in 55 gallon drums from Optima Chemicals and were compositionally characterized upon receipt. The unirradiated tetraphenylborate precipitate slurries simulated the composition of a Tank 48 product slurry and were prepared by combining five materials according to TNX Operating Procedure 677T-70184, Rev. 2[8]:

1) an aqueous solution of potassium and cesium salts
2) a monosodium titanate slurry
3) a simulated non-radioactive Purex sludge slurry simulant without noble metals
4) a mercury compound (diphenylmercury in PF-113, mercuric nitrate in PF-143)
5) an aqueous solution of sodium tetraphenylborate stabilized with 0.1 - 0.2 M sodium hydroxide.

The tetraphenylborate precipitate slurry was then gamma irradiated to the desired dose in the 774-A Co-60 source, and returned to TNX for analytical characterization and late washing. After analytical characterization, the slurries were processed through the late-washing operation. This involved adding sodium nitrite to adjust the nitrite concentration to about 0.13 M, adding

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additional sodium tetraphenylborate to re-precipitate soluble potassium, cesium and ammonium produced during the irradiation, and then washing the irradiated slurry in a continuous washing operation to reduce the nitrite concentration to ≤ 0.01 M. The washing was generally performed by pumping the irradiated slurry through a sintered-metal crossflow filter and adding wash water adjusted to 0.004 M sodium tetraphenylborate to the agitated slurry at the same rate at which filter permeate was withdrawn. The feeds hydrolyzed in runs 92-10 through 92-13, 92-17, and 92-18 were not re-precipitated because the re-precipitation of soluble potassium, cesium and ammonium was not yet incorporated in the late washing technical baseline.

After the late washing operation, the precipitate feeds were compositionally characterized, including analyses for nitrite, base equivalences, tetraphenylborate, etc. In runs 94-7, 17, and 18 the desired quantity of (zero-nitrite) Purex sludge simulant trimmed with noble metals and any additional sodium nitrite needed were added to the tetraphenylborate precipitate feeds prior to hydrolysis. In runs 94-3, 4, 5, 12, 13, 14, the late-washed, irradiated precipitate feed was irradiated to an additional 4.6 E+07 rads to simulate 90 days of layup prior to the hydrolysis processing. Additional details on the precipitate preparation recipes, salt solutions, sodium tetraphenylborate solutions, and preparation of sludge with noble metals are provided in the appendix tables A.1, A.2, A.3, A.4, A.5, A.6, and A.7.

Precipitate Hydrolysis Processing

The late-washed irradiated precipitate slurries were compositionally characterized by the process control analyses for the Precipitate Hydrolysis Process, including insoluble solids (wt%), base equivalence's to pH 5.5 (M), tetraphenylborate concentration (wt%), and nitrite concentration (mg/L). The formic acid and copper catalyst charges were calculated and the batch processed per the same technical bases for precipitate hydrolysis as were used in DWPF Integrated Cold Runs[5,9]. The experiments were scaled to simulate processing a 3,600 gallon batch of precipitate in DWPF using a pre-reaction heel volume of 1650 gallons. The precipitate transfer times used with the scaled 3,600 gallon batch size corresponded to feedrates of 32 - 51 gpm. TNX Operating Procedure 677T-70183, Rev. 2[10] controlled the operation with relevant operating data recorded on a run sheet, which provided additional instructions required and a sample schedule.

The reactor system was disassembled and cleaned after each hydrolysis experiment or series of experiments. The system was then re-assembled and leak checked before performing the experiment. The cleaning and disassembly was only performed after the last run if the runs constituted a consecutive series of experiments. Consecutive series of experiments were performed in runs 92-10 through 92-13, runs 94-3 through 94-5, and runs 94-12 through 94-15.

The pre-reaction heel charge was prepared and batched to the reactor. This consisted of weighing out the target quantities of 90 wt% formic acid (Baker, 90 wt%) and copper formate (Sheppard Chemical Lot B49860, $Cu(HCO_2)_2 \cdot 2\ H_2O$ assay 33.1 ± 0.2 wt% copper) or copper nitrate (Fisher, $Cu(NO_3)_2 \cdot 2.5\ H_2O$) catalyst in ASTM Type I distilled and deionized water. In experiments which constituted a consecutive series, a portion of the PHA produced in the previous experiment was also added to the pre-reaction heel. A 100.0 g. sample of the

pre-reaction heel was taken for analysis, leaving the desired quantity of material in the reactor vessel. The decanter was inventoried with about 20 g. of deionized water. Heatup of the reactor contents to 90 °C was then initiated.

The reactor was purged with the appropriate purge gas (nitrogen or carbon dioxide) to sweep out oxygen. In runs 94-7, 94-17, and 94-18, the oxygen concentration was determined by gas chromatographic analysis to be less than 0.2 vol% before the run was started. The purge gas flowrate was then adjusted to 50 cc/min in the glass reactor vessel and to 20 cc/min in the metal reactor. After the temperature of the reactor contents had stabilized at 90 ± 2 °C, the peristaltic feed pump was started to initiate transfer of precipitate from the feed tank to the reactor. The pump setpoint was adjusted to transfer the precipitate in a period of about 71 - 112 minutes, corresponding to a feedrate of 32 - 51 gpm for a 3,600 gallon batch of precipitate. During the feed period, considerable benzene collected in the decanter. The organic was drained out of the organic overflow leg into a collection bottle when necessary.

After the precipitate transfer was finished, the feed tank was rinsed with about 50 g. of deionized water which was flushed through the transfer line into the reactor. The reactor was sampled after the post-feed water flush to obtain the initial sample for phenylboric acid analysis. The reactor contents were then maintained at 90 ± 2 °C and sampled at designated time intervals (generally every 15 minutes for the first two hours and every 30 minutes thereafter) while the phenylboric acid hydrolysis and diphenylmercury cleavage/reduction reactions occurred. The samples were cooled by placing them in ice water mixture to minimize additional phenylboric acid hydrolysis.

At the end of the five hour reaction period at 90 °C, the setpoint on the temperature controller was adjusted to 110 °C and the vessel contents were heated to boiling. Boiling of the reactor contents was achieved in from ten to thirty minutes after the setpoint change. The reactor contents were boiled for at least the target five hour boiling period. At the end of the boiling period, the reactor contents were cooled, sampled for analysis, and allowed to idle under inertant purge overnight. The reactor was re-sampled the next day, and the PHA was de-inventoried and assayed. Except in the runs that were part of a consecutive series, the decanter contents were drained and all the collected organic product was combined. The vent line connection to the condenser-decanter system was then disconnected and the condenser-decanter was rinsed with the organic product to collect any high-boilers that had deposited in the condenser. The decanter aqueous and organic product were then assayed and submitted for analysis. In the runs that were part of a consecutive series, these operations were performed only for the last run of the series.

Phenylboric Acid Analysis

The samples were run in a Hewlett Packard 1090 liquid chromatograph with a diode array detector. The instrument utilized reverse phase, gradient liquid chromatography using a water/acetonitrile solvent system. The analytical column was a 25 cm, 4.6 mm ID Chemcosorb 5-ODS-UH (30% carbon load, bonded phase C-18). Phenylboric acid was analyzed at 217 nm and diphenylmercury was analyzed using 225 nm. Standards were prepared from reagent grade chemicals without further purification. Quantitation was based upon external standards. Sample preparation consisted of dilution with "HPLC Grade" acetonitrile and filtration through a 0.2 micron nylon filter.

Data Analysis and Controls

The rate of a chemical reaction can be defined as the rate of change of the concentrations of the chemical species with respect to time under conditions of constant volume. Mathematically, $r = dC/dt$ where r is the rate, t is time, and C_A is the concentration of species A produced by the reaction. The chemical reaction rate must be a positive quantity. When a reactant, such as phenylboric acid, is considered then $r = - d[PBA]/dt$ where [PBA] is the phenylboric acid concentration. For the phenylboric acid hydrolysis reaction, the rate law depends on other factors including the acid and catalyst concentrations[4]. The rate law can be written using these other factors and a fundamental rate constant, k', as follows:

$$\text{rate} = -\frac{d[PBA]}{dt} = k'[PBA][H_3O^+]^n[Cu]^m = k[PBA]$$

The latter simplification is made by introducing the apparent rate constant $k = k'[H_3O^+]^n[Cu]^m$. Integrating the rate expression leads to the first order rate law shown below:

$$[PBA] = [PBA]_o \exp(-kt)$$

where [PBA] = phenylboric acid concentration at time t
$[PBA]_o$ = initial phenylboric acid concentration
k = apparent rate constant, hr^{-1}
t = time elapsed since end of feeding, hours.

This non-linear equation was used to model the analytical data for phenylboric acid concentration as a function of the elapsed time after the precipitate transfer to the reactor was stopped. The calculations were performed using JMP® statistical analysis computer software and a Macintosh Quadra 700 computer. The routine solved the regression equations and produced the upper and lower 95% confidence limits for the parameters k and $[PBA]_o$. Once the parameters k and $[PBA]_o$ and are calculated, the rate of phenylboric acid disappearance at any time may be calculated by differentiating the equation for [PBA] with respect to time. The initial rate of phenylboric acid disappearance immediately after the precipitate transfer is stopped may then be calculated by setting t = 0 hours in the rate equation:

$$r_o = \text{initial rate} = -\left.\frac{d[PBA]}{dt}\right|_{t=0} = k[PBA]_o \exp(-kt)\Big|_{t=0} = k[PBA]_o$$

The initial rate of benzene generation was then calculated assuming complete conversion of phenylboric acid to benzene and by multiplying by the ratio of the formula weights for the two compounds, i.e. by 121.9/78.1 = 1.561. It must be emphasized that the rate constant k reported here is in fact an apparent rate constant and that there has been no attempt to develop a complete rate equation for the phenylboric acid disappearance that includes an intrinsic rate constant and other concentration terms such as the acid and copper concentrations.

Qualification Process

Controls and quality assurance applied to produce these data were equivalent to those used in task activities requiring a task technical plan per the DWPT/TNX QA program description in SRL-PMC-91-0075, Rev. 4. The controls used included the DWP&HT Quality Assurance Procedures Manual, 1Q43, the SRTC 1Q Implementation Matrix, the WSRC Quality Assurance Manual 1Q, and the WSRC Quality Assurance Management Plan, WSRC-RP-92-225.

All experimental activities were controlled by approved TNX operating procedures. Accuracy of the analytical results was controlled by bracketing the analytical results with check standards which are controlled to within 5%, except liquid chromatography results which were controlled within 10% of their nominal values. All analytical results are stored in the TNX Laboratory Information System (TNXLIMS) as described in SRL-PMC-92-0002, Rev. 1 dated April 3, 1992. Analytical results are not official until they are entered into the TNXLIMS. Analytical balance calibration certifications were performed annually on the balances in 677-T and 772-T per developmental procedure 772T-70377, Rev. 0, "Procedure for Balance Calibration Certification". Balance accuracy was verified prior to each use and the data was trended using statistical process control charts to identify deviations in balance accuracy.

Results

Figure 2 is taken from the study reported by Bannochie et al[4] and contains phenylboric acid kinetic data from hydrolysis of a late-washed tetraphenylborate precipitate slurry containing diphenylmercury. The feed was irradiated to a dose of 1.9 E+08 rads prior to the late-washing operation. The hydrolysis conditions used were 90 °C, 950 ppm copper catalyst, 0.3 M total acidity, and a tetraphenylborate feed nitrite concentration of 0.01M. As noted by Bannochie et al from the curvature that appeared after about 1 hour in the ln [PBA] versus time plot, the reaction was not first order in phenylboric acid throughout the entire hydrolysis period. Additionally, the concentration of diphenylmercury ($Ø_2Hg$) remained essentially constant until the concentration of phenylboric acid had dropped to nearly zero. Only upon complete hydrolysis of the phenylboric acid was a reduction in the diphenylmercury concentration observed. These findings led to the hypothesis that phenylmercurate ion produced from acid cleavage of the diphenylmercury could react with phenylboric acid to regenerate diphenyl-mercury. The reaction with phenylmercurate ion could provide a second catalytic mechanism for the phenylboric acid hydrolysis, with a subsequent change in the order of the reaction.

Inspection of Figure 2 reveals that the ln [PBA] versus time plot is essentially a straight line over the range of ln [PBA] = 8.3 to ln [PBA] = 6 (or from time zero to 1 hour). Over this range, the PBA concentration is decreasing from about 4,000 mg/L to about 400 mg/L, or by about 90%. This implies that after the precipitate slurry transfer to the reactor was stopped, 90% of the remaining phenylboric acid was hydrolyzed by a reaction apparently first order in PBA. Significant quantities of PBA are also surely hydrolyzed while the precipitate is being fed to the reactor - if in fact no phenylboric acid hydrolysis occurred during the feed period then the resulting phenylboric acid concentration would be theoretically on the order of 20,000 mg/L after the precipitate transfer. Hence, the data strongly suggest that only 2 to 3% of the PBA is actually hydrolyzed when the reaction order has changed from one.

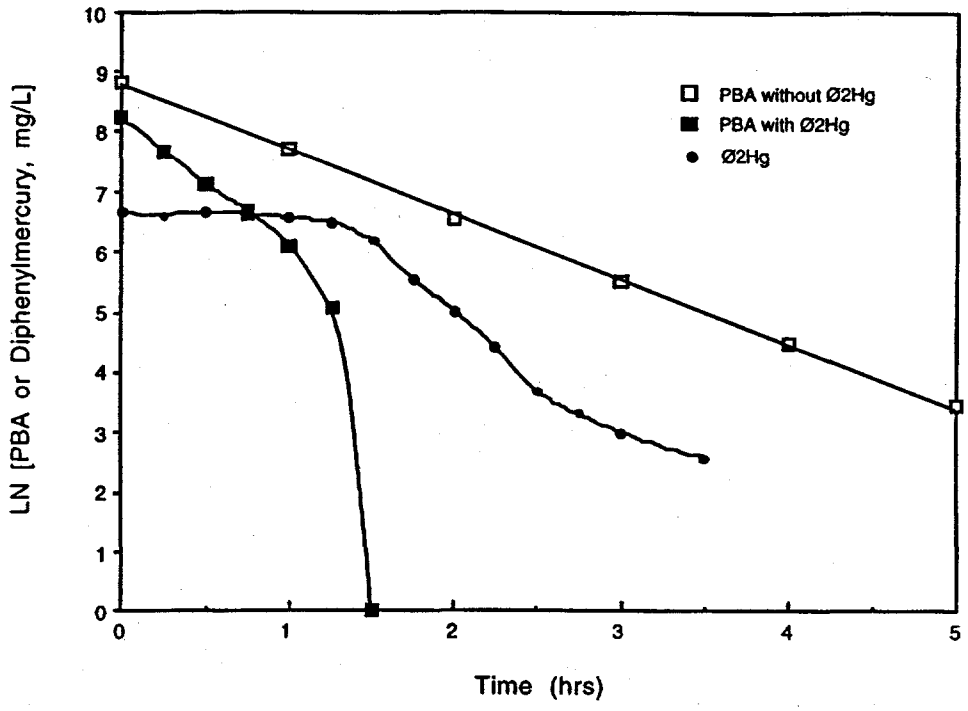


Figure 2. Effect of diphenylmercury on phenylboric acid hydrolysis kinetics at 90 °C with 950 ppm Cu(II), 0.3 M total acidity, and irradiated, late-washed tetraphenylborate slurry nitrite concentration of 0.01M. From Bannochie et al[4].

Figure 3 compares data obtained in run 92-13 of this study with the data reported earlier by Bannochie et al[4]. The two runs hydrolyzed the same feeds, with the main difference being that run 92-13 was performed at 0.20M acidity in a Hastelloy® C-276 vessel whereas the data reported by Bannochie et al. were obtained using a glass reactor and 0.30M acidity. The kinetics are slightly slower in run 92-13, presumably because of the lower acid concentration. Figure 3 also shows data obtained in runs 94-5 and 94 -14 to examine the effect of nitrite at essentially identical levels of diphenylmercury. The irradiation dose history of the tetraphenylborate slurry feeds are also somewhat different. The precipitate feed in run 92-13 was irradiated to a dose of 1.9 E+08 rads prior to the late wash operation, which reduced the nitrite concentration to 0.01M. In runs 94-5 and 94-14, the feeds were irradiated to doses of 2.0 E+08 rads and 5.1 E+08 rads, respectively, prior to late washing operation and afterwards with an additional 4.6 E+07 rads to simulate layup conditions. The additional irradiation dose reduced the nitrite to about 0.0002M. As expected based on findings with unirradiated precipitate feeds[4], the PBA kinetics for the slurry irradiated to 200 Mrads but containing only 0.0002M nitrite were much slower than for the slurries with comparable irradiation and 0.01M nitrite. Interestingly, the PBA kinetics for the slurry irradiated to 510 Mrad and containing 0.0002M nitrite in run 94-14 were essentially equivalent to those for the slurry irradiated 190 Mrad but containing 0.01M nitrite.

Figure 4 compares data obtained in runs 92-17, 92-18, 94-5, and 94 -14 to further examine the effect of mercury but at essentially zero nitrite conditions. The runs also differ in the irradiation dose history of the tetraphenylborate slurries. The feed used in runs 92-17 and 92-18 contained no mercury and very little nitrite (14 mg/L or ~ 0.0003M). The feed was irradiated to a dose of

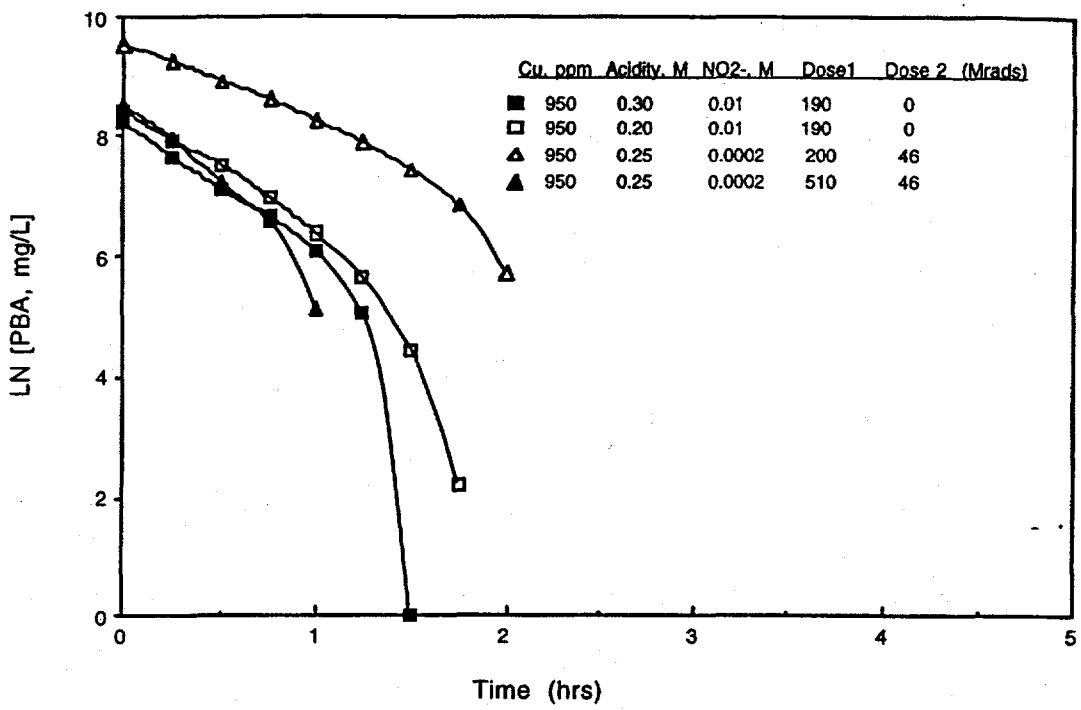


Figure 3. Phenylboric acid hydrolysis as a function of nitrite content and irradiation dose. All the precipitate slurries contained 3150 mg/L diphenylmercury. The slurries irradiated to 200 Mrads exhibit much slower PBA kinetics at low levels of nitrite.

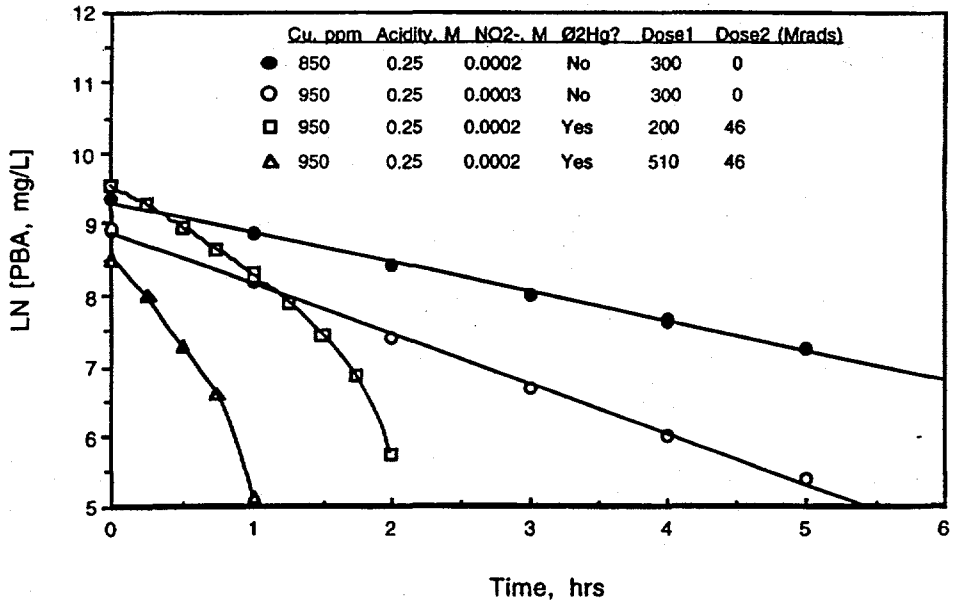


Figure 4. Phenylboric acid hydrolysis as a function of mercury content and irradiation dose at low nitrite content. Two of the feeds were re-irradiated to 4.6 E+07 rads after the late wash operation.

3.0 E+08 rads prior to the late washing operation, and was not re-irradiated after the late washing operation. In runs 94-5 and 94-14, the feeds contained 3150 mg/L diphenylmercury and were irradiated to doses of 2.0 E+08 rads and 5.1 E+08 rads, respectively, prior to late washing operation. The latter two feeds were irradiated with an additional 4.6 E+07 rads after late washing to simulate layup conditions. As expected, the combined lack of nitrite and mercury in runs 92-17 and 92-18 yielded much lower rates of phenylboric acid hydrolysis. The phenylboric acid concentration in the PHA product was 64 mg/L in run 92-18, which exceeds the TSR limit for DWPF. However, in run 92-17 performed using the identical feed and acid concentrations but at 950 ppm copper catalyst, the PHA produced contained less than 1 mg/L phenylboric acid, successfully meeting the TSR limit for PHA in the DWPF. All four feeds had similar nitrite concentrations prior to the hydrolysis run, but during the processing of the tetraphenylborate slurry without diphenylmercury much lower rates of phenylboric acid hydrolysis resulted, demonstrating the effect of diphenylmercury on hydrolysis kinetics. Of the two slurries that contained diphenylmercury, the rate constant for phenylboric acid hydrolysis with the slurry irradiated to 5.1 E+08 rads was nearly twice that of the slurry irradiated to 2.0 E+08 rads.

Conditions for the nineteen hydrolysis runs, the resulting kinetic data, and the derived kinetic rate constants are summarized in Tables 1 through 4. The nonlinear regressions performed using JMP® statistical analysis software are contained in Appendix B. Of the nineteen experiments performed, thirteen are considered to be within the nominal process operating conditions. Two experiments were performed at low nitrite levels (14 mg/L) and with no mercury, two experiments were performed using only 400 ppm of copper catalyst, and two were performed using excess copper catalyst (1200 ppm). The feeds used in the runs with layup irradiation doses of 4.6 E+07 rads were at low levels of nitrite, but the reduction in nitrite content was a direct consequence of the layup irradiation dose. Hence, these six runs could be considered to be within the range of normal operating conditions.

The maximum rate constant for phenylboric acid hydrolysis was $2.63 \pm 0.26\ hr^{-1}$ in run 94-18, which processed a precipitate slurry containing 0.02M nitrite at target conditions of 0.36M acidity and 1200 ppm copper catalyst. The maximum rate constant for runs within the recommended process operating parameters was $2.52 \pm 0.44\ hr^{-1}$ in run 94-14, which processed a precipitate slurry irradiated to 5.10 E+08 rads, late-washed to 0.01M nitrite, and re-irradiated to a dose of 4.6 E+07 rads. The slurry was hydrolyzed using 950 ppm copper and 0.25M total acidity. The maximum rate of benzene generation for any run within the recommended process operating parameters was 11.8 ± 2.0 g/hr•L in run 94-5, which processed a precipitate slurry irradiated to 2.0 E+08 rads, late-washed to 0.01M nitrite, and was re-irradiated to a dose of 4.6 E+07 rads. The slurry was hydrolyzed using 950 ppm copper and 0.25M total acidity.

Figure 5 shows a graph of $[PBA]_o$ versus the rate constant, k. The data fall on approximately a straight line with negative slope equal to -6096.8 mg•hr/L and intercept of 19,334 mg/L. Intuitively, one would expect that the higher the rate of reaction, the lower the value of $[PBA]_o$ will be, assuming there are no significant differences in the inlet concentration of tetraphenylborate. Conversely, in comparing two runs with equal tetraphenylborate concentrations in the feed, the lower the rate of reaction is the greater the accumulation of unreacted phenylboric acid will be in the vessel leading to higher observed values of $[PBA]_o$.

Table 1. Summary of Run Conditions and Kinetic Data from Hydrolysis of Tetraphenylborate Slurries Late-Washed with No Re-precipitation Step. Runs 92-10, 11, 12, 13, 17, and 18.

Run No.:		Run 92-10	Run 92-11	Run 92-12	Run 92-13	Run 92-17	Run 92-18
Processing Conditions:	Units						
Feed Processed		LWRDPW3	LWRDPW3	LWRDPW3	LWRDPW3	IR-8	IR-8
Target Ø2Hg Concentration	ppm	3150	3150	3150	3150	0	0
Irradiation Dose, pre- Late Wash	Mrad	190	190	190	190	300	300
Irradiation Dose, post- Late Wash	Mrad	0	0	0	0	0	0
Sludge & Noble Metals	ppm	0	0	0	0	0	0
Nitrite Concentration	mg/L	369	369	369	369	14	14
Precipitate TPB- Conc.	wt%	6.44	6.44	6.44	6.44	6.06	6.06
Precipitate Feed Mass	g	650.2	651.3	650.08	650	651.3	554.2
Precipitate Transfer Time	min	71	75	85	98	91	95
Target Cu Conc.	ppm	950	950	950	950	950	800
Target Acidity	Molar	0.2	0.2	0.2	0.2	0.25	0.25
Pre-Reaction Heel Data							
Pre-Reaction Heel (PRH) mass	g	289.03	289.03	289.03	289	289.02	244.22
Soluble Cu Analysis of PRH	ppm	3001	3002	3002	3002	3503.8	2582
Total Cu Analysis of PRH	ppm	2828	3388	3388	3471	3946.8	2937
PHA Product Data							
PHA Product Mass	g	862.8	889.1	906.1	887.9	847.9	697.74
Batch Kinetic Samples Mass	g	56.36	41.34	53.74	56.11	60.3	47.94
Corrected PHA Mass	g	919.16	930.44	959.84	944.01	908.2	745.68
Anal. Total Cu	ppm	1052	1039	983	1060	1373.2	1053.6
Anal. Soluble Cu	ppm	663	623	623	683	566.8	441
Anal. Acidity	Molar	0.22	0.21	0.2	0.20	0.30	0.28
PBA Kinetic Data Results		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Time @ 90 °C	0 hrs	9081	6148	5706	4657	7501	11306
	0.25 hrs		4301	3969	2842		
	0.5 hrs	3328	2891	2737	1905		
	0.75 hrs		1760	1810	1095		
	1 hrs	1560	978	662	596	3487	7122
	1.25 hrs		526	287	286		
	1.5 hrs	378	222	42	85		
	1.75 hrs		<1	<1	9		
	2 hrs	33			<1	1637	4525
	2.5 hrs	8					
	3 hrs	<1				793	2975
	4 hrs					406	2062
	5 hrs					222	1399
PBA after 5 hours boiling		<1	<1	<1	<1	<1	64
Kinetic Model Parameters							
PBA Rate Constant	1/hr	1.942	1.749	1.798	1.99	0.756	0.441
PBA 95% CL Max Rate Const.	1/hr	2.128	1.983	2.17	2.18	0.773	0.462
PBAo	mg/L	9068	6331	5914	4694	7489	11225
PBAo 95% CL Max. Value	mg/L	9444	6803	6581	4938	7572	11509
Nom. Benzene Generation Rate	g/hr•L	11.28	7.09	6.81	5.98	3.63	3.17
Max. Benzene Generation Rate	g/hr•L	12.88	8.64	9.15	6.90	3.75	3.41

Table 2. Summary of Run Conditions and Kinetic Data from Hydrolysis of Late-Washed Irradiated Tetraphenylborate Slurries in Runs 92-28, 92-29, 93-1, and 93-2.

Run No.:			Run 92-28	Run 92-29	Run 93-1	Run 93-2
Processing Conditions:		Units				
Feed Processed			LWRDPW13	LWRDPW13	LWRDPW13	LWRDPW13
Target Ø2Hg Concentration		ppm	3150	3150	3150	3150
Irradiation Dose, pre- Late Wash		Mrad	190	190	190	190
Irradiation Dose, post- Late Wash		Mrad	0	0	0	0
Sludge & Noble Metals		ppm	0	0	0	0
Nitrite Concentration		mg/L	368	368	368	368
Precipitate TPB- Conc.		wt%	7.78	7.78	7.78	7.78
Precipitate Feed Mass		g	2599.6	2601.3	649.7	650.4
Precipitate Transfer Time		min	103	98	84	85
Target Cu Conc.		ppm	950	950	400	400
Target Acidity		Molar	0.2	0.2	0.2	0.2
Pre-Reaction Heel Data						
Pre-Reaction Heel (PRH) mass		g	1156	1156	289.02	289.05
Soluble Cu Analysis of PRH		ppm	2861	2819	1211	1203
Total Cu Analysis of PRH		ppm	3271	2875	999	1190
PHA Product Data						
PHA Product Mass		g	3409.6	3372	786.6	773
Batch Kinetic Samples Mass		g	153.8	153.3	88.38	93.51
Corrected PHA Mass		g	3563.4	3525.3	874.98	866.51
Anal. Total Cu		ppm	954.3	896.05	400	400
Anal. Soluble Cu		ppm	751.2	730.95	278.9	382.4
Anal. Acidity		Molar	0.20	0.20	0.18	0.17
PBA Kinetic Data Results			mg/L	mg/L	mg/L	mg/L
Time @ 90 °C	0	hrs	5992	6113	14625	12204
	0.25	hrs	3170	4083	9736	9718
	0.5	hrs	2304	2125	8073	7964
	0.75	hrs	1436	1701	6186	6430
	1	hrs	682	1046	5168	5266
	1.25	hrs	355	342	5270	4247
	1.5	hrs	134	165	3482	3001
	1.75	hrs	38	60	2880	2130
	2	hrs	4	6	2345	1904
	2.5	hrs	6	4	1542	696
	3	hrs	3	6	691	203
	4	hrs	1	4	83	5
	5	hrs	2	5	7	
PBA after 5 hours boiling			<1	<1	<1	<1
Kinetic Model Parameters						
PBA Rate Constant		1/hr	2.101	1.928	0.937	0.93
PBA 95% CL Max Rate Const.		1/hr	2.313	2.126	1.074	1.007
PBAo		mg/L	5908	6212	13625	12413
PBAo 95% CL Max. Value		mg/L	6223	6562	14712	13012
Nom. Benzene Generation Rate		g/hr•L	7.95	7.67	8.18	7.40
Max. Benzene Generation Rate		g/hr•L	9.22	8.94	10.12	8.40

Table 3. Summary of Run Conditions and Kinetic Data from Hydrolysis of Late-Washed Irradiated Tetraphenylborate Slurries in Runs 94-3, 94-4, 94-5, and 94-7.

Run No.:			Run 94-3	Run 94-4	Run 94-5	Run 94-7
Processing Conditions:		Units				
Feed Processed			PF-143A200-46	PF-143A200-46	PF-143A200-46	PF-113PW
Target Ø2Hg Concentration		ppm	3150	3150	3150	3150
Irradiation Dose, pre- Late Wash		Mrad	200	200	200	200
Irradiation Dose, post- Late Wash		Mrad	46	46	46	0
Sludge & Noble Metals		ppm	0	0	0	3000
Nitrite Concentration		mg/L	<10	<10	<10	465
Precipitate TPB- Conc.		wt%	7.63	7.63	7.63	6.84
Precipitate Feed Mass		g	701.9	700.7	703	2500.5
Precipitate Transfer Time		min	112	79	77	92
Target Cu Conc.		ppm	950	950	950	950
Target Acidity		Molar	0.25	0.25	0.25	0.25
Pre-Reaction Heel Data						
Pre-Reaction Heel (PRH) mass		g	321.1	320.97	320.8	1145.89
Soluble Cu Analysis of PRH		ppm	2910	2670	2680	2770
Total Cu Analysis of PRH		ppm	2930	2700	2910	2890
PHA Product Data						
PHA Product Mass		g	862.4	879.4	927.9	3358
Batch Kinetic Samples Mass		g	92.7	82.8	81	67.9
Corrected PHA Mass		g	955.1	962.2	1008.9	3425.9
Anal. Total Cu		ppm	822	834.5	645	621
Anal. Soluble Cu		ppm	601	575.5	499	179
Anal. Acidity		Molar	0.24	0.25	0.23	0.26
PBA Kinetic Data Results			mg/L	mg/L	mg/L	mg/L
Time @ 90 °C	0	hrs	12790	13349	13700	7620
	0.25	hrs	9715	9980	10600	5430
	0.5	hrs	6964	7095	7690	3800
	0.75	hrs	5170	5193	5610	2460
	1	hrs	3974	3693	3940	1270
	1.25	hrs	2721	2530	2700	828
	1.5	hrs	1904	1592	1730	430
	1.75	hrs	1098	928	951	206
	2	hrs	543	297	305	<1
	2.5	hrs				
	3	hrs				
	4	hrs				
	5	hrs				
PBA after 5 hours boiling			<1	<1	<1	<1
Kinetic Model Parameters						
PBA Rate Constant		1/hr	1.258	1.347	1.305	1.645
PBA 95% CL Max Rate Const.		1/hr	1.347	1.458	1.441	1.847
PBAo		mg/L	13003	13625	14141	7856
PBAo 95% CL Max. Value		mg/L	13535	14269	14987	8404
Nom. Benzene Generation Rate		g/hr•L	10.48	11.76	11.82	8.28
Max. Benzene Generation Rate		g/hr•L	11.68	13.33	13.84	9.95

Table 4. Summary of Run Conditions and Kinetic Data from Hydrolysis of Late-Washed Irradiated Tetraphenylborate Slurries in Runs 94-12, 94-13, 94-14, 94-17, and 94-18.

Run No.:		Run 94-12	Run 94-13	Run 94-14	Run 94-17	Run 94-18
Processing Conditions:	Units					
Feed Processed		PF-143A510-46	PF-143A510-46	PF-143A510-46	PF-143PW	PF-113PW
Target Ø2Hg Concentration	ppm	3150	3150	3150	3150	3150
Irradiation Dose, pre- Late Wash	Mrad	510	510	510	200	200
Irradiation Dose, post- Late Wash	Mrad	46	46	46	0	0
Sludge & Noble Metals	ppm	0	0	0	12000	12000
Nitrite Concentration	mg/L	<10	<10	<10	476	972
Precipitate TPB- Conc.	wt%	6.17	6.17	6.17	7.86	4.52
Precipitate Feed Mass	g	700.3	700.2	700.00	2500.1	2201.6
Precipitate Transfer Time	min	97	75	82.00	89	85
Target Cu Conc.	ppm	950	950	950	1200	1200
Target Acidity	Molar	0.25	0.25	0.25	0.36	0.36
Pre-Reaction Heel Data						
Pre-Reaction Heel (PRH) mass	g	320.8	320.6	320.8	1145.6	1008.3
Soluble Cu Analysis of PRH	ppm	2720	2760	2780	3340	3410
Total Cu Analysis of PRH	ppm	2820	2830	2860	3440	3630
PHA Product Data						
PHA Product Mass	g	879.7	853.9	850.4	3276.7	2881.1
Batch Kinetic Samples Mass	g	100.5	119	125.38	128.8	165.63
Corrected PHA Mass	g	980.2	972.9	975.78	3405.5	3046.73
Anal. Total Cu	ppm	896.5	768.5	962.5	1046.3	842
Anal. Soluble Cu	ppm	409.5	613.5	756	24.9	85
Anal. Acidity	Molar	0.234	0.235	0.243	0.296	0.267
PBA Kinetic Data Results		mg/L	mg/L	mg/L	mg/L	mg/L
Time @ 90 °C	0 hrs	5680	7360	4970	7580	4600
	0.25 hrs	3650	4960	2960	4410	2600
	0.5 hrs	2300	3100	1430	2670	1200
	0.75 hrs	1060	1790	743	1550	614
	1 hrs	505	802	170	818	251
	1.25 hrs	48	281	<1	345	95
	1.5 hrs	<1	<1		142	<1
	1.75 hrs				56	
	2 hrs				30	
	2.5 hrs					
	3 hrs					
	4 hrs					
	5 hrs					
PBA after 5 hours boiling		<1	<1	<1	<1	<1
Kinetic Model Parameters						
PBA Rate Constant	1/hr	2.137	1.964	2.521	2.185	2.627
PBA 95% CL Max Rate Const.	1/hr	2.537	2.301	2.964	2.304	2.889
PBAo	mg/L	5836	7578	5074	7612	4664
PBAo 95% CL Max. Value	mg/L	6411	8272	5520	7835	4901
Nom. Benzene Generation Rate	g/hr•L	7.99	9.54	8.20	10.66	7.85
Max. Benzene Generation Rate	g/hr•L	10.42	12.20	10.48	11.57	9.07

The data in Figure 5 confirm this phenomenon. Furthermore, since the initial rate r_o is equal to $k*[PBA]_o$ and the data indicate that $[PBA]_o = -6096.8*k + 19{,}334$, then $r_o = 19334k - 6096.8*k^2$.

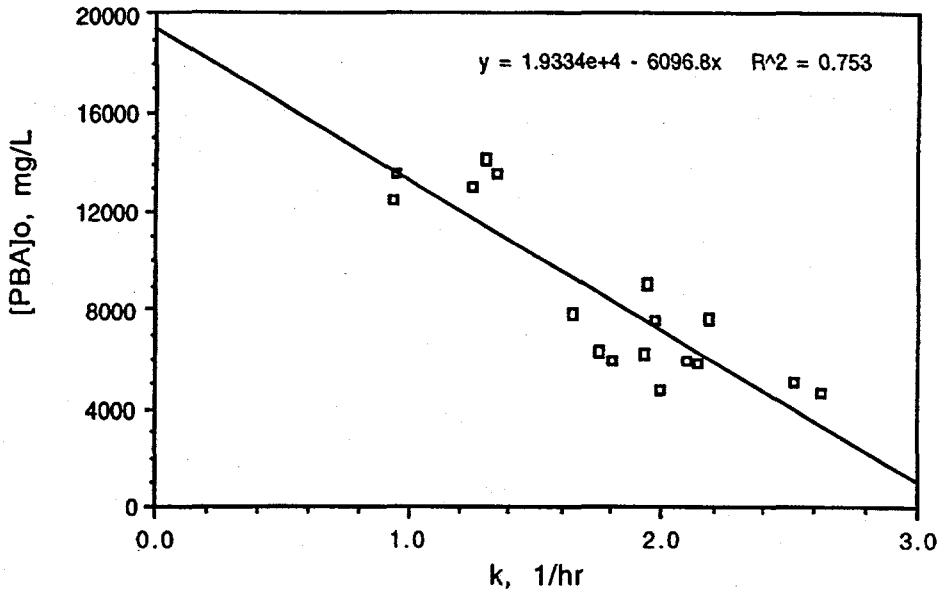


Figure 5. Initial phenylboric acid concentration immediately after the precipitate transfer is stopped, $[PBA]_o$, as a function of the rate constant, k. The higher the rate constant, the greater the rate of reaction and consequently the lower the value of $[PBA]_o$.

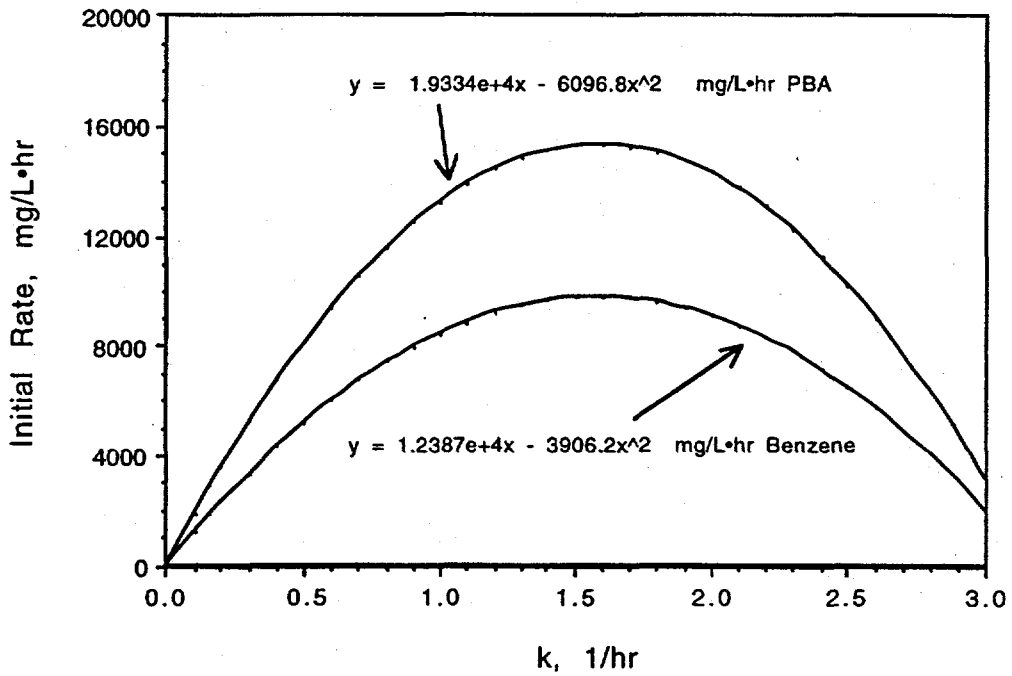


Figure 6. Initial rates of phenylboric acid disappearance and benzene generation immediately after the precipitate transfer is stopped as a function of the rate constant, k, as predicted by the correlation of $[PBA]_o$ with k determined in Figure 5.

Figure 6 shows the predicted initial rate of phenylboric acid disappearance and benzene generation immediately after the precipitate transfer is stopped as a function of the rate constant k over the range of k's determined in this study, from 0 to 2.7 hr^{-1}. Extrapolation of the data beyond this range is not recommended since there are no experimental data to support the results.

Conclusions

A change in the order of the phenylboric acid hydrolysis reaction in the presence of diphenylmercury is confirmed by these data and was a certainly a key finding to develop precipitate hydrolysis process operating parameters that met the process limits for phenylboric acid concentration in the aqueous product and diphenylmercury concentration in the organic product. However, over 90 - 98% of the phenylboric acid still disappears via a reaction first order in phenylboric acid, and only a relatively small fraction of the phenylboric acid reacts once the reaction order becomes different from one. This finding can be used to derive kinetic data that predicts the rate of phenylboric acid disappearance once the precipitate feed is completed. The maximum rate constant of any run within the recommended process operating parameters was found to be 2.52 ± 0.44 hr^{-1} and the maximum rate of benzene generation for any run within the recommended process operating parameters was found to be 11.8 ± 2.0 g/hr•L.

Acknowledgments

The author appreciates the efforts of a number of coworkers within the SRTC Defense Waste Processing Technology (DWPT) Section that were instrumental in completing this work. Support during the long and extensive experimental runs was provided by Sammie King and Irene Reamer. Technical assistance and consultations from Russ Eibling, Mark Baich, Chris Bannochie, and Roy Jacobs proved to be invaluable. The data also could not have been obtained without the rapid turnaround of sample analyses by the Analytical Development Section (ADS) and in particular the efforts of Curtis Johnson, Henry Franks, Vicki Williams, and Sherry Vissage.

References

1) Ainley, A. D. and Challenger, F., J. Chem. Soc., p. 2171, (1930).

2) Kuivila, H. G., Reuwer, J. F., Mangravite, J. A., J. Am. Chem. Soc., 86, p. 2666, (1964).

3) Doherty, J. P., Marek, J. C., U. S. Patent No. 4,840,765, "Precipitate Hydrolysis Process for the Removal of Organic Compounds from Nuclear Waste Slurries", June 20, 1989.

4) Bannochie, C. J., Marek, J. C., Eibling, R. E., Baich, M. A., ACS Symposium Series No. 554, Emerging Technologies in Hazardous Waste Management IV, Chapter 17, "Factors Affecting the Rate of Hydrolysis of Phenylboronic Acid in Laboratory-Scale Precipitate Reactor Studies", (1994).

5) Bannochie, C. J. and Lambert, D. P., WSRC-TR-92-458, Rev. 1, "Technical Bases for Precipitate Hydrolysis Process Operating Parameters", November 9, 1992.

6) Marek, J. C., WSRC-TR-92-0067, "Defense Waste Processing Facility: Report of Task Force to Mitigate the Effect of Nitrite on DWPF Operations", March, 1992.

7) McCabe, D. L., WSRC-RP-94-188, "Curie Concentration in the Influent to Late Wash", March 9, 1994.

8) Marek, J. C., TNX Operating Procedure 677T-70184, Rev. 2, "Preparation of Precipitate Feed Simulant", December, 1992.

9) Landon, L. F., WSRC-RP-92-737, "DWPF Integrated Cold Runs Revised Technical Bases for Precipitate Hydrolysis", May 27, 1992.

10) Marek, J. C., TNX Operating Procedure 677T-70183, Rev. 2, "Operation of Lab Scale Hydrolysis Reactor (LSHR) Unit", December, 1992.

11) Morrissey, M. F., WSRC-RP-92-1030, "Late Washing Efficiency", August 31, 1992.

Appendices

Appendix Table A.1: Preparation of Feeds PF-50, 51, 53, and 54 for Irradiation

	Salt Solution Makeup, grams	
Salt Solution No.	PF-49	PF-52
H_2O, g.	6378.4	6178.35
K_2CO_3, g.	3.45	3.45
KNO_2, g.	268.95	268.95
$CsNO_3$, g.	6.72	6.72
KNO_3, g.	25.02	25.02
KCl, g.	0.24	0.24
KF, g.	0.13	0.13
$Na2SO_4$, g.	2.87	2.87
$K2CrO_4$, g.	0.10	0.09
$Na_2SiO_3 \cdot 9H_2O$, g.	0.16	0.16
C_6H_5OH, g.	0.06	0.06

Feed Makeup No.	PF-50	PF-51	PF-53	PF-54
Salt Solution No.	PF-49	PF-49	PF-52	PF-52
Salt Solution, g.	3344.3	3344.8	3247.3	3238.8
Order of Addition	1st	1st	1st	1st
Sludge Slurry, g.	0	0	0	
Wt% Insolubles	NA	NA	NA	NA
Order of Addition	NA	NA	NA	NA
$NaTi_2O_5H$ Slurry, g.	100.0	100.0	120	120
Wt% Insolubles	14.00	14.00	11.67	11.67
Order of Addition	2nd	2nd	2nd	2nd
Diphenylmercury, g.	22.1	22.1	22.07	22.1
Order of Addition	3rd	3rd	3rd	3rd
NaTPB Drum	#1519	#1519	#1519	#1519
NaTPB Solution, g.	3534.9	3534.9	3534.9	3534.9
Order of Addition	4th	4th	4th	4th
Deionized Water, g.	0	0	75.7	84.2
Order of Addition	NA	NA	5th	5th
Net Makeup, g.	7001.3	7001.8	7000.0	7000.0
Irradiation Dose, rads	1.9 E+08	1.9 E+08	1.9 E+08	1.9 E+08

Feed LWRDPW3 was prepared by washing 6871.7 g of the irradiated material in a continuous wash operation with 13740 mL of wash water with no re-precipitation operation. Additional details of the preparation of this feed were reported previously by Morrissey[11].

Appendix Table A.2: Preparation of Feed I-8 for Irradiation

Salt Solution Makeup, grams	
H_2O, g.	2575.0
KOH, g.	7.07
KNO_2, g.	91.6
$CsNO_3$, g.	2.89
KNO_3, g.	23.8
KCl, g.	0.21
KF, g.	0.11
$B(OH)_3$	0.002
$K_2CO_3 \cdot 1.5H_2O$	3.66
$Na2SO_4$, g.	2.54
$K2CrO_4$, g.	0.08
$Na_2SiO_3 \cdot 9H_2O$, g.	0.14
C_6H_5OH, g.	0.06
Net	2707.16
Order of Addition	1st
Sludge Slurry, g.	0
$NaTi_2O_5H$ Slurry, g.	0
Diphenylmercury, g.	0
NaTPB Solution Makeup, g.	
NaTPB Mass, g.	547.9
H_2O, g.	2642.5
NaOH, g.	2.38
Net	3192.78
Order of Addition	2nd
Deionized Water, g.	100.06
Order of Addition	3rd
Net Makeup, g.	6000.00
Irradiation	
Dose, rads	300

Feed IR-8 was prepared by washing 1300.0 g of the irradiated material in a batch wash operation with 3306 mL of distilled, de-ionized water with no re-precipitation operation. The slurry was recovered by decantation and filtration of the supernate.

Appendix Table A.3: Preparation of Feeds PF-84 and PF-85 for Irradiation

Salt Solution Makeup, grams

Salt Solution No.	PF-83
H_2O, g.	5782.19
K_2CO_3, g.	3.50
KNO_2, g.	269.0
$CsNO_3$, g.	6.70
KNO_3, g.	25.03
KCl, g.	0.24
KF, g.	0.13
$Na2SO_4$, g.	2.87
$K2CrO_4$, g.	0.09
$Na_2SiO_3 \cdot 9H_2O$, g.	0.16
C_6H_5OH, g.	0.06
Net	6089.96

Feed Makeup No.	PF-84	PF-85
Salt Solution No.	PF-83	PF-83
Salt Solution, g.	3045.0	3045.0
Order of Addition	1st	1st
Sludge Slurry, g.	152.5	153.0
Wt% Insolubles	9.18	9.18
Order of Addition	2nd	2nd
$NaTi_2O_5H$ Slurry, g.	198.1	198.1
Wt% Insolubles	10.60	10.60
Order of Addition	3rd	3rd
Diphenylmercury, g.	22.07	22.07
Order of Addition	4th	4th
NaTPB Drum	#1519	#1519
NaTPB Solution, g.	3534.9	3466.7
Order of Addition	5th	5th
Deionized Water, g.	47.9	115.6
Order of Addition	6th	6th
Net Makeup, g.	7000.47	7000.47
Irradiation Dose, rads	1.9 E+08	1.9 E+08

Feed LWRDPW13 was prepared by re-precipitating 16.0 L of the irradiated material with NaTPB and adding sodium nitrite to adjust the nitrite concentration to 0.13 M. 15.237 L of the material was concentrated to 10 wt% solids by removing 1.66 L of supernate. The remaining 13.577 L of material was washed in a continuous wash operation with 34.725 L of wash water adjusted to 0.004 M NaTPB.

Appendix Table A.4: Preparation of Feed PF-113 (Blend of six feeds post-irradiation)

	Salt Solution Makeup, grams		
Salt Solution No.	PF-96	PF-99	PF-102
H_2O, g.	5782.3	6182.3	5795.0
K_2CO_3, g.	3.45	3.45	3.45
KNO_2, g.	268.95	268.95	268.95
$CsNO_3$, g.	6.72	6.72	6.72
KNO_3, g.	25.02	25.02	25.02
KCl, g.	0.24	0.24	0.24
KF, g.	0.13	0.13	0.13
Na2SO4, g.	2.87	2.87	2.88
K2CrO4, g.	0.09	0.13	0.11
$Na_2SiO_3 \cdot 9H_2O$, g.	0.16	0.16	0.18
C_6H_5OH, g.	0.06	0.10	0.08

Feed Makeup No.	PF-97	PF-98	PF-100	PF-101	PF-103	PF-104
Salt Solution No.	PF-96	PF-96	PF-99	PF-99	PF-102	PF-102
Salt Solution, g.	3045.0	3045.0	3245.8	3244.0	3052.0	3052.0
Order of Addition	1st	1st	1st	1st	1st	1st
Sludge Slurry, g.	198.1	198.1	0	0	0	0
Wt% Insolubles	10.6	10.6	NA	NA	NA	NA
Order of Addition	2nd	2nd	2nd	2nd	2nd	2nd
$NaTi_2O_5H$ Slurry, g.	152.5	152.5	152.5	152.6	152.5	152.6
Wt% Insolubles	9.18	9.18	9.18	9.18	9.18	9.18
Order of Addition	3rd	3rd	3rd	3rd	3rd	3rd
Diphenylmercury, g.	22.07	22.07	22.00	22.00	22.10	22.10
Order of Addition	4th	4th	4th	4th	4th	4th
NaTPB Drum	#1610	#1610	#1633	#1633	#1633	#1633
NaTPB Solution, g.	3470.8	3470.8	3466.8	3466.8	3466.8	3470.2
Order of Addition	5th	5th	5th	5th	5th	5th
Deionized Water, g.	111.53	111.53	115.8	116.0	306.6	307.1
Order of Addition	6th	6th	6th	6th	6th	6th
Net Makeup, g.	7000.0	7000.0	7002.9	7001.4	7000.0	7004.0
Irradiation Dose, rads	2.0 E+08	2.0 E+08	2.0 E+08	2.0 E+08	2.0 E+08	2.0 E+08
Mass Added to PF-113 Blend, g.	6076.0	5316.3	6309.0	6366.7	6072.4	6406.8

Feed PF-113PW was prepared by re-precipitation with NaTPB and then washing 8165 g of the material in a continuous wash operation with 21079 mL of wash water adjusted to 0.004 M NaTPB.

Appendix Table A.5: Preparation of Feeds PF-143, PF-143A200-46 and PF-143A510-46

Feed Makeup No.	PF-143
Salt Solution Preparation:	
H_2O, g.	67760.1
K_2CO_3, g.	42.0
KNO_2, g.	3271.8
$CsNO_3$, g.	81.71
KNO_3, g.	304.3
KCl, g.	2.95
KF, g.	1.55
$Na2SO_4$, g.	35.0
$K2CrO_4$, g.	1.20
$Na_2SiO_3 \cdot 9H_2O$, g.	1.92
C_6H_5OH, g.	0.18
$C_6H_5B(OH)_2$., g.	0.13
$B(OH)_3$, g.	0.05
Order of Addition:	4th
Sodium Titanate Slurry	
$NaTi_2O_5H$ Slurry, g.	2604.8
Wt% Insolubles	13.08
Order of Addition:	2nd
Sodium Tetraphenylborate Solution	
NaTPB Drum	#1760
NaTPB Solution, g.	91763.0
NaOH	14.3
Order of Addition:	1st
Mercuric Nitrate Solution	
H_2O, g.	1868.0
$Hg(NO_3)_2 \cdot H_2O$, g.	518.0
70 wt% HNO_3, g.	33.6
Order of Addition:	3rd
Deionized Water, g.	1996.0
Order of Addition:	5th
Net Makeup, g.	170301.1
Irradiation Dose, rads	2.0 E+08

Feed PF-143PW was prepared by re-precipitating the irradiated PF-143 material with NaTPB. The 125.5 L of feed material was concentrated from 9.91 wt% to 10.0 wt% by removing 1.1 L of permeate. The 124.4 L of remaining material was then washed with 328.8 L wash water adjusted to 0.004 M NaTPB to reduce the nitrite concentration from 0.146 M to 0.008 M.

Feed PF-143A200-46 was prepared by washing 7933 g of the irradiated PF-143 material in a continuous wash operation with 27753 mL of wash water adjusted to 0.004 M NaTPB. The washed material was then irradiated to an additional dose of 4.6 E+07 rads in the 774-A Cobalt source.

Feed PF-143A510-46 was prepared by first irradiating the PF-143 material to an additional dose of 3.1 E+08 rads in the 774-A cobalt well to achieve a net dose of 5.1 E+08 rads. 4560 g of the material was then washed in a continuous wash operation with 13178 mL of wash water adjusted to 0.004 M NaTPB. The washed material was then irradiated to an additional dose of 4.6 E+07 rads in the 774-A Cobalt source.

Appendix Table A.6: Sodium Tetraphenylborate Solution Analyses

Drum No.	#1519	#1610	#1633	#1760
Tetraphenylborate, wt%	16.80	17.10	17.09	16.00
Hydroxide, M	0.18	0.23	0.23	0.09
Organics, mg/L:				
Phenylboric Acid	552	613	917	593
N-Phenylformamide	<1	<1	42	NA
Phenol	173	262	663	1138
4-Phenylphenol	<1	27	7	11
2-Phenylphenol	7	36	41	6
Diphenylamine	22	31	37	3
Biphenyl	126	416	554	159
o-Terphenyl	<1	27	<1	3
m-Terphenyl	<1	<1	<1	<1
p-Terphenyl	<1	<1	<1	2
Benzene	537	1475	3643	536
Sodium, ppm	10,222	10,745	11,405	10,033
Copper, ppm	1.77	1.21	1.04	0.08
pH	13.23	13.14	13.23	12.2

Table A.7 Preparation of Sludge with Noble Metals for Trimming Precipitate

Constituent	Assay	Mass Added, g.	Mass Noble Metal or Solid	Noble Metal Wt% dry basis*
Purex Sludge	NA	2402.3	0	NA
$RuCl_3$	41.74 wt% Ru	1.7306	0.722 g. Ru	0.216
$Rh(NO_3)_3$ solution	4.93 wt% Rh	3.002	0.148 g. Rh	0.044
$Pd(NO_3)_3$ solution	8.77 wt% Pd	3.602	0.316 g. Pd	0.095
Trimmed Mixture	12.88 wt% insolubles 13.86 wt% total solids	2410.6	310.49 g. net insolubles 334.11 net solids	

Calculations for precipitate trimmed with 6000 g. sludge insolubles:

6000 ppm sludge insolubles * 0.722 g. Ru / 310.49g. sludge insoluble = 13.95 ppm Ru

6000 ppm sludge insolubles * 0.148 g. Rh / 310.49 g. sludge insoluble = 2.86 ppm Rh

6000 ppm sludge insolubles * 0.316 g. Pd / 310.49 g. sludge insoluble = 6.11 ppm Pd

* These values indicate the ratio of Ru:Pd:Rh is expected to be about 1:0.44:0.20. Analysis of the sludge material using x-ray fluorescence measured a ratio of 1:0.43:0.225, which compares favorably with the expected values. Analysis of the material using a ICP/ mass spectrometer determined the ruthenium concentration to be 0.23 wt%, which also compares favorably with the target values. The combined analysis indicates the noble metal concentrations were 0.23 wt% Ru, wt% Pd, and wt% Rh.

Appendices

Appendix B: JMP® Nonlinear Regression Statistical Data Analyses

Non-linear Regression of PBA Kinetic Data for Run 92-10

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=0.00004
Converged in Objective Function

Warning: 7 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000036	0.0000001	
D Criterion	0.0075436157	0.0000001	
G Criterion	0.0003622072	0.000001	
CL Criterion	•	0.00001	

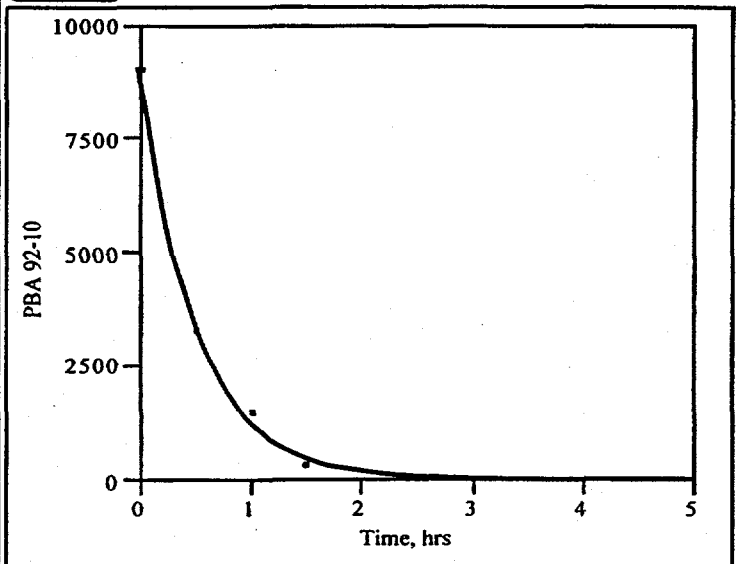
Parameter	Current Value	Lock	SSE
PBAo	9067.7848918	☐	119362.30461
k	1.9415188868	☐	263920.07224

Solution

SSE	DFE	MSE	RMSE
119362.30461	4	29840.576	172.74425

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	9067.7848918	170.968076	8691.87984	9444.20816
k	1.9415188868	0.07979637	1.77600223	2.12782823

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.3544
k	0.3544	1.0000

Non-linear Regression of PBA Kinetic Data for Run 92-11

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=1.87e-6
Converged in Objective Function

Warning: 5 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000154	0.0000001	
D Criterion	0.0208733439	0.0000001	
G Criterion	0.0017395888	0.000001	
CL Criterion	.	0.00001	

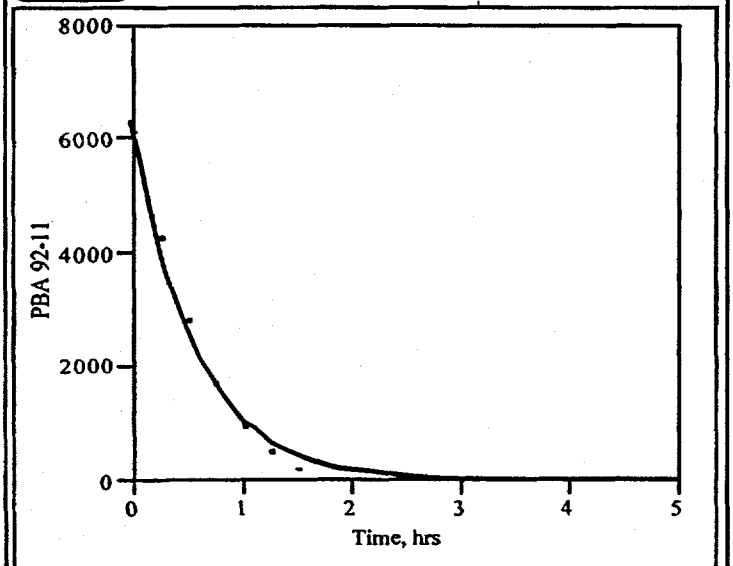
Parameter	Current Value	Lock	SSE
PBAo	6330.9556916	☐	337557.03032
k	1.7489203154	☐	610096.9577

Solution

SSE	DFE	MSE	RMSE
337557.03032	6	56259.505	237.19086

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	6330.9556916	216.586893	5864.40219	6802.67416
k	1.7489203154	0.10588357	1.54021997	1.98347537

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5480
k	0.5480	1.0000

Non-linear Regression of PBA Kinetic Data for Run 92-12

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=0.00038
Converged in Objective Function

Warning: 5 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000042	0.0000001	
D Criterion	0.0111200958	0.0000001	
G Criterion	0.0004993516	0.000001	
CL Criterion	.	0.00001	

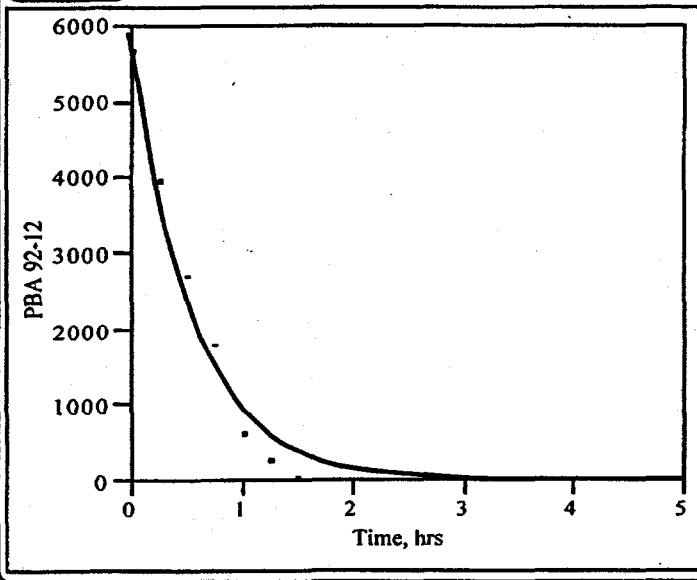
Parameter	Current Value	Lock	SSE
PBAo	5914.1679312	☐	672487.3393
k	1.7984237407	☐	1215446.4074

Solution

SSE	DFE	MSE	RMSE
672487.3393	6	112081.22	334.78534

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	5914.1679312	307.047894	5258.06588	6580.87674
k	1.7984237407	0.16569017	1.48694562	2.17010027

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5425
k	0.5425	1.0000

Non-linear Regression of PBA Kinetic Data for Run 92-13

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=3.43e-7
Converged in Objective Function

Warning: 5 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000031	0.0000001	
D Criterion	0.0082187329	0.0000001	
G Criterion	0.0002856605	0.000001	
CL Criterion	.	0.00001	

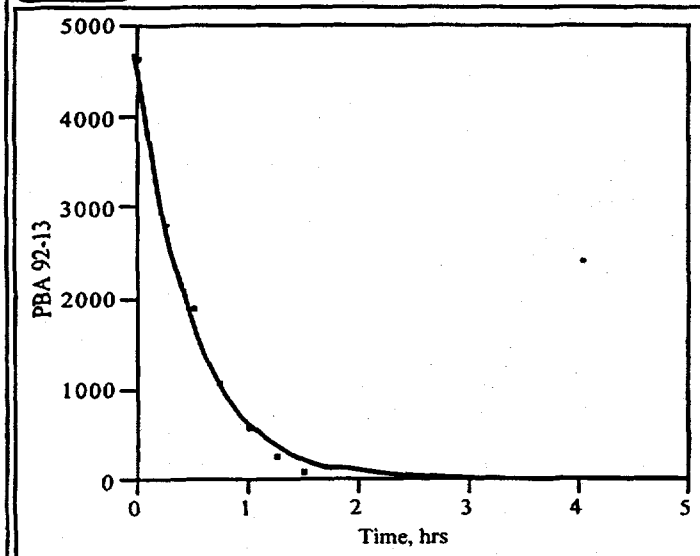
Parameter	Current Value	Lock	SSE
PBAo	4693.9170457	☐	86231.194328
k	1.9894598444	☐	155853.33616

Solution

SSE	DFE	MSE	RMSE
86231.194328	6	14371.866	119.88272

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	4693.9170457	111.626557	4451.31563	4938.22606
k	1.9894598444	0.08508249	1.81632698	2.17930874

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5224
k	0.5224	1.0000

Non-linear Regression of PBA Kinetic Data for Run 92-17

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=1.8e-10
Converged in Objective Function

Warning: 7 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000008	0.0000001	
D Criterion	0.0008876458	0.0000001	
G Criterion	0.0000045631	0.000001	
CL Criterion	.	0.00001	

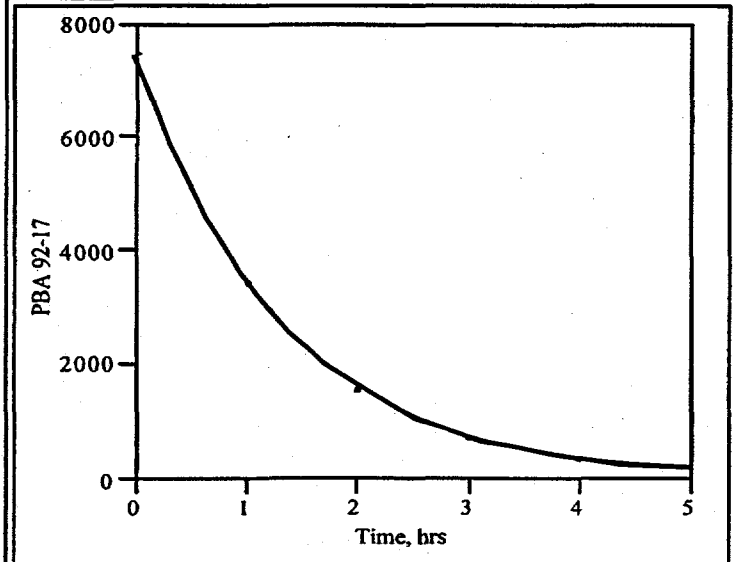
Parameter	Current Value	Lock	SSE
PBAo	7489.4482059	☐	5892.7407055
k	0.7561615928	☐	13029.344211

Solution

SSE	DFE	MSE	RMSE
5892.7407055	4	1473.1852	38.382094

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	7489.4482059	37.4627238	7406.90385	7572.04773
k	0.7561615928	0.00755781	0.73960655	0.77314224

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.4261
k	0.4261	1.0000

Non-linear Regression of PBA Kinetic Data for Run 92-18

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=1.86e-7
Converged in Objective Function

Warning: 7 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000032	0.0000001	
D Criterion	0.0079528878	0.0000001	
G Criterion	0.0002404628	0.000001	
CL Criterion	.	0.00001	

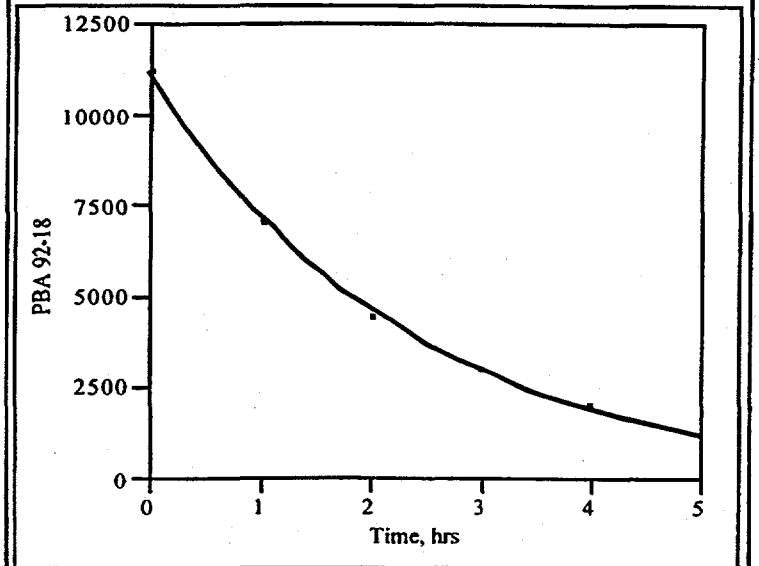
Parameter	Current Value	Lock	SSE
PBAo	11225.486197	☐	76811.332182
k	0.4407616682	☐	169836.30136

Solution

SSE	DFE	MSE	RMSE
76811.332182	4	19202.833	138.57429

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	11225.486197	127.923656	10943.2464	11508.6586
k	0.4407616682	0.00936473	0.42025254	0.46204325

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5559
k	0.5559	1.0000

Non-linear Regression of PBA Kinetic Data for Run 92-28

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=0.00002
Converged in Objective Function

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	3.31123e-11	0.0000001	
D Criterion	0.000874246	0.0000001	
G Criterion	0.00000335	0.000001	
CL Criterion	.	0.00001	

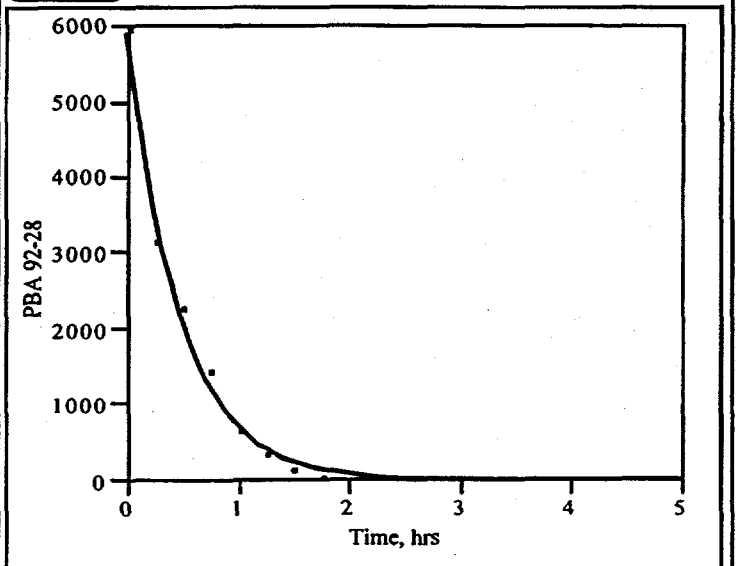
Parameter	Current Value	Lock	SSE
PBAo	5908.4317747	☐	255533.14815
k	2.10139847	☐	368068.45231

Solution

SSE	DFE	MSE	RMSE
255533.14815	11	23230.286	152.41485

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	5908.4317747	142.861323	5595.65144	6223.53789
k	2.10139847	0.09175656	1.91059936	2.31349539

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5097
k	0.5097	1.0000

Non-linear Regression of PBA Kinetic Data for Run 92-29

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=2.25e-6
Converged in Objective Function

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000026	0.0000001	
D Criterion	0.0081746694	0.0000001	
G Criterion	0.0002816518	0.000001	
CL Criterion	.	0.00001	

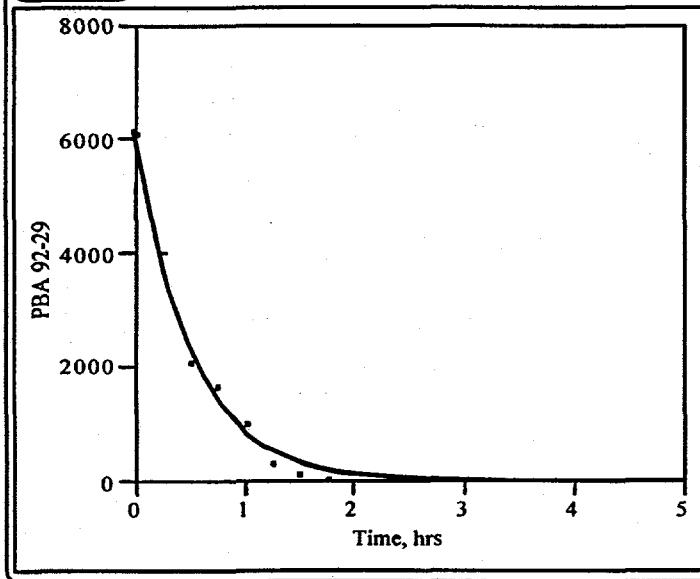
Parameter	Current Value	Lock	SSE
PBAo	6212.0672742	☐	327477.85555
k	1.9284092332	☐	471697.18813

Solution

SSE	DFE	MSE	RMSE
327477.85555	11	29770.714	172.54192

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	6212.0672742	159.651372	5865.32975	6561.67016
k	1.9284092332	0.08799086	1.75015068	2.12578208

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5265
k	0.5265	1.0000

Non-linear Regression of PBA Kinetic Data for Run 93-1

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=0.0113
Converged in Objective Function

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000006	0.0000001	
D Criterion	0.0037532682	0.0000001	
G Criterion	0.0000545243	0.000001	
CL Criterion	.	0.00001	

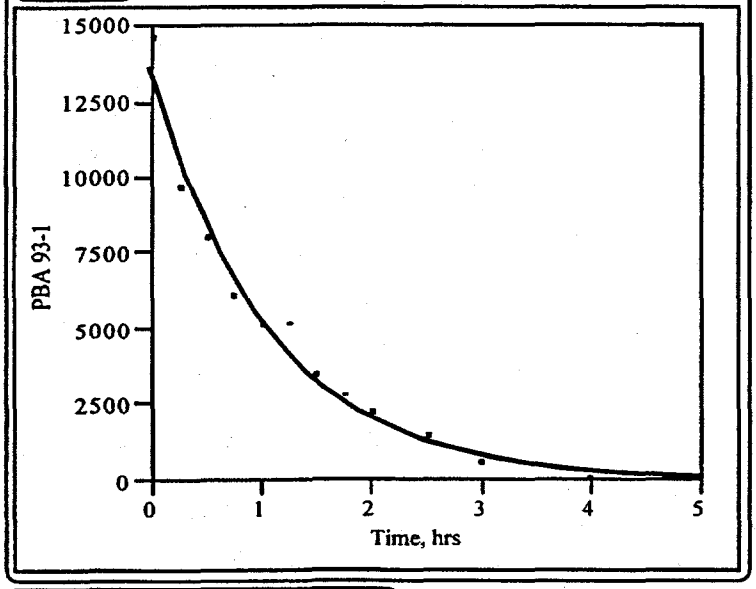
Parameter	Current Value	Lock	SSE
PBAo	13625.287579	☐	4017276.1894
k	0.9373263145	☐	5786461.1313

Solution

SSE	DFE	MSE	RMSE
4017276.1894	11	365206.93	604.32353

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	13625.287579	482.013001	12563.112	14711.7999
k	0.9373263145	0.05687696	0.81492767	1.07413183

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.6373
k	0.6373	1.0000

Non-linear Regression of PBA Kinetic Data for Run 93-2

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=2 Converged g=0.0492
Converged in Objective Function

Warning: 1 missing Y's,

	Current	Limit	Alpha
Iteration	2	60	0.050
Shortening	0	15	
O Criterion	0.0000000653	0.0000001	
D Criterion	0.0427596439	0.0000001	
G Criterion	0.0070641405	0.000001	
CL Criterion	.	0.00001	

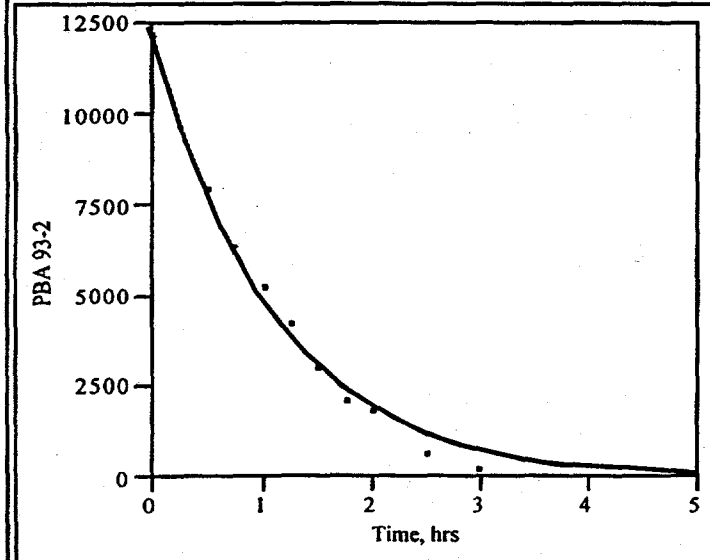
Parameter	Current Value	Lock	SSE
PBAo	12413.181644	☐	1187842.8207
k	0.9293282552	☐	1763273.756

Solution

SSE	DFE	MSE	RMSE
1187842.8207	10	118784.28	344.65096

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	12413.181644	274.464923	11821.5646	13012.1323
k	0.9293282552	0.0353164	0.85657851	1.00663299

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.6387
k	0.6387	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-3

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=2 Converged g=0.01942
Converged in Objective Function

Warning: 4 missing Y's,

	Current	Limit	Alpha
Iteration	2	60	0.050
Shortening	0	15	
O Criterion	0.0000000594	0.0000001	
D Criterion	0.0408116733	0.0000001	
G Criterion	0.006239702	0.000001	
CL Criterion	.	0.00001	

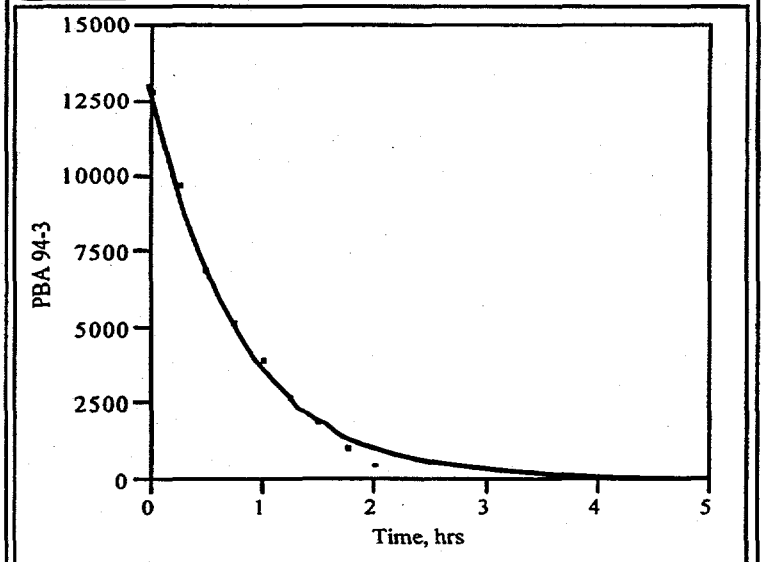
Parameter	Current Value	Lock	SSE
PBAo	13002.573018	☐	562691.52173
k	1.257568129	☐	952101.03782

Solution

SSE	DFE	MSE	RMSE
562691.52173	7	80384.503	283.52161

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	13002.573018	243.17233	12473.9821	13535.454
k	1.257568129	0.0405851	1.17259992	1.34732651

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.6027
k	0.6027	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-4

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=2 Converged g=0.01124
Converged in Objective Function

Warning: 4 missing Y's,

	Current	Limit	Alpha
Iteration	2	60	0.050
Shortening	0	15	
O Criterion	0.000000007	0.0000001	
D Criterion	0.0142319175	0.0000001	
G Criterion	0.0007533986	0.000001	
CL Criterion	.	0.00001	

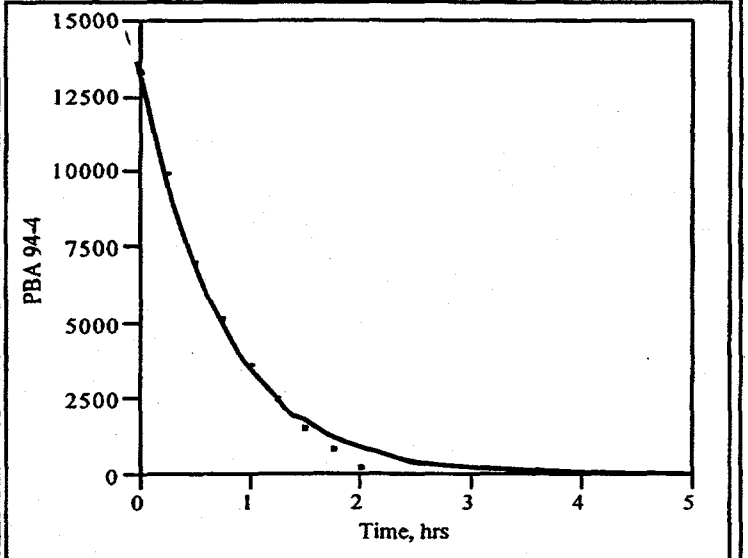
Parameter	Current Value	Lock	SSE
PBAo	13624.794951	☐	803618.17396
k	1.3474204226	☐	1359760.4867

Solution

SSE	DFE	MSE	RMSE
803618.17396	7	114802.6	338.82532

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	13624.794951	294.47969	12986.5252	14268.8025
k	1.3474204226	0.05015832	1.2438311	1.45810864

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5912
k	0.5912	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-5

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=2 Converged g=0.00266
Converged in Objective Function

Warning: 4 missing Y's,

	Current	Limit	Alpha
Iteration	2	60	0.050
Shortening	0	15	
O Criterion	0.0000000022	0.0000001	
D Criterion	0.008039409	0.0000001	
G Criterion	0.0002433867	0.000001	
CL Criterion	.	0.00001	

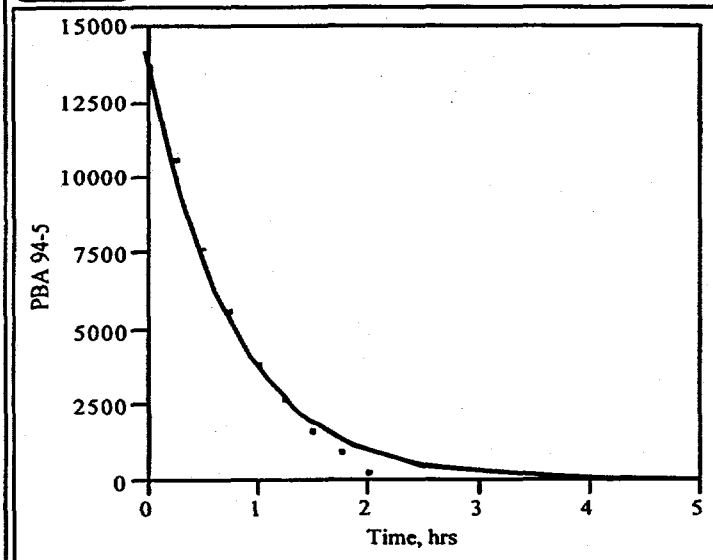
Parameter	Current Value	Lock	SSE
PBAo	14140.597112	☐	1411890.8411
k	1.304982629	☐	2388987.0083

Solution

SSE	DFE	MSE	RMSE
1411890.8411	7	201698.69	449.10877

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	14140.597112	387.947518	13303.6968	14987.0559
k	1.304982629	0.06169535	1.17962161	1.44087688

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5966
k	0.5966	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-7

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=2.39e-7
Converged in Objective Function

Warning: 4 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000042	0.0000001	
D Criterion	0.0109676482	0.0000001	
G Criterion	0.0004775089	0.000001	
CL Criterion	.	0.00001	

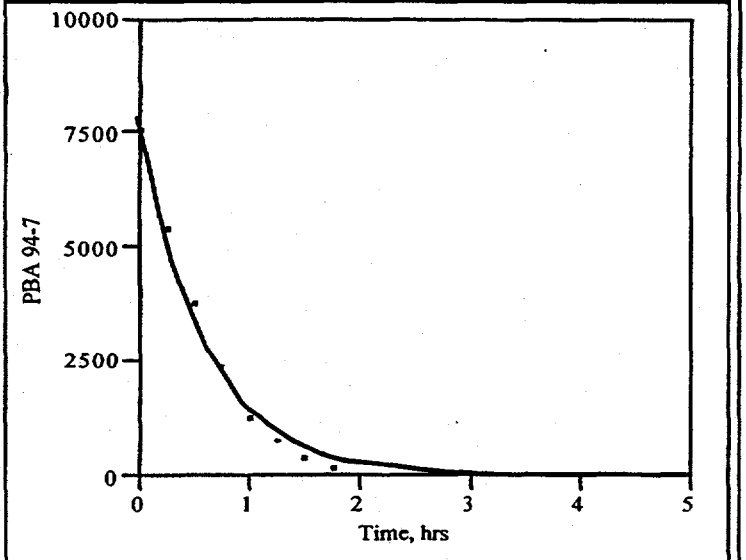
Parameter	Current Value	Lock	SSE
PBAo	7856.1732785	☐	544933.59502
k	1.6448385662	☐	922053.77428

Solution

SSE	DFE	MSE	RMSE
544933.59502	7	77847.656	279.01193

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	7856.1732785	251.563311	7314.57094	8403.90135
k	1.6448385662	0.09162885	1.46360514	1.84700854

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5567
k	0.5567	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-12

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

- ☐ Second Deriv. Method
- ☐ Continuous Update
- ☐ Iteration Log
- ☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=0.00023
Converged in Objective Function

Warning: 6 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000036	0.0000001	
D Criterion	0.0098329647	0.0000001	
G Criterion	0.0004199881	0.000001	
CL Criterion	.	0.00001	

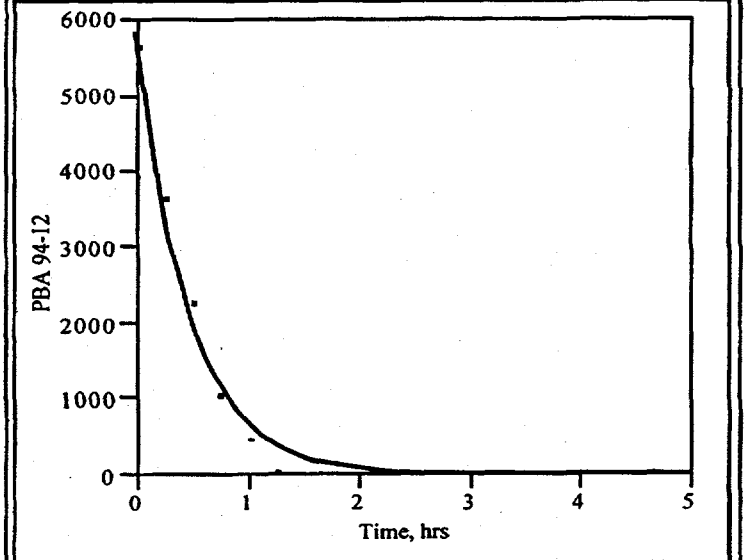
Parameter	Current Value	Lock	SSE
PBAo	5836.4675592	☐	393097.27784
k	2.1368250547	☐	773956.31119

Solution

SSE	DFE	MSE	RMSE
393097.27784	5	78619.456	280.39161

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	5836.4675592	264.085509	5268.05722	6411.32355
k	2.1368250547	0.17753284	1.79874258	2.53691576

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5095
k	0.5095	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-13

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=0.00011
Converged in Objective Function

Warning: 6 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000144	0.0000001	
D Criterion	0.0200062982	0.0000001	
G Criterion	0.0016567333	0.000001	
CL Criterion	.	0.00001	

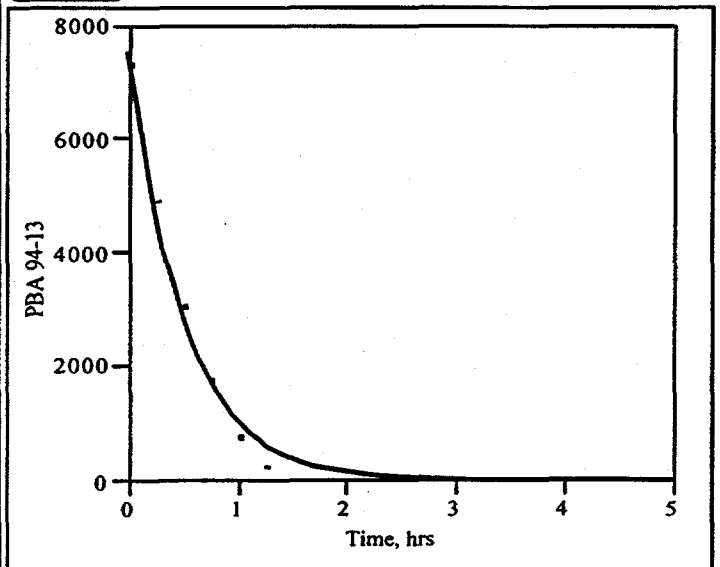
Parameter	Current Value	Lock	SSE
PBAo	7578.3817067	☐	585169.85064
k	1.9643409437	☐	1152121.6873

Solution

SSE	DFE	MSE	RMSE
585169.85064	5	117033.97	342.10228

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	7578.3817067	318.689826	6892.37891	8272.30765
k	1.9643409437	0.15007337	1.67428168	2.30050642

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5277
k	0.5277	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-14

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=0.00018
Converged in Objective Function

Warning: 7 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	0.0000000023	0.0000001	
D Criterion	0.0073749062	0.0000001	
G Criterion	0.000262759	0.000001	
CL Criterion	•	0.00001	

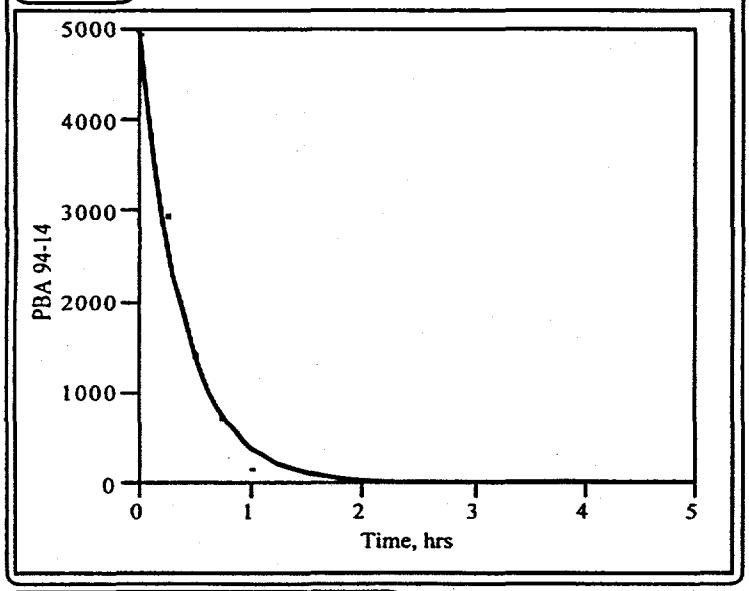
Parameter	Current Value	Lock	SSE
PBAo	5073.5554935	☐	181432.14726
k	2.521144632	☐	401161.70314

Solution

SSE	DFE	MSE	RMSE
181432.14726	4	45358.037	212.97426

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	5073.5554935	204.714103	4630.05109	5520.46352
k	2.521144632	0.1946391	2.14557113	2.96393557

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.4734
k	0.4734	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-17

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=0.00018
Converged in Objective Function

Warning: 4 missing Y's,

	Current	Limit	Alpha
Iteration	2	60	0.050
Shortening	0	15	
O Criterion	0.0000000005	0.0000001	
D Criterion	0.0029971092	0.0000001	
G Criterion	0.0000401324	0.000001	
CL Criterion	.	0.00001	

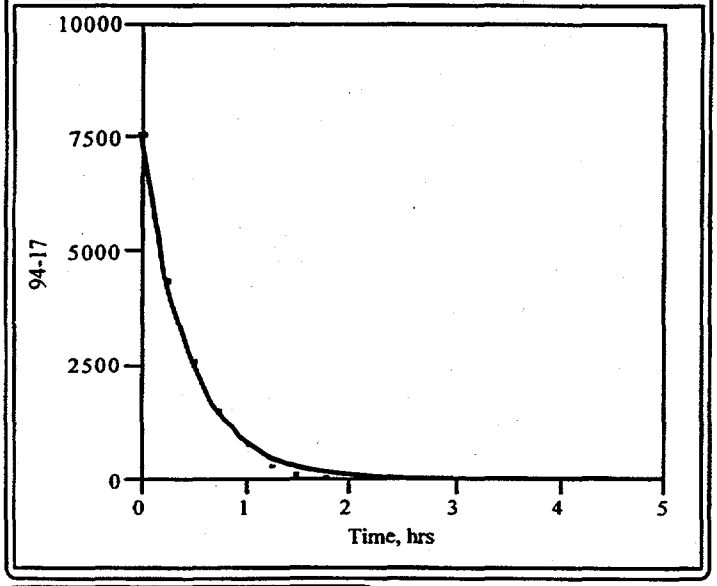
Parameter	Current Value	Lock	SSE
PBAo	7612.0483052	☐	81697.216068
k	2.1854981945	☐	138235.60726

Solution

SSE	DFE	MSE	RMSE
81697.216068	7	11671.031	108.03255

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	7612.0483052	101.830606	7389.56999	7835.33792
k	2.1854981945	0.05328473	2.07396528	2.30354688

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.5018
k	0.5018	1.0000

Non-linear Regression of PBA Kinetic Data for Run 94-18

Nonlinear Fitting Control Panel

Go | Step | Stop | Reset | Confid Limits

☐ Second Deriv. Method
☐ Continuous Update
☐ Iteration Log
☐ Loss is -LogLikelihood

PLCI iter=3 Converged g=5.07e-7
Converged in the Gradient

Warning: 6 missing Y's,

	Current	Limit	Alpha
Iteration	3	60	0.050
Shortening	0	15	
O Criterion	4.517481e-14	0.0000001	
D Criterion	0.000001574	0.0000001	
G Criterion	0.0000000032	0.000001	
CL Criterion	.	0.00001	

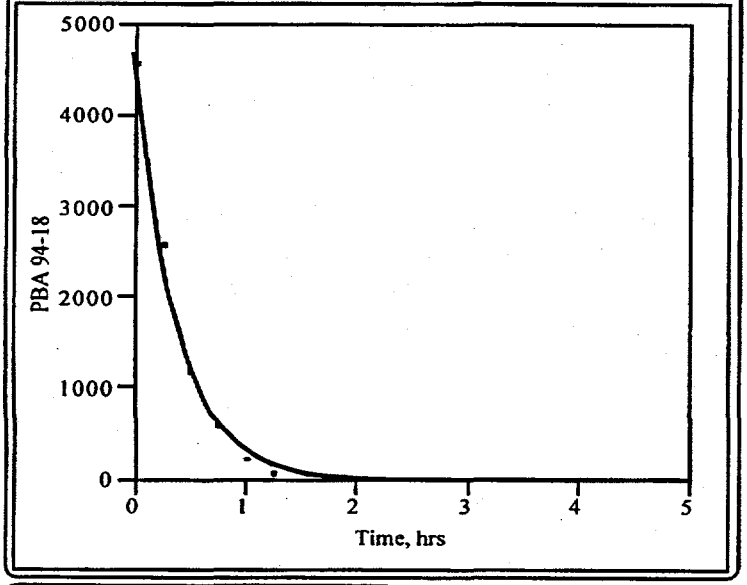
Parameter	Current Value	Lock	SSE
PBAo	4663.8410416	☐	63136.415082
k	2.6273286382	☐	124307.21268

Solution

SSE	DFE	MSE	RMSE
63136.415082	5	12627.283	112.37118

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
PBAo	4663.8410416	108.309737	4427.80877	4900.89782
k	2.6273286382	0.11679787	2.39165053	2.88860172

Graph



Correlation of Estimates

	PBAo	k
PBAo	1.0000	0.4614
k	0.4614	1.0000