ORNL/TM-2001/42

Evaluation of the Small-Tank Tetraphenylborate Process Using a Bench-Scale, 20-L Continuous Stirred Tank Reactor System at Oak Ridge National Laboratory: Results of Test 5

D. D. Lee
J. L. Collins

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via the U.S. Department of Energy (DOE) Information Bridge:

Web site: http://www.osti.gov/bridge

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-605-6000 (1-800-553-6847)
TDD: 703-487-4639
Fax: 703-605-6900
E-mail: info@ntis.fedworld.gov
Web site: http://www.ntis.gov/support/ordernowabout.htm

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and International Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Telephone: 865-576-8401
Fax: 865-576-5728
E-mail: reports@adonis.osti.gov
Web site: http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL-2001/42

Chemical Technology Division

Evaluation of the Small-Tank Tetraphenylborate Process Using a Bench-Scale, 20-L Continuous Stirred Tank Reactor System at Oak Ridge National Laboratory: Results of Test 5

D. D. Lee and J. L. Collins

Date Published: August 2001

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
managed by
UT-BATTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

	Page
LIST OF FIGURES	v
LIST OF TABLES	vii
ACRONYMS	ix
ACKNOWLEDGMENTS	xi
EXECUTIVE SUMMARY	xiii
1. INTRODUCTION	1
1.1 BACKGROUND	1
1.2 SYSTEM DESIGN	2
2. PLAN FOR TEST 5	4
2.1 TEST DESIGN	4
2.2 PREPARATION OF FEED FOR TEST 5	14
3. MEASUREMENTS AND SAMPLING	16
3.1 SAMPLING PLANS	16
3.2 MEASURING AND TEST EQUIPMENT	16
4. RESULTS OF TEST 5	17
4.1 RUN SUMMARY	17
4.2 CESIUM DECONTAMINATION AND SYSTEM CHEMISTRY IN TEST 5	20
4.2.1 Cesium Removal	20
4.2.2 Analysis of Recycle Wash-Water Feed	23
4.2.3 TPB Decomposition Data	24
4.2.4 ICP-AES Analyses for Potassium and Boron	29
4.2.5 Benzene Production Rate as a Measure of TPB Decomposition	33
4.3 SUBSYSTEMS OPERATION	38
4.3.1 Feed System Operations	38
4.3.2 Antifoam Operations	38
4.3.3 Problems with MST/Catalyst Feed Mixture	38
4.3.4 Performance of the Slurry Concentration System	39
4.3.5 Hydraulic Performance of the CSTR	41
4.3.6 Performance of the Control and Data Acquisition System	41
4.4 SLURRY WASHING	41
5. EVALUATION OF 20-L CSTR SYSTEM PERFORMANCE	43
5.1 CESIUM REMOVAL	43
5.2 STRONTIUM REMOVAL	46
5.3 URANIUM REMOVAL	48
5.4 BEHAVIOR OF SOLUBLE TPB DURING DECOMPOSITION	49
5.5 TPB DECOMPOSITION AND BENZENE PRODUCTION	52
5.5.1 Test Conditions for Catalyst Activation	52
5.5.2 Benzene Production in CSTR 1: Tests 4 and 5	53
5.5.3 Benzene Production in CSTR 2: Tests 4 and 5	55
5.5.4 Benzene Production in the SCT and the Combined System: Tests 4 and 5	56

5.5.5 Comparison with 1-L CSTR Test Results 57
5.5.6 Summary of Findings from Decomposition Studies..... 58
5.6 SLURRY WASHING AND TPB RECOVERY..... 59

6. CONCLUSIONS AND RECOMMENDATIONS FOR THE 20-L CSTR TEST PROGRAM... 63

7. REFERENCES..... 65

LIST OF FIGURES

Figure		Page
1	Simplified flow diagram of the 20-L CSTR system	3
2	Diagram showing the CSTR feed systems	5
3	Diagram showing the CSTR antifoam and MST/catalyst delivery systems	6
4	Redesigned slurry concentrate system	7
5	Redesigned slurry wash filter system	8
6	Flowsheet for the benzene monitoring system	9
7	Valves and piping for the benzene monitoring system	10
8	STTP 20-L CSTR, SCT, and SWT configurations in the ORNL hot cell	11
9	STTP 20-L slurry concentration and slurry wash cross-flow filtration systems in the ORNL hot cell	12
10	Feed systems for the STTP 20-L CSTR at ORNL	13
11	Material balances for Test 5	18
12	Average flow rates for Test 5	18
13	Sodium and potassium concentration profiles in CSTR 1 if no reactions occur	19
14	On-site cesium DF results	21
15	Cesium DF results for samples analyzed by RMAL	21
16	Cesium removal results for CSTR 1 in Test 5: comparison of the sample-analysis results for on-site and RMAL instruments	22
17	Cesium removal results for CSTR 2 in Test 5: comparison of sample-analysis results for on-site and RMAL instruments	22
18	Cesium removal results for SCT filtrate in Test 5: comparison of sample-analysis results for on-site and RMAL instruments	23
19	HPLC results for CSTR 1 in Test 5	26
20	1PB HPLC results for CSTRs and SCT in Test 5	26
21	Soluble NaTPB and potassium in CSTRs 1 and 2	27
22	HPLC results for CSTR 2 in Test 5	27
23	HPLC results for SCT filtrate in Test 5	28
24	HPLC results for TPB in CSTRs and SCT in Test 5	28
25	HPLC results for 3PB concentration in CSTRs and SCT in Test 5	30
26	NaTPB behavior in CSTR 1 during Test 5	30
27	NaTPB behavior in CSTR 2 during Test 5	31

28 NaTPB behavior in SCT during Test 5 31
29 CSTR 1 results for boron and potassium in Test 5 32
30 CSTR 2 results for boron and potassium in Test 5 32
31 SCT filtrate results for boron and potassium in Test 5 33
32 Benzene generation results for CSTR 1 35
33 Benzene generation results for CSTR 2 35
34 Benzene generation results for SCT 37
35 Benzene generation results from conversion of TPB to 3PB in Test 5 37
36 Performance of SCT cross-flow filter in Test 5 40
37 Performance of SCT cross-flow filter in Tests 3, 4, and 5 40
38 Nitrite and NaTPB concentrations in wash water during slurry washing in Test 5 42
39 Comparison of cesium DFs for all CSTR tests 44
40 Comparison of cesium DFs for all CSTR tests (CSTR 1) 45
41 Comparison of cesium DFs for all CSTR tests (CSTR 2) 45
42 Strontium concentrations during Tests 1a and 3 47
43 Strontium DFs in system vessels during Tests 1a and 3 47
44 Uranium concentrations during Tests 1a and 3 48
45 Uranium DFs in system vessels during Tests 1a and 3 49
46 Soluble TPB results for CSTR 1 in Tests 1–5 50
47 Soluble TPB results for CSTR 2 in Tests 1–5 51
48 Soluble TPB results for SCT filtrate in Tests 1–5 51
49 Benzene generation in CSTR 1 in Tests 4 and 5 54
50 Benzene generation in CSTR 2 in Tests 4 and 5 55
51 Benzene generation in concentration system in Tests 4 and 5 56
52 Cumulative benzene generation for CSTR system in Tests 4 and 5 57
53 NaTPB concentrations in slurry wash water during slurry washing in Tests 1–5 62
54 Nitrite concentrations in slurry wash water during slurry washing in Tests 1–5 62

LIST OF TABLES

Table		Page
1	Preparation of average SRS salt feed for Test 5	14
2	Feed materials and feed rates for Test 5	15
3	Process feed and product volumes for Test 5	19
4	Chronology of IITB52 feed problems and other events for Test 5	20
5	Analysis of recycle wash water	24
6	Wash-water results for batch 1 slurry washed at 20 mL/min in Test 5	42
7	Results for batch 2 slurry washed at 20 mL/min in Test 5	42
8	Summary of benzene generation for Tests 4 and 5	53
9	NaTPB recovery in slurry washing process in CSTR tests	59
10	Nitrite removal wash results for slurry washing in Tests 2–5	61

ACRONYMS

ALARA	as low as reasonably achievable
CERS	Chemical and Energy Research Section
CSTR	continuous-flow stirred-tank reactor
DF	decontamination factor
ECC	Enhanced Comprehensive Catalyst
FTIR	Fourier transform infrared analyzer
HLW	high-level waste
HPLC	high-performance liquid chromatography
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma–atomic emission spectroscopy
IIT	Illinois Institute of Technology
KTPB	potassium tetraphenylborate
MST	monosodium titanate
NaTPB	sodium tetraphenylborate
NIST	National Institute of Standards and Technology
ORNL	Oak Ridge National Laboratory
QA	quality assurance
RCS	recommended catalyst system
RMAL	Radioactive Materials Analytical Laboratory
RWW	recycle wash water
RWWT	recycle wash water tank
SCT	slurry concentrating tank
SP	sample port
SPP	Savannah River Salt Waste Processing Program
SRL	Savannah River Laboratory
SRS	Savannah River Site
SRTC	Savannah River Technology Center
STTP	Small-Tank Tetraphenylborate Process
SWT	slurry washing tank
TPB	tetraphenylborate
TMP	cross-flow filter transmembrane pressure
WAC	waste acceptance criteria
WSRC	Westinghouse Savannah River Company
3PB	triphenylborane
2PB	diphenylborinic acid
1PB	phenylboronic acid

ACKNOWLEDGMENTS

The authors wish to thank their colleagues at the Westinghouse Savannah River Company and Savannah River Technology Center for the invaluable assistance they provided in ensuring that the 20-L CSTR Demonstration Program was a success. In addition to participating in the actual tests, the Savannah River Salt Processing Program Team provided excellent guidance relative to design, operation, and chemistry. Some of the many key contributors were as follows (in alphabetical order): Mark Barnes, Seth Campbell, Joe Carter, Hank Elder, Sam Fink, Jim Firth, Rick Fowler, Roy Jacobs, Rocci Norcia (the Control Company), Reid Peterson, Michael Poirier, Ken Rueter, Tony Tipton, and Walter Tamosaitis.

The efforts of the ORNL staff were greatly appreciated. Kim Anderson, Bill Chase, Bob Cummins, Jim Hewitt, Rodney Hunt, Hal Jennings, Tim Kent, Steve Richardson, Paul Taylor, Jim Travis, and Betty Evans, of the Chemical Technology Division, participated in preparing and conducting the tests. Max Cronan, Greg Knox, and other members of the Plant and Equipment Division, as well as Vern McClain, Don Raby, and members of the Instrumentation and Controls Division, did an excellent job in the construction and installation of the experimental equipment in the hot cells. John Keller, Joe Giaquinto, and the technicians at the Radioactive Materials Analysis Laboratory conducted the hundreds of required analyses in a timely manner. John Slaten and the staff of the Office of Radiation Protection provided excellent support through the long days and nights of continuous operations. The authors also appreciate the efforts of Richard Shoun for his guidance on safety-related matters and the ALARA Plan; Bob Jubin and Phil McGinnis for their managerial help and support; Roger Jones for his assistance with the QA plan; and Beulah Brock for her help and patience in handling the large volume of paperwork that this project entailed. Special thanks go to Tim Kent and Roger Spence for their technical reviews of this document.

This study was sponsored by the Tanks Focus Area of the U.S. Department of Energy's Environmental Management (EM-50) Program under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

EXECUTIVE SUMMARY

The goal of the Savannah River Salt Waste Processing Program (SPP) is to evaluate the presently available technologies and select the most effective approach for treatment of high-level waste salt solutions currently stored in underground tanks at the U.S. Department of Energy's Savannah River Site in Aiken, South Carolina. One of the three technologies currently being developed for this application is the Small-Tank Tetraphenylborate Process (STTP). This process uses sodium tetraphenylborate (TPB) to precipitate and remove radioactive cesium from the waste and monosodium titanate (MST) to sorb and remove radioactive strontium and actinides. Oak Ridge National Laboratory is demonstrating this process at the 1:4000 scale using a 20-L-capacity continuous-flow stirred-tank reactor (CSTR) system. Since March 1999, five operating campaigns of the 20-L CSTR have been conducted. The ultimate goal is to verify that this process, under certain extremes of operating conditions, can meet the minimum treatment criteria necessary for processing and disposing of the salt waste at the Savannah River Saltstone Facility. The waste acceptance criteria (WAC) for ^{137}Cs, ^{90}Sr, and total alpha nuclides are <40 nCi/g, <40 nCi/g, and<18 nCi/g, respectively. However, to allow for changes in process conditions, the SPP is seeking a level of treatment that is about 50% of the WAC. The bounding separation goals for ^{137}Cs and ^{90}Sr are to obtain decontamination factors (DFs) of 40,000 (99.998% removal) and 26 (96.15% removal), respectively. (DF is mathematically defined as the concentration of contaminant in the waste feed divided by the concentration of contaminant in the effluent stream.)

Tests 1a and 2 were conducted in June and July 1999; the results are documented in ORNL/TM/1999/234. These initial tests, which were conducted using simulants traced with radioactive materials, verified that the STTP process could achieve the necessary cesium, strontium, and actinide decontamination under standard operating conditions, with and without the recovery and recycle of the unreacted TPB. TPB decomposition, the major side reaction of the process, did not occur in Test 2 despite the addition of materials [SRS synthetic sludge and modified "Enhanced Comprehensive Catalyst" (ECC)] that were known to cause TPB to degrade. However, there was evidence of decomposition of 3PB, 2PB, and 1PB constituents that were added in the salt feed as part of the catalyst system.

Test 3 was a 72-h demonstration that was conducted in August 2000; the detailed test description and results are documented in ORNL/TM-2000/300. The objectives were to examine the effectiveness of an improved antifoam agent (IITB52) in minimizing foam formation and to determine if its presence had a deleterious effect on the removal of ^{137}Cs, ^{85}Sr and uranium from simulated waste. To more aggressively test the antifoam, the slurry in each vessel was mixed at 1200 to 1250 rpm while maintaining the temperature at 25ºC. This rate of mixing was found to cause heavy foam formation in a control test that was conducted prior to Test 3. There was no evidence of significant foam formation in Test 3 as indicated by (1) lack of foam in the analytical samples taken from the vessels, (2) absence of foam in the clear plastic slurry transfer lines between the vessels, (3) lack of changes in the level probe readings in the process vessels, and (4) lack of significant decrease in fluid density measurements in the slurry concentration loop.

Cesium removal performance in Test 3 indicated that IITB52 did not interfere with the TPB-cesium precipitation reaction. Both CSTRs were filled with feed before the TPB flow was initiated. A DF_{Cs} (DFs are referred to the original feed concentration to CSTR 1) of 40,000 was obtained in 14 h in CSTR 1 and afterward ranged between 41,000 and 270,000. About 32 h was required to reach a DF_{Cs} of 40,000 in CSTR 2, and the DF ranged from 49,000 to 77,000 for the remainder of the test. A DF_{Cs} of 37,000 was obtained in the slurry concentration tank (SCT) in about 32 h. It subsequently fluctuated between 21,000 and 59,000 and consistently exceeded 40,000 near the end of the test. In comparing the cesium concentration-versus-time profiles for previous tests where the antifoam was not used, there was no clear evidence that the rate of cesium removal was adversely impacted by the antifoam.

No impact of the IITB52 on the sorption of strontium and uranium by the monosodium titanate (MST) was observed in Test 3. A DF_{Sr} of 26 was needed to reach the WAC standard for saltstone. After

24 h of operation, a DF of 30 was obtained for strontium in the SCT; near the end of the test, the DF climbed to 100. A DF of 5 was obtained for uranium in the SCT at the end of the test — which is indicative of the removal of other actinides (neptunium and plutonium) and meets the WAC standards for saltstone.

At the end of Test 3, the concentrated slurry in the concentrating system was transferred to the slurry washing tank (SWT) and washed with deionized water to recover unutilized TPB. IITB52 was added continuously to the tank during the washing step to provide an effective concentration of 100 mg/L. Calculations indicated that 0.33 mol of excess soluble NaTPB was available in the slurry concentrating system for recovery during water washing. The concentration of NaTPB in the resulting wash water was 0.0033 mol/L (0.095 mol of TPB, total), which was equivalent to 29% of the available TPB. This amount was greater than that recovered in Tests 1a and 2, in which only 12 and 20% of the available TPB were recovered, respectively, and in which no IITB52 was used. This indicates that the antifoam did not interfere with the recovery of the precipitated NaTPB under these test conditions. The higher mixing rate in Test 3 (1200 vs 600 rpm) may have slightly enhanced the recovery of TPB in this case.

Test 4 was conducted in October 2000 with the primary goal of verifying that the STTP process could achieve and maintain the necessary cesium decontamination while TPB was actively decomposing. The detailed description and results for Test 4 are documented in a separate publication (*Test Results for CSTR Test 4*, ORNL/TM-2001/8). As in Test 3, antifoam IITB52 was added to the system vessels to minimize foam formation. The recommended catalyst system (RCS), consisting of Pd(0) on alumina powder, Hg(II) salt, phenylboronic acid (1PB), and benzene, was continuously added during the test. Sample analysis results show that the decomposition reaction was successfully initiated and sustained. The testing verified that the rate of decomposition was sensitive to temperature. The system vessels were controlled at 25ºC during the first 76 h of operation. The temperature was then increased to 45ºC over the next 13 h and maintained at that temperature for the remainder of the test. As expected, the TPB decomposition rate increased at the elevated temperature. At 25ºC, the decomposition/benzene generation rate was about 1.5 mg benzene/(L•h) in CSTR 1 and 3 mg/(L•h) in the SCT, while at 45ºC the rate in CSTR 1 was greater than 5 mg/(L•h) and 3.0 mg/(L•h) in the SCT. The target for benzene generation was 2.5 mg/(L•h), based on the single decomposition reaction of TPB to triphenylborane (3PB). If all of the TPB molecule were decomposed, the rate would be four times higher, or 10 mg/(L•h). At the end of the test, about 4.2% of the total TPB in the first CSTR vessel was being decomposed as indicated by 3PB concentration. This behavior was confirmed by on-line measurement of benzene concentration in the vapor space of each vessel. Despite the high rate of TPB decomposition experienced in this test, the DF for ^{137}Cs obtained for the filtrate from the SCT ranged from 47,000 to 646,000, exceeding the WAC standard.

Overall, the system control and hydraulic behavior for Test 4 were good, and the IITB52 antifoam successfully prevented foam formation in all vessels. More than 162 L of radioactive, simulated waste was treated during the test, and ~218 L of decontaminated filtrate was collected. About 13 L of 10 wt % TPB precipitate/MST slurry was collected and washed to recover the excess TPB (that was not precipitated as potassium and cesium). Only about 10 to 11% of the available TPB was recovered during slurry washing with water. As compared with the results from test 3 slurry washing, the TPB recovery in Test 4 was significantly lower — and lower than Test 2 TPB recoveries under similar agitation conditions. This result contradicts the conclusion from Test 3 and suggests that the use of IITB52 antifoam may interfere with TPB recovery. Both batches of recycle wash water (RWW) were saved for use in Test 5.

The objective of Test 5 was to demonstrate the acceptable performance of the 20-L CSTR system in a fully integrated, closed-loop operation (with TPB recovery and recycle) with TPB actively decomposing under steady-state conditions. The RCS was used to cause TPB degradation by adding (1) the palladium/alumina and inorganic mercury along with the MST slurry to CSTR 1, and (2) the 1PB along with the NaTPB feed to CSTR 1. With the approval of the SPP team, the benzene component of the RCS was not used in Test 5. However, if TPB decomposition had not been initiated early in the test, benzene would have been used. Since benzene was not added to the process vessels, any benzene

detected in the off-gas of these vessels would provide a real-time indication of TPB decomposition. The test plan called for production of three to four batches of slurry and recycle of slurry wash water (with unreacted TPB) to CSTR 1. Recycle wash water from slurry produced in Test 4 was used during the initial startup of Test 5. The slurry wash water from Test 5 was to be used when it became available later in the operation.

Few operational problems were experienced throughout most of the campaign; however, the test had to be terminated 2.5 days prematurely due to the failure of the fluid seals on the progressive-cavity (Moyno) pump in the slurry concentration system. The failure occurred while the third batch of slurry was being processed. No loss of cesium DF in the concentration filtrate occurred during the test. The cesium DF was maintained at >40,000 in the filtrate product. Hydraulic performance occasionally indicated fluid flow problems in the piping between the CSTRs, with the MST/palladium/mercury feed mixture, and with the IITB52 antifoam feed. However, these problems were managed effectively during the test and did not impact the overall quality of the data.

During the test, more than 300 kg (235 L) of radioactive, simulated waste was processed and 320 kg (267 L) of decontaminated filtrate was produced. About 21 L (three batches) of 10 wt % concentrated TPB/MST reaction product was produced, and two of these batches were washed to evaluate TPB recovery. The TPB recovery for the washing tests was poor, with 11% recovered in the first test and 3.0% in the second. TPB concentration in both wash solutions was low as compared with wash solutions from Tests 4 and 2, further confirming that the presence of IITB52 antifoam interferes with TPB recovery.

During production of the first batch of concentrated slurry and the first half of the second batch, the TPB decomposition monitored by the formation of 3PB and the production of benzene in the off-gas of the system vessels indicated slight TPB decomposition in CSTR 1. The low decomposition rate was expected because about 36 h was required to reach a steady-state concentration of the RCS in CSTR 1. While in the later stage of processing the second batch of concentrated slurry and during the processing of the third batch, the TPB decomposition in each CSTR increased and stabilized at a combined benzene rate of about 2.4–2.5 mg/(L·h) (equivalent to ~10 mg/(L·h) benzene for complete TPB decomposition) as measured by both 3PB production and benzene in the off-gas of each vessel. The increase in decomposition activity in the CSTRs for Test 5 could have been related to the changes in RWW composition, the change in antifoam batch source, and/or a prolonged activation period for the catalyst system. The fluctuation in the data and the time relationship of these changes complicated the ability to narrow the cause to a single factor. Decomposition reactions in the SCT system were less stable. During the later stage of processing for the second slurry batch, the 3PB concentration increased rapidly, providing a benzene rate of more than 6 mg/(L·h) just before the batch was finished. When concentration of the third batch was started, the benzene rate was about 2.5–3 mg/(L·h), and it continued to fluctuate at that rate until processing of the third batch was complete. The overall average benzene rate during the last 60 h of the test was about 5 mg benzene/(L·h) (computed for the TPB to 3PB reaction only), with the majority produced in the SCT and CSTR 1. It is likely that the increased decomposition activity in the SCT was due to the increase in the palladium catalyst content, which would have overwhelmed any possible effects from changes in RWW or antifoam.

The operating data for Test 5 indicated that acceptable performance of the 20-L CSTR system could be maintained in closed-loop operation with TPB actively decomposing. However, the data trends for the TPB decomposition products detected in the process vessels did not support the achievement of steady-state conditions in all cases. The concentrations of 3PB in CSTRs 1 and 2 are reasonably consistent in the time frame of 100 to 186 h. However, during generation of the second batch of concentrated TPB/MST slurry in the 70- to 130-h time frame, the 3PB data for the filtrate from the SCT indicated a clearly increasing rate of TPB decomposition, corresponding to a clearly decreasing trend in soluble NaTPB. During the processing of the third batch of slurry (130- to 186-h time frame), the trends in the 3PB and TPB filtrate concentrations were quite different. The 3PB showed a slightly decreasing trend, and the TPB was fairly constant at a slightly higher concentration than was observed while processing the second slurry batch. To establish that steady-state conditions existed, it would have been

necessary to observe consistent 3PB and TPB trends while processing an additional two or three batches of concentrated slurry. Although the system performance was acceptable throughout the operation, it is not possible to predict similar performance in a longer operation without observing consistent TPB decomposition behavior in all vessels. Therefore, it is recommended that an additional 20-L CSTR test be performed in order to verify acceptable performance for a longer-term operation.

The 20-L CSTR performance data from all five tests were compared to determine if additional influences were revealed that were not obvious when evaluating system performance within a particular data set. Comparison of data from Tests 1a and Test 3 indicated that the increased mixing speed used in Test 3 for all process vessels not only enhanced the recovery of TPB in the washing process, but also improved the reaction rate and the DF associated with strontium and uranium removal. In comparing the cesium removal performance for all of the tests, the rate of cesium removal or DF achieved for the process vessels did not appear to be influenced by the presence of antifoam IITB52 or by TPB degradation. Evaluation of the TPB degradation data for Tests 4 and 5 indicated that the targeted decomposition rate was obtained in both tests. The addition of benzene added as a component of the catalyst system and the use of aged Test 3 process fluids in Test 4 appeared to enhance the TPB decomposition reaction while operating at 25ºC. Data from CSTR 2 operations in both tests indicated a reduction in decomposition activity for this vessel, possibly due to poor transport of the palladium/alumina component of the catalyst system to this vessel. The SCT in Test 4 also showed a declining trend in 3PB generation, possibly due either to deactivation of the palladium catalyst (resulting from oxidation at the elevated temperature) or to further decomposition of 3PB to 2P, although boron analytical data suggest that this was not the case. In the SCT for Test 5, a significant amount of additional TPB decomposition occurred, possibly as a result of the increased concentration of the palladium component of the catalyst system.

Comparison of washing data used to evaluate the efficiency of TPB recovery gave further evidence that IITB52 is detrimental to the washing process. This comparison also revealed design limitations that may have limited the ability of the washing system to provide adequate mass transfer conditions for slurry washing and TPB recovery. It is recommended that future testing focus on three aspects of the STTP: (1) longer-term operations to evaluate steady-state behavior in the slurry concentration system; (2) monitoring of 2PB during operations; and (3) evaluation of process improvements for enhancing TPB recovery.

1. INTRODUCTION

1.1 BACKGROUND

The Small-Tank Tetraphenylborate Process (STTP) is one of three separations processes currently being examined by the Savannah River High-Level Waste (HLW) Salt Waste Processing Program (SPP) as an alternative to the In-Tank Precipitation (ITP) process for treatment of Savannah River Site (SRS) highly radioactive tank waste. The STTP was designed with the objective of overcoming the processing limitation of undesirable TPB decomposition and benzene generation by providing rapid throughput and temperature control. In addition, to provide a safety factor, the vapor space above the slurries in the system tanks is made inert (nonflammable) by purging it with nitrogen. The ultimate goal of STTP is to decontaminate the SRS salt waste so that it meets the waste acceptance criteria (WAC) for immobilization processing and disposal at the Savannah River Saltstone Facility. The WAC for ^{137}Cs, ^{90}Sr, and alpha are <40 nCi/g, <40 nCi/g, and <18 nCi/g, respectively. However, to allow for changes in process conditions, the SPP is seeking a level of treatment that is about 50% of the WAC. Supernatants in "High-OH^-" SRS tanks that are 6.4 *M* in Na^+ have cesium concentrations in the range of 0.000415 *M*. Cesium concentrations for average SRS waste with the same Na^+ concentration are in the range of 0.000157 *M*. The radioactivity levels associated with the ^{137}Cs present in these wastes are 1.1 Ci/L and 0.41 Ci/L, respectively. The STTP must obtain a process filtrate that contains less than 35 nCi of ^{137}Cs/g. The SPP treatment process goal is to achieve a DF of 40,000 (99.998% cesium removal) that would treat supernatants with ^{137}Cs concentrations of 2.44 Ci/L. Only a few SRS tanks have concentrations that high.

During the period March–June 1999, a 20-L continuous-flow stirred-tank reactor (CSTR) system was designed and fabricated at ORNL for development of this process. The goal of the 20-L CSTR test program is to evaluate the performance of the 20-L CSTR system under conditions that simulate the anticipated full-scale operation of the STTP. The basic chemistry of the process makes use of tetraphenylborate (TPB) to remove cesium by precipitation and monosodium titanate (MST) to remove strontium and actinides (Pu, Np, and U) by sorption. The CSTR system is operated in a contained and shielded hot-cell environment to allow the use of radioactive materials. Testing of the CSTR system would determine if this approach (1) could provide the necessary cesium, strontium, and actinide separations needed for treatment of the SRS salt waste; (2) could satisfactorily function with an improved antifoam agent; and (3) could perform satisfactorily while active decomposition of TPB was taking place — with and without the recovery and recycle of unreacted TPB.

Tests 1a (Tests 1b and 1c were not needed) and 2 were conducted in FY1999. Test 1a was a single-pass configuration (no recycle of TPB recovered from slurry washing), while Test 2 was conducted using an integrated closed-loop system (including recycle of TPB recovered from slurry washing). Tests 1a and 2 were operated at 25ºC for 61 and 230 h, respectively, and met performance objectives in verifying that the required separations of cesium, strontium, and actinides could be provided by this process, achieving DFs for ^{137}Cs, ^{85}Sr, and ^{235}U (uranium was used as a surrogate for the other actinides) of >40,000, ~100, and ~2, respectively.[1]

Test 3 was a single-pass, 72-h demonstration successfully conducted during August 14–18, 2000. The objectives of the test were to examine the effectiveness of an improved antifoam material in minimizing foam formation and to determine if its presence had a damaging effect on the removal of cesium, strontium, and uranium from simulated waste.[2] The antifoam (trade name IITB52) was developed by the Illinois Institute of Technology and consists of bis(2-ethylhexyl)sulfosuccinate sodium salt—$C_{20}H_{37}O_7SNa$—in ethanol or ethylene glycol. The antifoam was pumped continuously with syringe pumps into each process vessel. There was no evidence of excessive foam formation as indicated by the lack of foam in slurry samples and by the absence of foam-related operational difficulties. Cesium, strontium, and uranium removals were not significantly impacted by the antifoam, and the DFs for

product filtrate (40,000, ~50, and ~5, respectively) were comparable to those obtained in earlier tests and exceeded the WAC standards needed for filtrate disposal in saltstone.

Test 4 was conducted during October 2000 for 125.5 h to demonstrate the ability to initiate and control the rate of TPB decomposition and to verify that acceptable system performance could be maintained while TPB was decomposing, at operating temperatures of both 25ºC and 45ºC.[3] Antifoam, IITB52, was used and the TPB decomposition–recommended catalyst system (RCS), consisting of Pd(0) on alumina powder, Hg(II) salt, phenylboronic acid (1PB), and benzene, was continuously added during the test, successfully initiating and sustaining TPB decomposition. The TPB decomposition goal was to obtain an equivalent benzene generation rate in the slurry concentrating tank (SCT) of about 10 mg/(L•h). This rate is based on the complete decomposition of TPB to four benzene molecules. In terms of the decomposition of TPB to triphenylborane (3PB) and one benzene molecule, the equivalent rate of benzene generation is 2.5 mg/(L•h). From the standpoint of TPB utility, the decomposition to 3PB renders the compound ineffective for cesium removal. The testing also verified that the rate of decomposition was sensitive to temperature. The system vessels were controlled at 25ºC during the first 76 h of operation. The temperature was then increased to 45ºC over the next 13 h and maintained at that level for the remainder of the test. As expected, the TPB decomposition rate increased at the elevated temperature. The measured 3PB concentration at the end of the test indicated that about 4.3% of the original TPB (10 to 11 % of the excess TPB) had decomposed. On-line measurement of the benzene concentration in the vapor space of each vessel confirmed this decomposition. Despite the high rate of TPB decomposition experienced in this test, the DF for ^{137}Cs obtained for the filtrate from the SCT ranged from 47,000 to 646,000, exceeding the WAC standard.

Several evaluations of slurry washing for recovery of unreacted TPB, with and without IITB52, were conducted in the previous four tests. Efforts to remove excess TPB by washing the slurries with water were not very successful. The washing efforts only removed 10–20% of the available excess TPB in Tests 1a and Test 2, in which antifoam IITB52 was not used. In Test 3, IITB52 was used to control foaming and a mixing speed of 1200 to 1400 rpm was used. In this test, about 29% of the available TPB was recovered. IITB52 was also used in Test 4, and the results of wash tests indicated that about 10 to 11% of the available TPB as NaTPB was recovered. The mixing speeds in the slurry washing tank (SWT) for Tests 1a, 2, and 4 were about 600 to 700 rpm. Detailed analysis of the washing data indicates that a higher mixing speed and increased washing time improved TPB recovery, but the recovery rate falls short of the targeted 60%. The data also indicated that the addition of IITB52 inhibits TPB recovery. However, additional research is needed to determine the optimum conditions for slurry washing and TPB recovery.

1.2 SYSTEM DESIGN

The basis for the design of the ORNL CSTR system was derived from a preconceptual design using continuous-flow stirred-tank reactors of 15,000-gal working volume. The apparatus used in the test system was sized and designed to provide reliable data for scale-up to larger systems. Figure 1 shows a simplified process flowsheet for the system. The 1:4000-scale 20-L CSTR test system is located in Hot Cell B, Building 4501, and includes two CSTRs in series, each with a 15.4-L working volume, a slurry concentrating tank (SCT, 8-L working volume) with a cross-flow filter to concentrate the slurry, a slurry washing tank (SWT, 8-L working volume) with a cross-flow filter, and various tanks and pumps to integrate the operation. Two 55-gal feed tanks with mixing systems were located in Hot Cell A. The 15-L CSTRs provide a residence time (actually space time = vessel volume/volumetric flow rate) of 8.15 h. Process fluid passes from CSTR 1 to CSTR 2, and the reaction product from CSTR 2 is concentrated to 10 wt % precipitated solids (principally KTPB, NaTPB, and MST reaction products) in the SCT using the cross-flow filtration system. It takes approximately 60–72 h to accumulate a batch of concentrated precipitate. Four- to five-liter batches of 10 wt % precipitate are then transferred to the SWT and cross-flow filtration system for batch washing. The batch washing requires about 24 h at constant volume. The

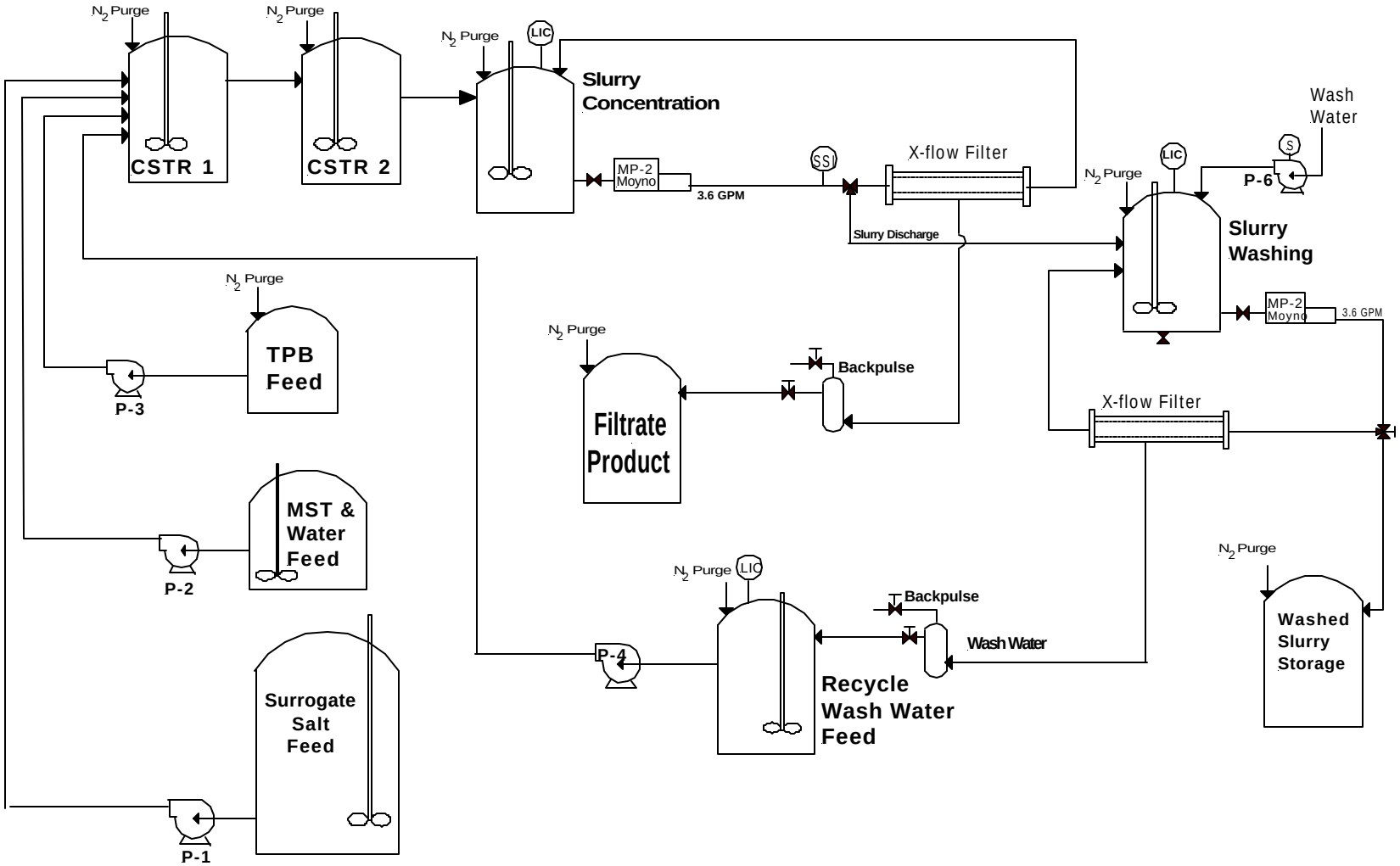

Fig. 1. Simplified flow diagram of the 20-L CSTR system.

filtered wash liquid is transferred to the recycle wash water tank (RWWT) for recycle to CSTR 1, and the washed solids are transferred to the washed slurry storage tank. The cross-flow filter elements are 0.5-µm stainless steel sintered-metal filters that are 24 in. long with a 0.5-in. inside diameter (ID). A progressive-cavity (Moyno) pump is used to circulate the slurry through the filter element and apply the driving pressure for filtration. The backpulse system for each cross-flow filter system is designed to remove accumulated filter cake from the filter surface and restore high filtrate production. The backpulse equipment consists of a filtrate holding vessel with a nitrogen supply capable of applying a 100-psi sustained pressure on the vessel to drive the backpulse system.

Figures 2–7 are drawings that provide the updated flowsheets for the TPB process test system in Hot Cell B. Figures 2, 3, and 4 show the CSTR feed systems, the antifoam feed system, and the slurry concentrate system, respectively. Figure 5 is a diagram of the slurry wash system, and Figs. 6 and 7 are the CSTR benzene monitoring flowsheets. Design changes implemented to prepare the system for Test 5 are highlighted on the drawings. Figure 8 is a photograph of the CSTR, SCT, and SWT configurations in the hot cell. Figure 9 is a photograph of the slurry concentration and slurry wash cross-flow filtration systems. Figure 10 is a photograph of the feed systems for NaTPB, excess TPB, slurry wash water, and MST/catalyst; it also includes some of the electronic control and monitoring system and balances that record the mass of feed materials sent to CSTR 1.

2. PLAN FOR TEST 5

2.1 TEST DESIGN

The primary goal of Test 5 was to catalytically activate the decomposition of NaTPB in the CSTRs and SCT, using the RCS additives, and to demonstrate a sustained cesium DF at flowsheet conditions during steady-state closed-loop operation at 25ºC using the average SRS salt feed shown in Table 1.[4] The RCS components included Pd^0 supported on an alumina carrier, mercury(II) nitrate, and 1PB. With the approval of the SPP team, the benzene component of the RCS was not used in Test 5. However, plans were that if TPB decomposition had not been initiated early in the test, benzene would have been added. Since benzene was not added to the process vessels, any benzene detected in the off-gas of these vessels would provide a real-time indication of TPB decomposition. The foam suppressant (IITB52) was to be added continuously with syringe pumps into each CSTR to provide a concentration of IITB52 of 50 ppmv in each CSTR and 100 ppmv in the SCT and SWT. It was anticipated that the three to four batches of concentrated TPB/MST reaction product slurry would have to be generated to establish steady-state operating conditions for this test.

The first RWW used in Test 5 was collected from water washing the batch of concentrated slurry produced during the 25°C phase of Test 4. It was followed by Test 4 RWW that was obtained from washing the batch of concentrated slurry produced during the phase of testing at 45°C. It was used until RWW from the first batch of concentrated slurry produced in Test 5 became available. Because the NaTPB molarities of the Test 4 RWW batches were too low, NaTPB was added to adjust the concentrations to 0.033 *M* to provide the 60% excess. The supported palladium catalyst and $Hg(NO_3)_2 \cdot H_2O$ of the RCS were added to the MST/water supply feed. This feed mixture provided concentrations of about 7.8 mg/L palladium and 85 mg/L mercury in the CSTR slurries. The other component of the RCS, 1PB, was added to the NaTPB feed solution and provided a concentration of ~500 mg/L. The average SRS salt-feed formulation was used for Test 5. The concentration of ^{137}Cs was set at 9 mCi/L; and the total cesium concentration, including stable cesium, was 0.00156 *M*. Strontium and uranium were not added to the salt feed in this test. The planned feed rates are shown in Table 2.

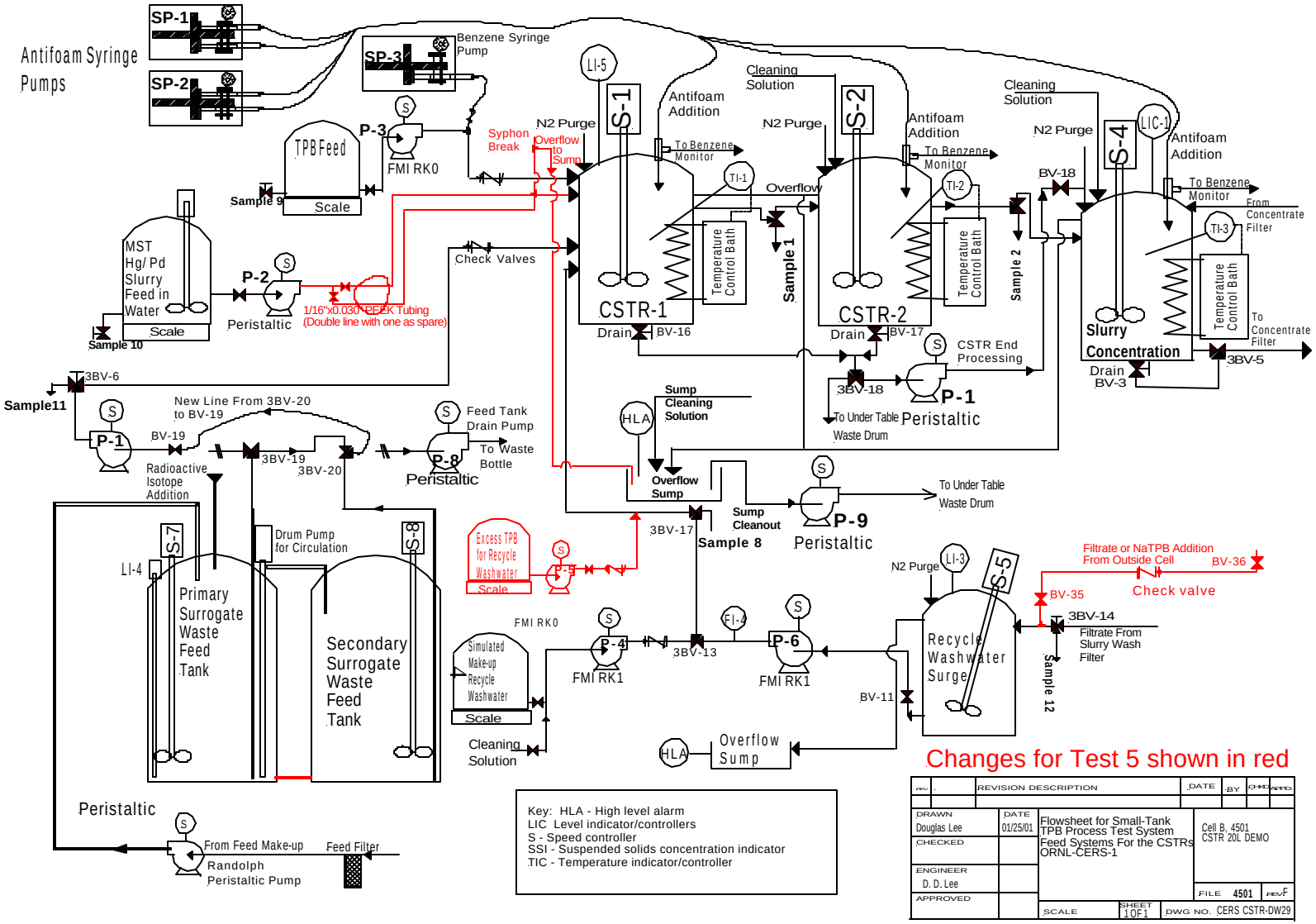

Fig. 2. Diagram showing the CSTR feed systems.

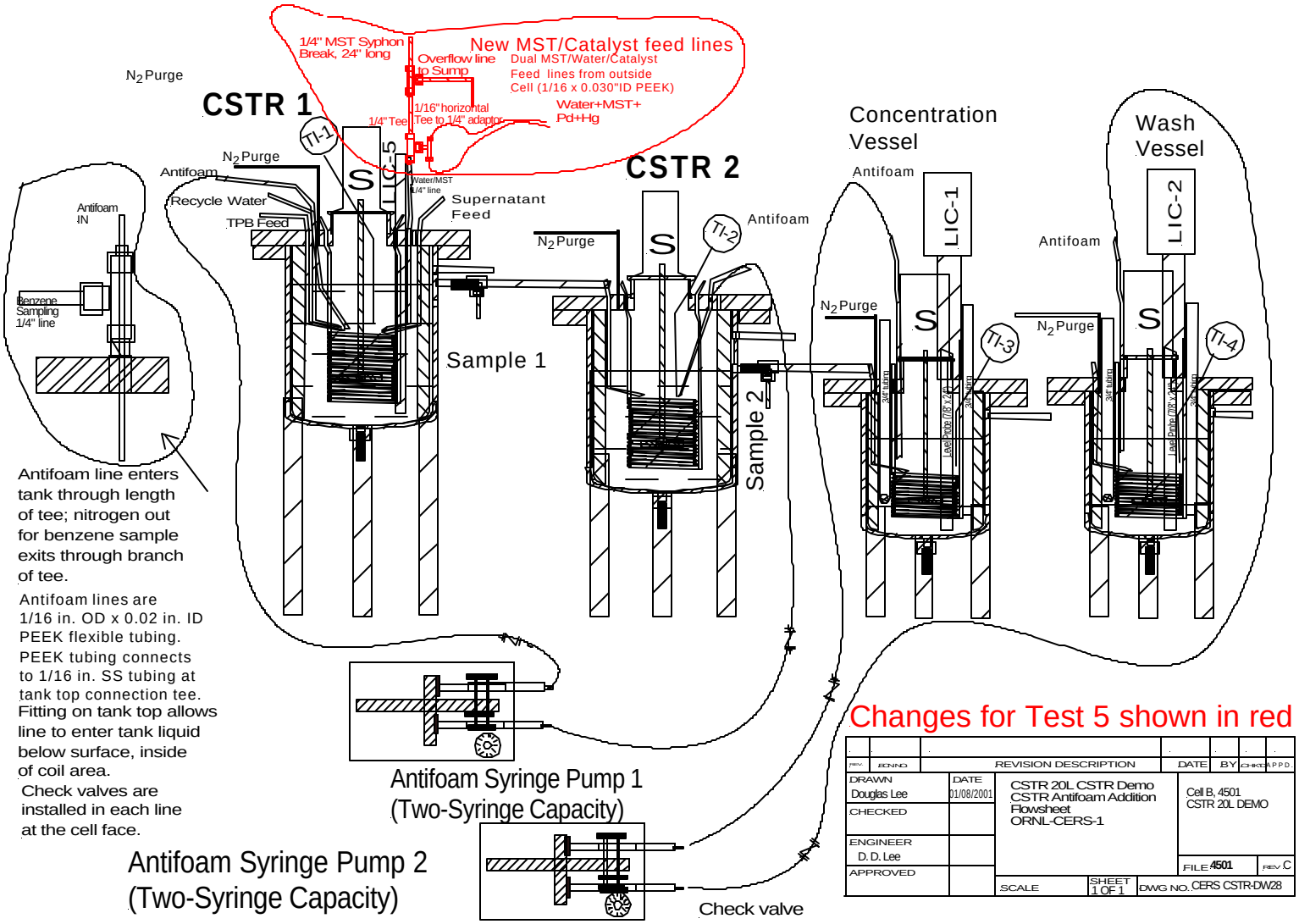

Fig. 3. Diagram showing the CSTR antifoam and MST/catalyst delivery systems.

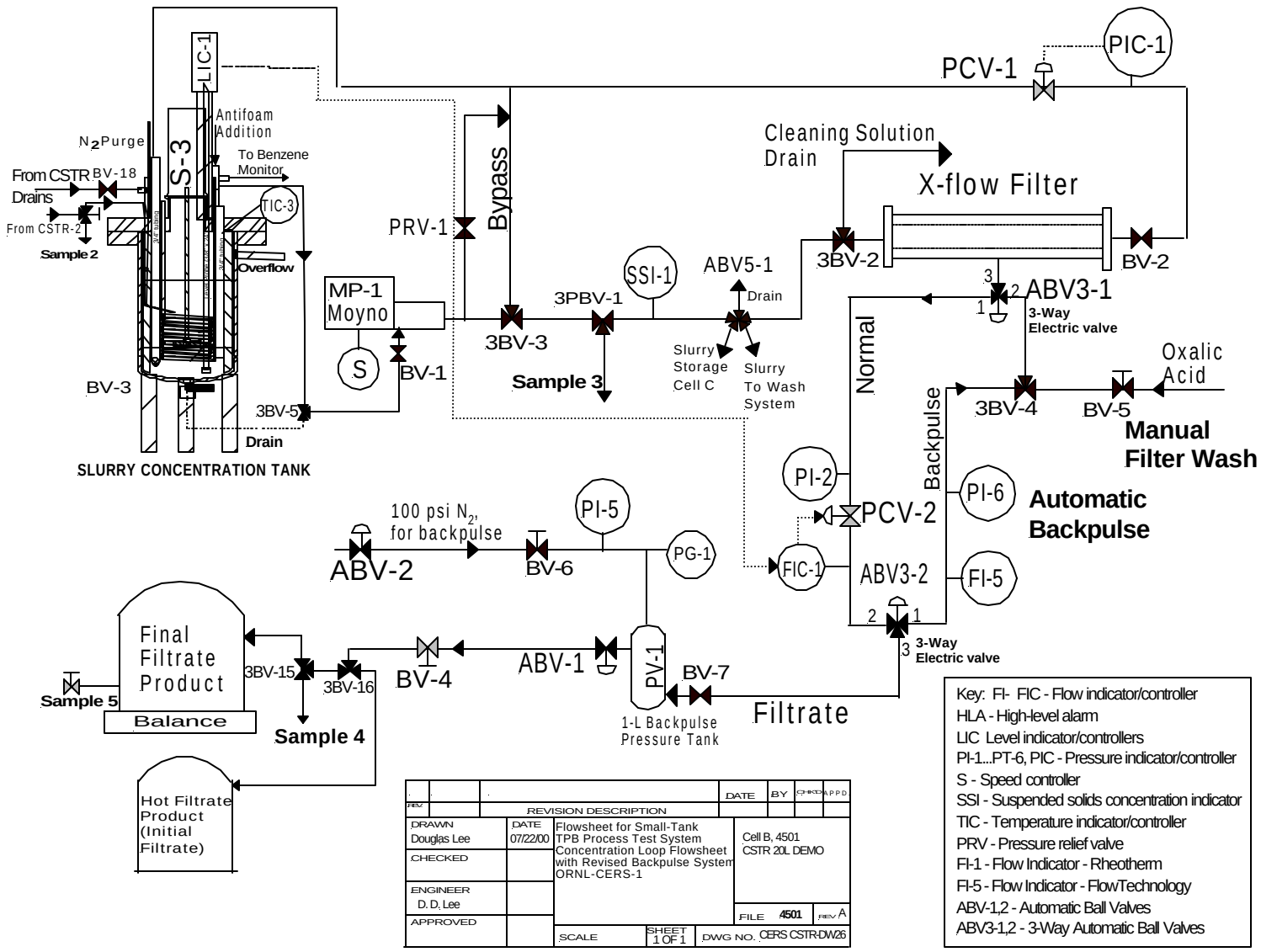

Fig. 4. Redesigned slurry concentrate system.

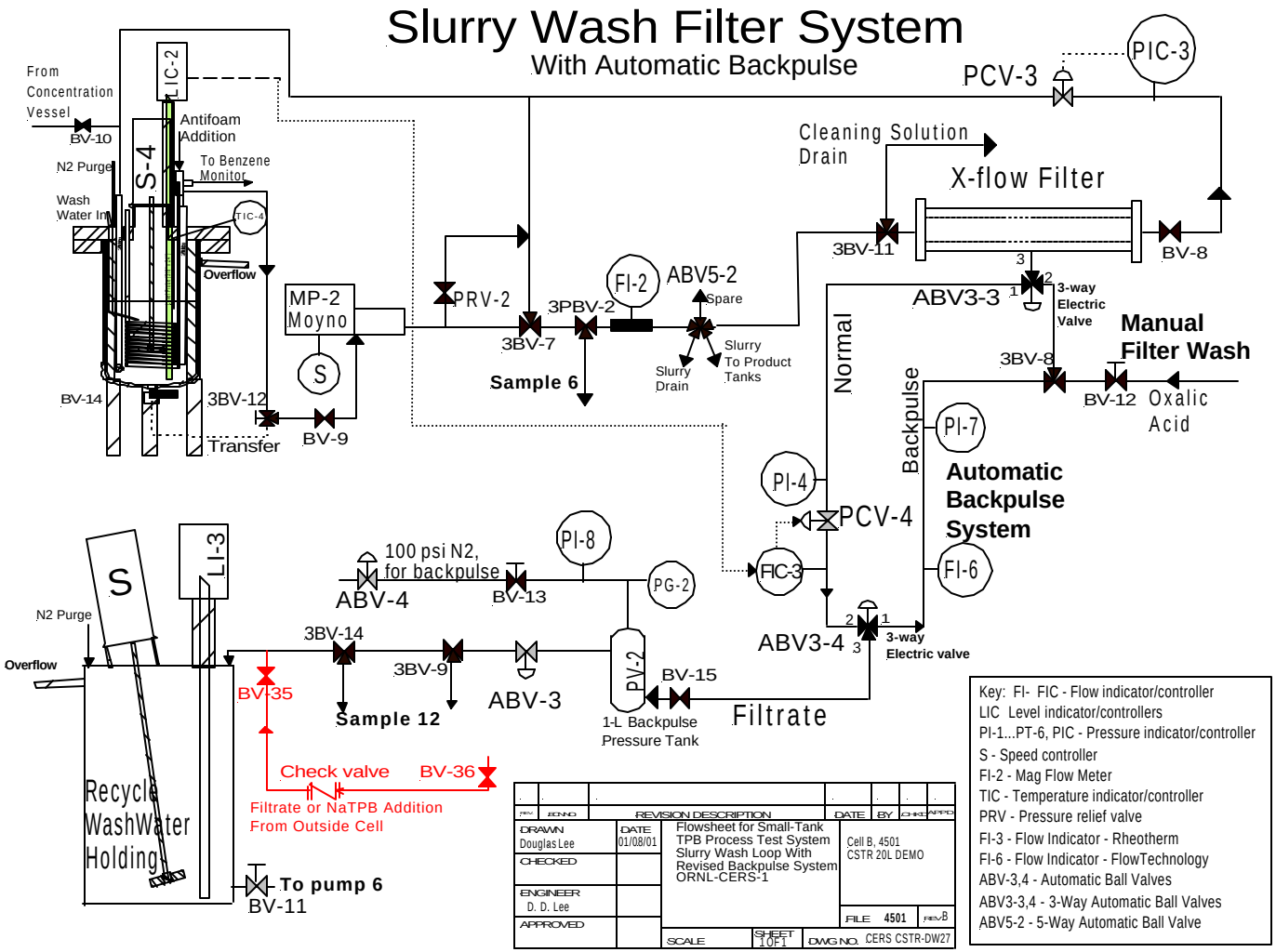

Fig. 5. Redesigned slurry wash filter system.

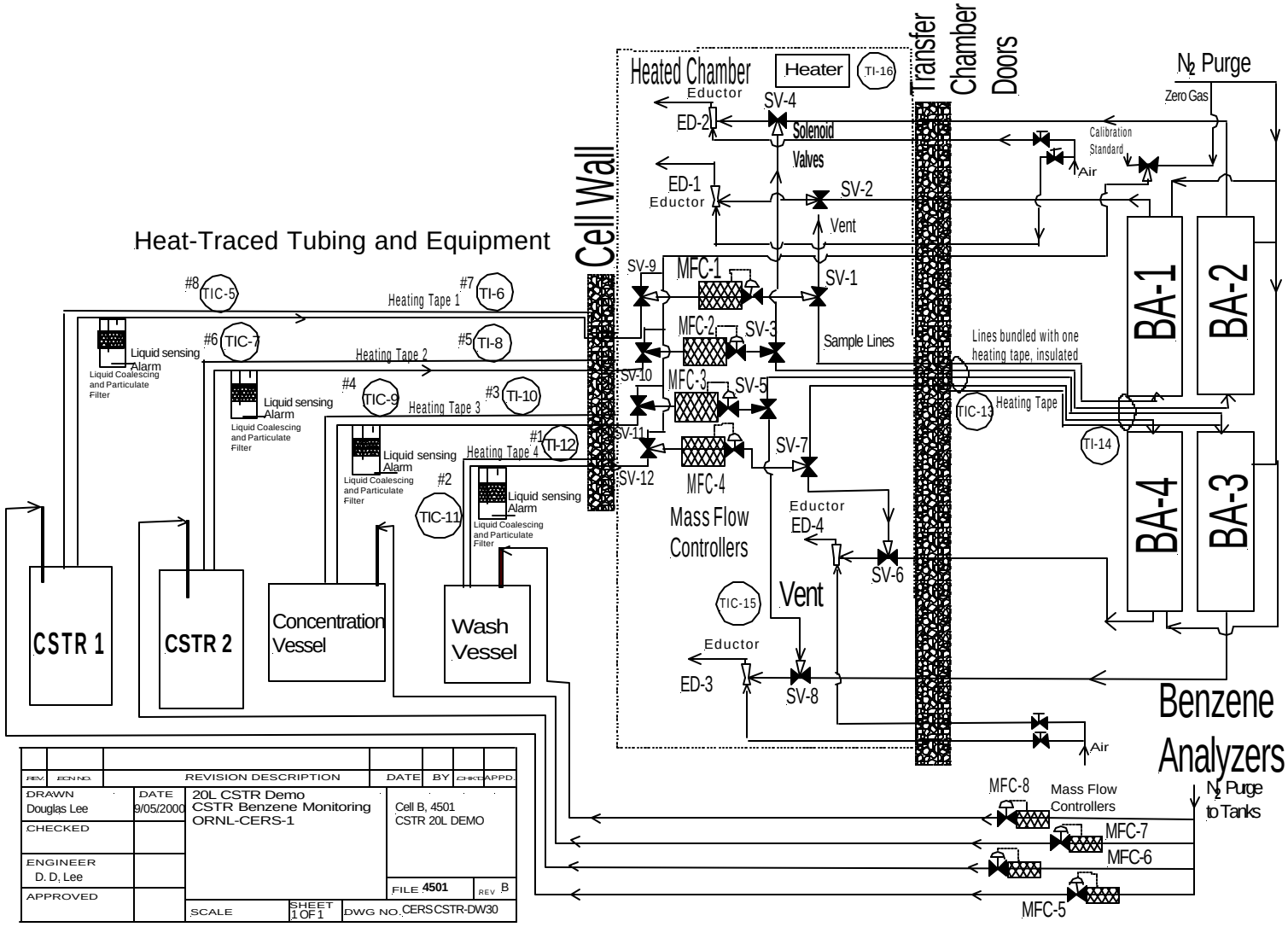

Fig. 6. Flowsheet for the benzene monitoring system.

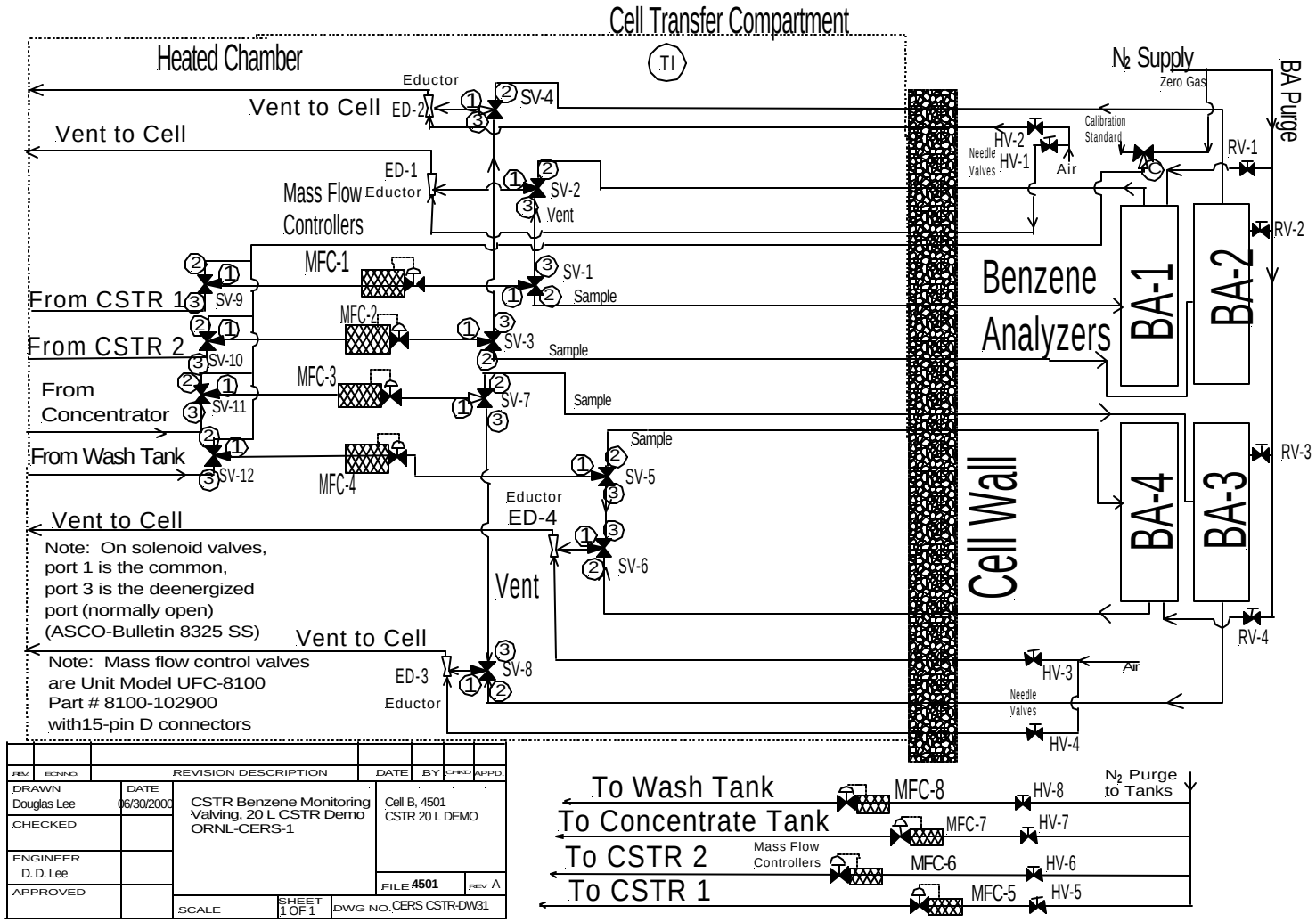

Fig. 7. Valves and piping for the benzene monitoring system.

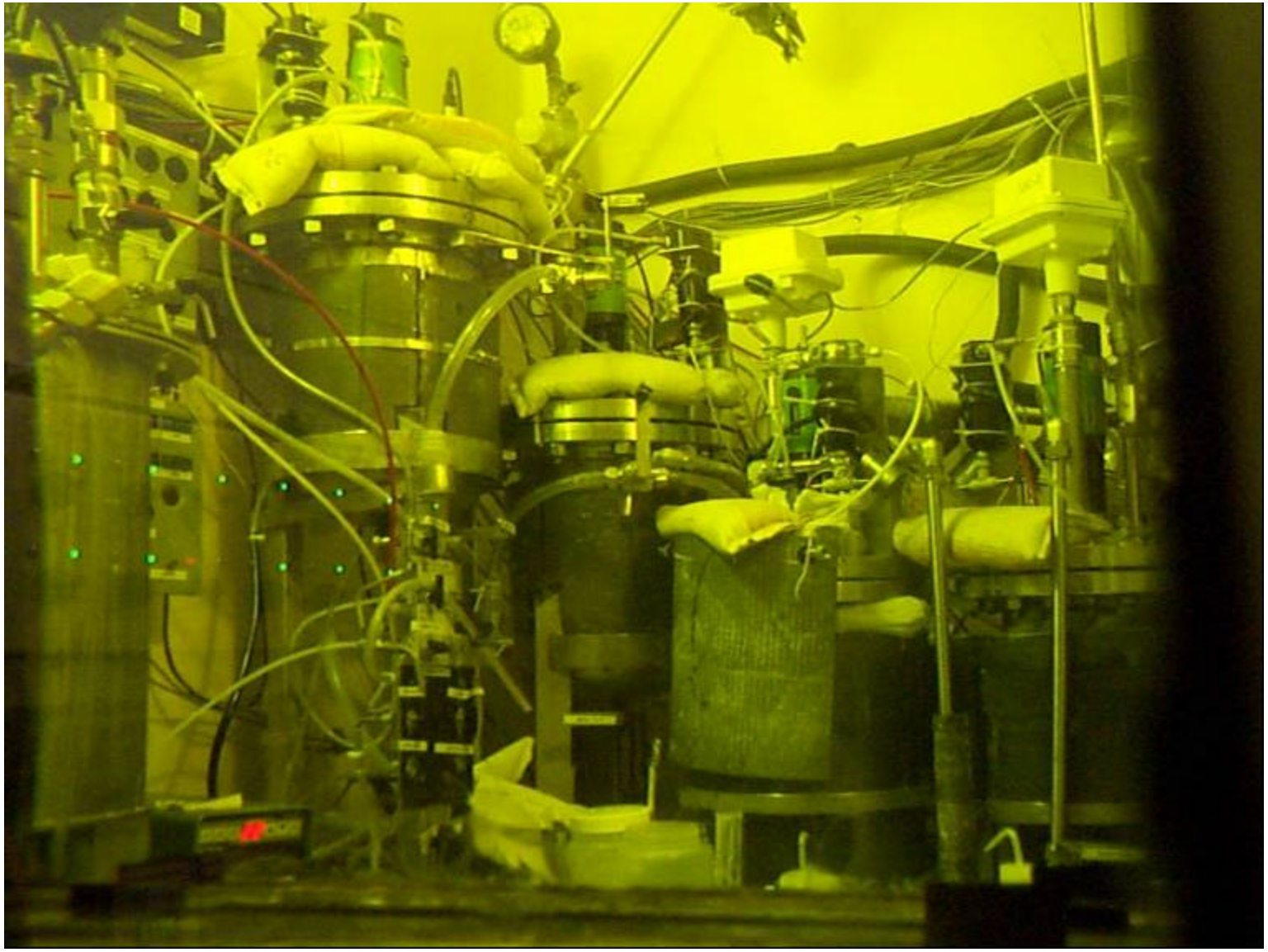

Fig. 8. STTP 20-L CSTR, SCT, and SWT configurations in ORNL hot cell.

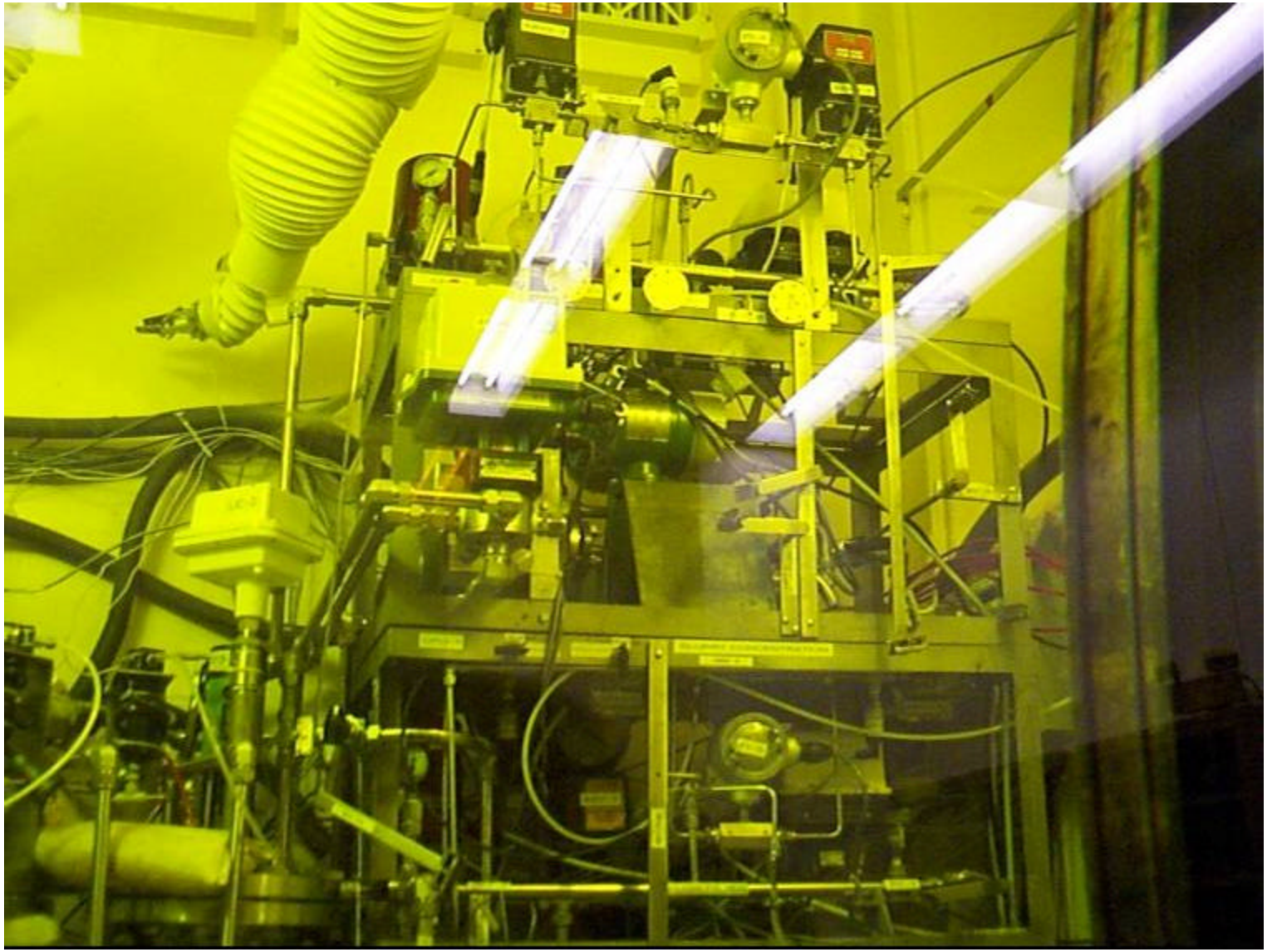

Fig. 9. STTP 20-L slurry concentration and slurry wash cross-flow filtration systems in ORNL hot cell.

Fig. 10. Feed systems for the STTP 20-L CSTR at ORNL.

Table 1. Preparation of average SRS salt feed for Test 5

Chemical species	Planned molarity (mol/L)	Compound	Molecular weight (g/mol)	Planned Concentration (g/L)	Test 5 mass[a,b] (g/382 L)	Test 5 molarity[c] (mol/L)
Cs^{+}[d]	0.00016	CsCl	168.36	0.027	10.3	0.000156
K^{+}	0.0171	KNO_3	101.1	1.729	660.5	0.0167
OH^{-}	3.611	NaOH	40.00	144.46	55,183.7	3.528
NO_3^{-}	1.371[e]	$NaNO_3$	84.99	116.01	44,315.8	2.43[f]
NO_2^{-}	0.594	$NaNO_2$	69.00	40.98	15,654.4	0.580
AlO_2^{-}	0.354	$Al(NO_3)_3 \cdot 9H_2O$	375.14	132.80	50,729.6	0.346
CO_3^{2-}	0.183	$Na_2CO_3 \cdot H_2O$	124.01	22.69	8,667.6	0.177
SO_4^{2-}	0.171	Na_2SO_4	142.04	24.29	9,278.8	0.167
Cl^{-}	0.0286	NaCl	58.4	1.671	638.3	0.0279
F^{-}	0.0366	NaF	41.99	1.537	587.1	0.0356
HPO_4^{2-}	0.0114	$Na_2HPO_4 \cdot 7H_2O$	268.09	3.056	1,167.3	0.0111
$C_2O_4^{2-}$	0.0091	$Na_2C_2O_4$	134.00	1.219	465.7	0.0088
SiO_3^{2-}	0.0046	$Na_2SiO_3 \cdot 9H_2O$	284.2	1.307	499.3	0.0045
MoO_4^{2-}	0.00023	$Na_2MoO_4 \cdot 2H_2O$	241.95	0.056	21.4	0.00022
Na^{+}	6.394					6.28
H_2O				796	304,072	
		Totals		1,287.8	491,952	

[a]Calculated density for preparation = (491,940 g)/(382,000 mL) = 1.288 g/mL.

[b]Assumes 260-h run time at 21.5 mL(salt feed)/min (or 1.29 L(salt feed)/h); also accounts for salt feed added to CSTRs and SCT at the beginning of the test, and 23 L extra in tanks.

[c]About 9 L of solution containing the ^{137}Cs and 12.4 mol each of Na^{+} and NO_3^{-} were added to the salt feed in Hot Cell C, increasing the volume to 391 L of salt feed.

[d]A total of 10.44 g of CsCl (8.25 g cesium) in 70 mL water was mixed well with ~4 Ci of ^{137}Cs tracer (mass of ^{137}Cs was 0.047 g, but total cesium mass in tracer was 0.225 g). The total mass of ^{133}Cs and ^{137}Cs used in Test 5 was 8.47 g, which provided the needed 0.00016 *M* cesium in the salt feed. The estimated ^{137}Cs activity in the salt feed was ~10.26 mCi/L. The RMAL analysis of the salt feed gave 10.27 ± 0.3 mCi/L.

[e]The target molarity for NO_3^{-} is 2.45 mol/L. The addition of $Al(NO_3)_3 \cdot 9H_2O$ and KNO_3 provides 1.062 and 0.017 mol NO_3^{-} /L, respectively. [2.45–(1.062 + 0.017)] = 1.371 mol ($NaNO_3$)/L extra needed].

[f]This is the total NO_3^{-} molar concentration.

2.2 PREPARATION OF FEED FOR TEST 5

Test 5 was scheduled to run about 260 h to provide about 32 CSTR volume turnovers and three to four batches of 10 wt % TPB/MST reaction product slurry. About 350 L of the salt feed was prepared for the test (see Table 1). The ^{137}Cs tracer was supplied from several sources and provided an effective concentration of 10.26 mCi/L. Recycle wash water from Test 4 was used in Test 5 during the first 74 h until wash water became available from Test 5 slurry washing. The concentration of NaTPB in the recycle wash water was amended to 0.033 *M* to provide the needed 60% excess by adding makeup NaTPB to the wash water stream as it was fed to the CSTR. Table 2 provides a list of the feed materials and feed rates that were planned and achieved in Test 5.

A total of 490.22 kg (382 L or 101 gal) of the salt feed, with a density of 1.283 g/mL, was prepared in the two salt feed supply tanks in Hot Cell C. One of the cesium tracer sources for the test was a strip solution from the alkaline-side solvent extraction experiments that were conducted in Hot Cell A (also supported by the SPP). This solution was pumped to Hot Cell C for purification. The purification and

Table 2. Feed materials and feed rates for Test 5

	Feed rates	
	Planned (mL/min)	Actual (mL/min)
Salt feed	21.5	21.50
Recycle wash water	6.86	6.60
NaTPB/1PB	0.68	0.701
Excess NaTPB	0.33	0.348
MST/Pd/Hg/water slurry	2.14	2.25
IITB52 feed to CSTRs	0.00156	0.00129[a]
IITB52 feed to SCT	0.00312	0.00258[a]
Total feed	31.19	31.37

RCS component	Planned (mg/h)	Planned concentration in CSTR fluid (mg/L)	Actual (mg/h)	Actual concentration in CSTR fluid (mg/L)
Mercury	159.0	85	167.	88.7
Palladium	14.6	7.8	15.3	8.1
MST	935.7	500	983.8	523
1PB	935.7	500	954.8	507

[a]Average based on total run time; actual rate based on time feeding IITB52 was 0.00152 mL/min to CSTRs and 0.00303 mL/min to SCT. The IITB52 syringe pumps were off for ~29 h due to plugging of the feed lines, but operation of the CSTR system was continued.

preparation of this source are described in CERS/SR/TPB/005 (Rev. 5).[5] The cesium in this solution was sorbed on zirconium monohydrogen phosphate ion-exchange material that was subsequently washed with deionized water several times to remove any remaining traces of organic contaminant. Afterward, the cesium was eluted with 1 *M* HNO_3 containing $NaNO_3$. The acid in the eluate was neutralized with an equivalent amount of 19.3 *M* NaOH added directly to the eluate. The eluate was then added to the salt feed tanks. The balance of the ^{137}Cs required for the test was provided by adding 75 mL of water containing about 1.2 Ci of ^{137}Cs from a purified $^{137}CsCl$ source material. Addition of the two solutions containing ^{137}Cs increased the total salt feed volume, ~9 L, to ~391 L (103 gal) and added 12.4 mol of Na^+ and NO_3^-. The volume change decreased the Na^+ and NO_3^- concentrations to 6.28 and 2.43 *M*, respectively. The concentrations of all the other chemical species in Table 1 were then 97.7% of the planned molarities. For example, the molarities of K^+, Cs^+, and Al^{3+} decreased to 0.0167, 0.000156, and 0.346, respectively. The calculated new density for the diluted salt feed was 1.278 g/mL. The analytical results for salt feed samples as obtained by the ORNL Radioactive Materials Analytical Laboratory (RMAL) were 6.13 *M* Na^+, 0.331 *M* Al^{3+}, and 0.0194 *M* K^+. The ICP analytical error was ±10%. Based on the masses of NaTPB and 1PB added in the preparation of the NaTPB supply, the NaTPB and 1PB concentrations were 0.5458 *M* (186.8 g/L) and 22.7 g/L. The excess NaTPB supply was prepared so that it would provide a 50% excess of NaTPB to the CSTR system for the feed rate used. (The other 10% of the total 60% excess TPB came from the slurry wash water.) Based on the mass of NaTPB added, its concentration was 0.554 *M* (189.6 g/L). HPLC analyses of these feeds by RMAL gave concentrations that were lower than those based on known masses added. For the NaTPB feed, the measured values for NaTPB and 1PB were 0.478 *M* (163.6 g/L) and 18.2 g/L, respectively. For the excess NaTPB feed, the measured concentration was 0.469 *M* (160.5 g/L). The analytical error for HPLC analyses is ±20%.

3. MEASUREMENTS AND SAMPLING

3.1 SAMPLING PLANS

During the tests, samples were taken for analysis according to the sampling plan given in CERS/SR/TPB/006, Rev.3.[6] After preparation, the salt feed solution was analyzed for potassium and ^{137}Cs. During Test 5, effluent samples were taken for each CSTR (sample ports 1 and 2); a filtrate sample was withdrawn from the SCT filtration system (sample port 4) every 4 h (each sample of 55–65 mL volume, collected over a 2-min duration). Each sample was analyzed using an on-site gamma counter for ^{137}Cs and was also analyzed by RMAL for NaTPB and TPB decomposition products. Every 8-h sample was also analyzed by RMAL for ^{137}Cs, potassium, and boron. The RWW feed samples (sample port 8, downstream from the excess TPB injection point) were taken and analyzed periodically for ^{137}Cs, NaTPB, and 3PB. Wash-water samples (sample port 12) were taken during slurry washing and analyzed for TPB and nitrite.

Samples from sample port 1 (SP-1) and sample port 2 (SP-2) were prepared for analysis by passing the sample through a 0.45-μm filter or a 0.80/0.22-μm double filter and placing the filtrate in new sample bottles for transfer to RMAL. Some of the samples were very difficult to filter with the 0.45-μm filter (which necessitated use of the double filter). The double-filter design facilitated easier and faster filtration of the sample, which reduced personnel radiation dose and the potential for contamination issues. Analytical results for the same sample, filtered using both methods, were comparable. The filtrate samples from the SCT (SP-4), the RWW feed (SP-8), and slurry wash water (SP-12) were sent as collected to RMAL for analysis after a small sample (1–3 mL) had been placed in a counting tube for on-site ^{137}Cs analysis. The on-site gamma counter had an error margin of ±10% and a minimum detectable level of 3×10^{-5} μCi/g for ^{137}Cs. Reverse-phase high-performance liquid chromatography (HPLC) was used by RMAL for analyses of NaTPB, 3PB, diphenylborinic acid (2PB), 1PB, and phenol. The error margin for all TPB and TPB decomposition product analysis was ±20%. Official gamma counting by RMAL was performed using either Canberra or ORTEC GMX closed-end coaxial detectors for ^{137}Cs with an error margin of ±10%. Inductively coupled plasma–atomic emission spectroscopy (ICP-AES) was used by RMAL for potassium and boron analyses with an error margin of ±10%. The potassium and boron samples were digested in nitric acid in a microwave oven prior to analysis. After preparation, all samples destined for RMAL were placed in a refrigerator, until they could be transported. A chain-of-custody procedure from the Sample Management Office was followed for all samples sent to RMAL.

3.2 MEASURING AND TEST EQUIPMENT

Electronic balances, which are calibrated annually by ORNL Plant and Equipment Division personnel, were used for solids and liquid mass measurements in preparing both the simulants and the samples for analysis. Class A volumetric flasks and graduated cylinders were used for simulant preparation. For on-site monitoring of ^{137}Cs during the CSTR tests, a gamma counting system consisting of an ORTEC model GMX-45220-P-S intrinsic germanium detector, an ORTEC model 672 counting system amplifier, a Canberra Accuspec-A MCA card, and Canberra Genie-2000 spectroscopy software were used. A National Institutes of Standards and Testing point source (S4275, 1988) was used for energy calibration and efficiency settings. All spectra are kept as part of the electronic data files for the final project.

All instrumentation used in the CSTR system was calibrated before startup. Calibration records are maintained in registered logbooks (B000510–B000512) and in a controlled project file. A revised list of instruments and corresponding calibration schedules was generated after modifications to the CSTR system had been reviewed and approved by the SPP and Oak Ridge investigators (CERS/SRS/TPB/009).[7]

4. RESULTS OF TEST 5

4.1 RUN SUMMARY

The initial startup of the CSTR system involved first adding simulated salt feed to fill CSTR 1 to 60% of the operating level. At this time the test was initiated by also starting the flow of the RWW, MST/palladium/mercury slurry, and NaTPB/1PB feeds to CSTR 1. This startup approach was used to reduce the time necessary to obtain the desired cesium DF in the concentrate filtrate. The required quantity of NaTPB feed was divided between the NaTPB/1PB feed and the 60% excess NaTPB added to the RWW feed. The IITB52 antifoam was metered to both CSTRs 1 and 2 after each had reached normal operating level. Addition of antifoam to the SCT began once the tank was partially filled with process fluids. After the SCT was filled with slurry, the cross-flow filter system was turned on to start concentrating the slurry from the CSTRs. For the CSTR system to reach steady state, the system needed to be operated continuously over an extended period (i.e., 11 days). After a batch of slurry was concentrated to about 10 wt % solids, which required about 60 h, about 5 L of the concentrated slurry was transferred to the SWT. The slurry in this tank was recirculated through the second cross-flow filter unit while water was added continuously at a rate that would dilute the nitrite present in the slurry to ~0.01 *M*. This operation required about 24 h. The filtrate from the cross-flow filter was then discharged to the RWWT. Afterward, the washed slurry was pumped to the washed slurry storage tank. During operation, the RWW that was initially provided from Test 4 was gradually displaced with Test 5 wash water.

A graph of the cumulative mass with time and a plot of the average flow rates during the test are shown in Figs. 11 and 12, respectively; a summary of the process feed and product volumes is provided in Table 3. In Fig. 11, a number at the end of each line gives the total mass fed for each of the streams at the conclusion of the test. In Fig. 11, the plot for the filtrate stream indicates the two times that slurry was transferred to the wash system by short horizontal lines at 75 and 130 h. Figure 12 shows the cumulative average flow rates for the feed streams. The flow averages were calculated for each 1-h increment during operations. No feed data are shown for the 8 h that the system was shut down to replace the sampling valve and for the 2 h that feeds were turned off to allow evaluation of problems with the Moyno pump used in the slurry concentrating system. The overall feed operation was stable and, with one exception, delivered the planned amounts and concentrations of all feed materials (for the shortened test time). The exception was the initially high rate of feed for the MST/palladium/mercury slurry that was fed at about 18% above the target rate for the first 40 h and then gradually reduced during the next 60 h to the target rate. This may have accounted for the initial unexpected production of benzene in CSTR 1 during the 20- to 40-h time frame.

Figure 13 shows the concentrations of soluble sodium and potassium that would result in CSTR 1 if no TPB precipitation took place. These data illustrate the slight dilution of the initial charge of salt feed delivered to CSTR 1 after the feeds of other materials began. At the start of the test, the potassium concentration was 8.6 % higher than steady state (0.0123 *M* initially as compared with 0.01132 *M* at steady state). This difference reduces the amount of NaTPB that is available to be removed from the concentrated slurry during slurry washing of the first batch of concentrated slurry and can also affect the second batch (see Sect. 4.4). This information was used in the mole analysis necessary to determine the amount of NaTPB available for recovery from the 10 wt % concentrated TPB/MST product slurry (Sect. 4.4).

Few operational problems were experienced throughout most of the campaign; however, the test had to be terminated 2.5 days prematurely due to the failure of the fluid seals on the progressive-cavity (Moyno) pump in the slurry concentration system. This failure occurred while processing the third batch of slurry. There was no loss of cesium DF in the concentration filtrate during the test; cesium decontamination was maintained at a DF of >40,000. Hydraulic behavior occasionally gave fluid-flow problems in the piping connections between the CSTRs, with the MST/palladium/mercury feed mixture, and with the IITB52 antifoam feed. TPB decomposition activity was observed in all vessels, as evidenced

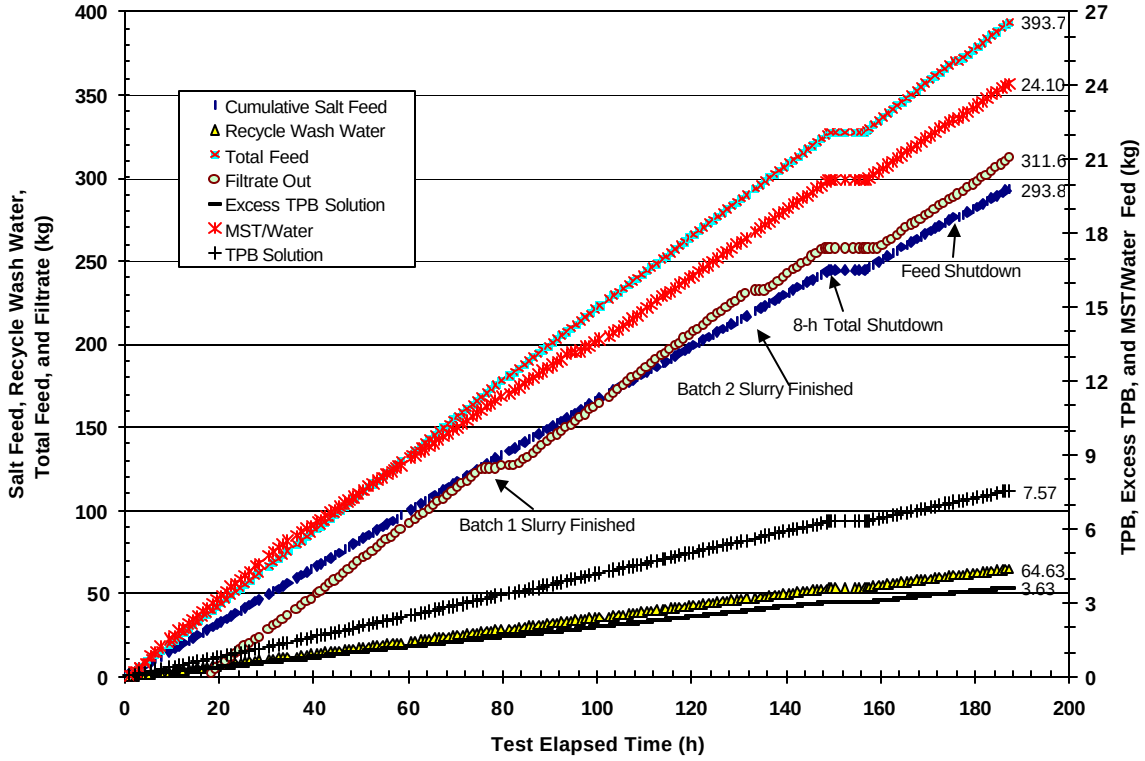

Fig. 11. Material balances for Test 5.

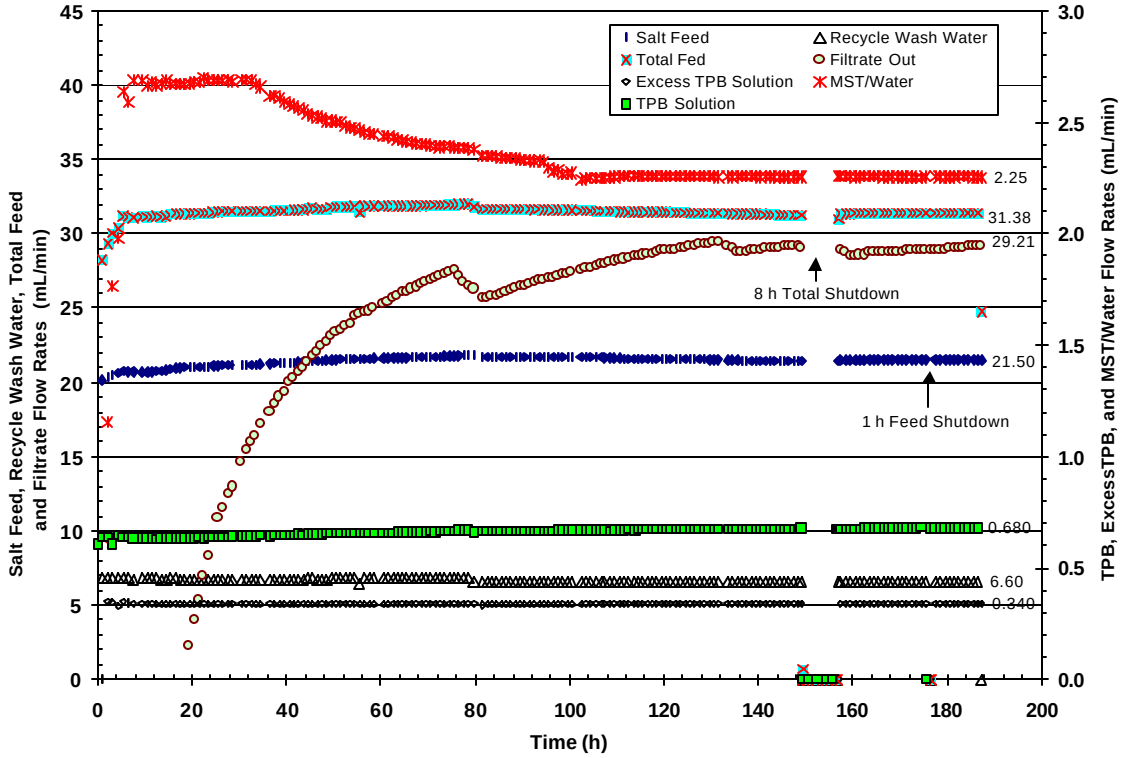

Fig. 12. Average flow rates in Test 5.

Table 3. Process feed and product volumes for Test 5

	Volume		Actual feed rate average (mL/min)
	Planned[a] (L)	Actual[b] (L)	
Salt feed	345.4	232.3 L	21.50
Recycle wash-water feed	106	64.6	6.60
NaTPB feed	15.6	10.77	0.680
Excess NaTPB feed	5.3	3.61	0.340
Water/MST/catalyst feed	33.85	24.1	2.25
Antifoam IITB52	0.111	0.050	0.00469[c]
Total feed	506.15	335.38	31.37
Product filtrate	463	314.4	29.21
Slurry produced	28	21	1.98

[a] Based on 260-h duration.
[b] Actual feeding duration was 177.5 h.
[c] Average for test; average during IITB52 pumping (137.5 h) was 0.00605 mL/min.

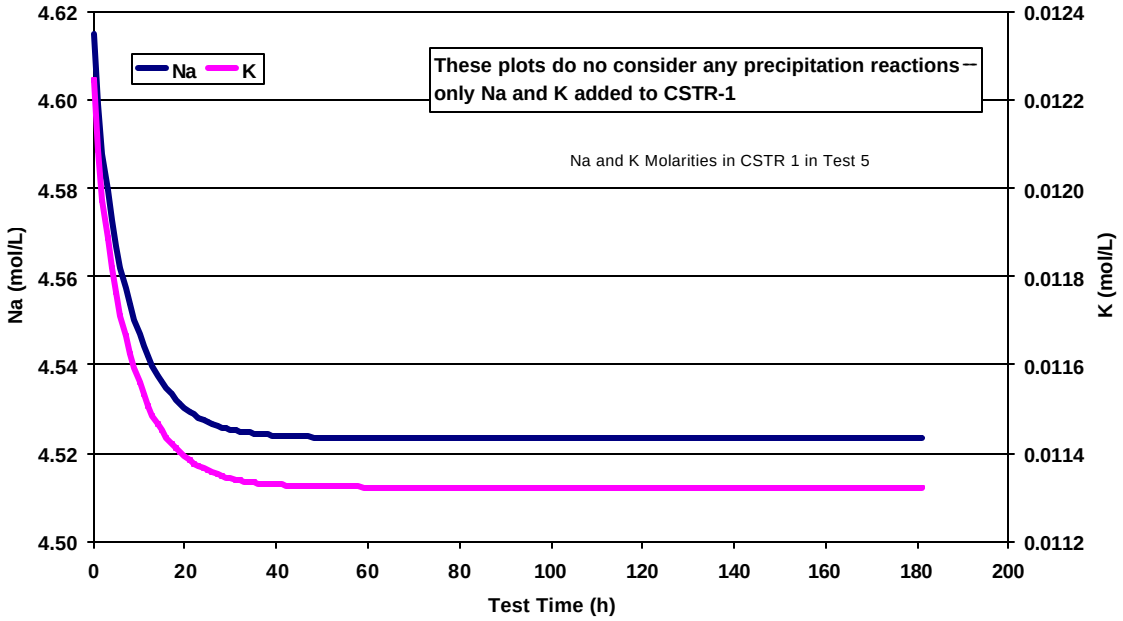

Fig. 13. Sodium and potassium concentration profiles in CSTR 1 if no reactions occur.

by benzene detection in the vessel off-gas and by analyses of TPB decomposition products in the fluid samples. During the test, more than 300 kg (235 L) of radioactive, simulated waste was processed and about 21 L of 10 wt % concentrated TPB/MST reaction product was formed and washed in three batches. In addition, more than 320 kg (267 L) of decontaminated filtrate was generated.

Recycle wash water from slurry produced at 25ºC in Test 4 was used for the first 48 h. In the 48- to 78-h time frame, RWW from slurry produced at 45ºC in Test 4 was used. The RWW from slurry produced in Test 5 was added to the RWWT beginning at 78 h. NaTPB was added to all wash water to provide the required 60% excess (50% in the excess TPB feed and 10% in the RWW feed).

Addition of undiluted IITB52 (Lot ANEAPG) to CSTRs 1 and 2 was started in accordance with the operating plan at about 12.5 h after the test began. At 14.0 h, the addition of IITB52 to the SCT began as planned. At 60.0 h, pumping of IITB52 to the vessels was discontinued because of the feed-line pluggage. After this problem had been discussed with the SPP antifoam development team, the decision was made to attempt to deliver a diluted IITB52 mixture (9 parts water to 1 part IITB52) to the system. At 70.0 h, after lines had been unplugged, pumping of the diluted IITB52 to vessels was started, but ended at 88.0 h when feed-line pluggage again occurred. It was decided after additional discussions with the antifoam team to attempt to deliver IITB52 Lot ANWEM (used in Test 4) to the system. After the feed lines had been cleared at 102.0 h, feed of undiluted IITB52 (ANWEM) was started to all vessels. No further IITB52 plugging problems developed through the end of the test. The pumping problem experienced with IITB52 Lot ANEAPG is undergoing further investigation by the SPP team. Table 4 provides a summary of the antifoam feed problems as related to other significant operating events.

Table 4. Chronology of IITB52 feed problems and other events for Test 5

Event	Elapsed time from start (h)
Started IITB52 (ANEAPG) feed to CSTRs	12
Started IITB52 (ANEAPG) feed to SCT	14
Backpulsed concentrate filter to empty pressure tank	33
Refilled RWWT with Test 4—45ºC wash water	48
Stopped all antifoam feed	59
Tried to feed diluted IITB52 (ANEAPG) antifoam	66
Stopped all antifoam feed	76
Transferred first slurry batch to SWT and started wash	76
Started refilling RWWT with Test 5 wash water	76.5
Started pumping IITB52 (ANWEM) to CSTRs and SCT	98
Transferred second slurry batch to SWT and started wash	132
Started refilling RWWT with second batch of wash water	133
Conducted 8-h shutdown to replace sample valve on CSTR 2	149
Stopped test because of slurry leakage from SCT Moyno pump seal	187.5

4.2 CESIUM DECONTAMINATION AND SYSTEM CHEMISTRY IN TEST 5

4.2.1 Cesium Removal

During Test 5, cesium decontamination of the salt feed met the requirements for saltstone. After 15 h, the DFs for filtered samples from the CSTR 1 slurry overflow to CSTR 2 ranged from 17,000 to 1,000,000, with most of the values >25,000. After 27 h, the DFs for filtered samples from the CSTR 2 slurry overflow to the SCT ranged from 27,000 to 148,000, with most values being >35,000. After 31 h of operation, the ^{137}Cs DFs (as measured by ORNL RMAL) for the filtrates from the SCT were greater than 31,000 and ranged between 46,000 and 682,000 for the remainder of the test, easily exceeding the DF goal of 40,000 (99.998% removal). The ^{137}Cs DF results for all the vessels are plotted in Fig. 14 (on-site counting). Figure 15 shows the counting results submitted by RMAL and indicates that the filtrate DF remained greater than 40,000 for the last 140 h of the test. The sample-analysis results for individual process vessels, comparing the on-site and RMAL data, are shown in Figs. 16–18. These data clearly show that the DFs for each vessel were fairly stable and maintained at the overall process DF requirement, while the TPB was actively decomposing. Each figure shows close agreement between the on-site counting used for process control and the analytical results supplied by RMAL. The agreement is

not as good at very low concentrations (near the background), where the RMAL counting system superior performs because it uses a detector with superior geometry for low-level samples.

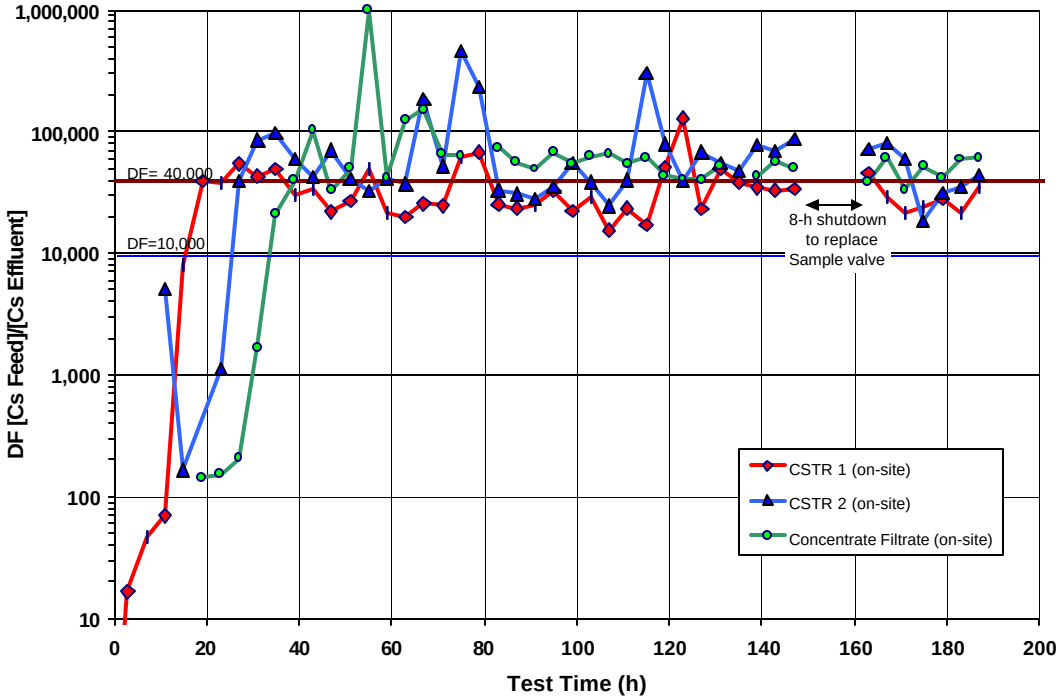

Fig. 14. On-site cesium DF results.

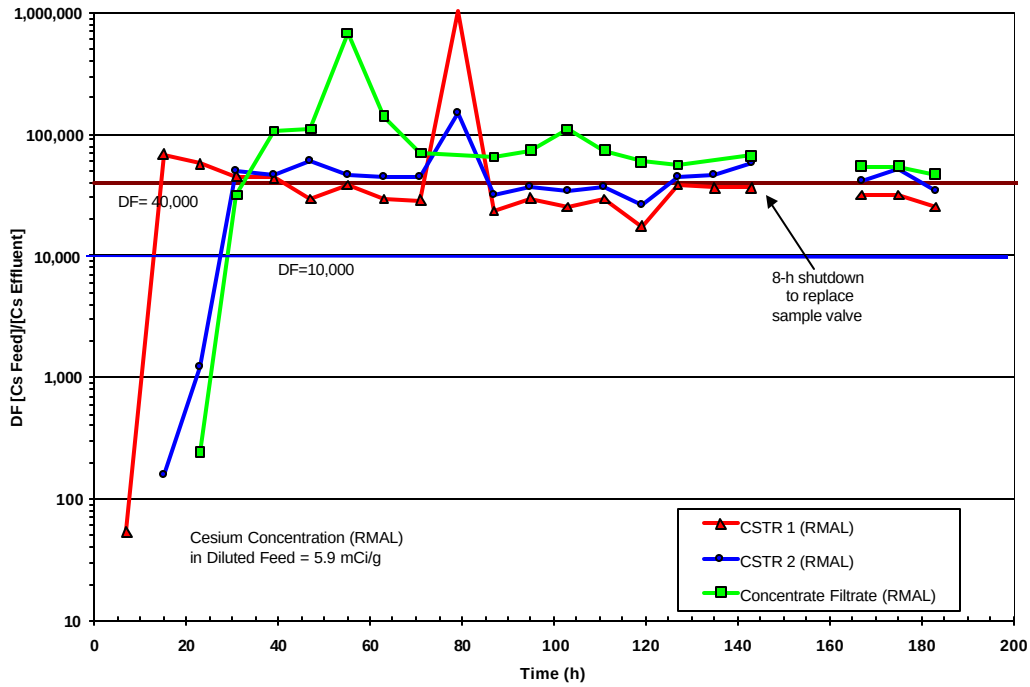

Fig. 15. Cesium DF results for samples analyzed by RMAL.

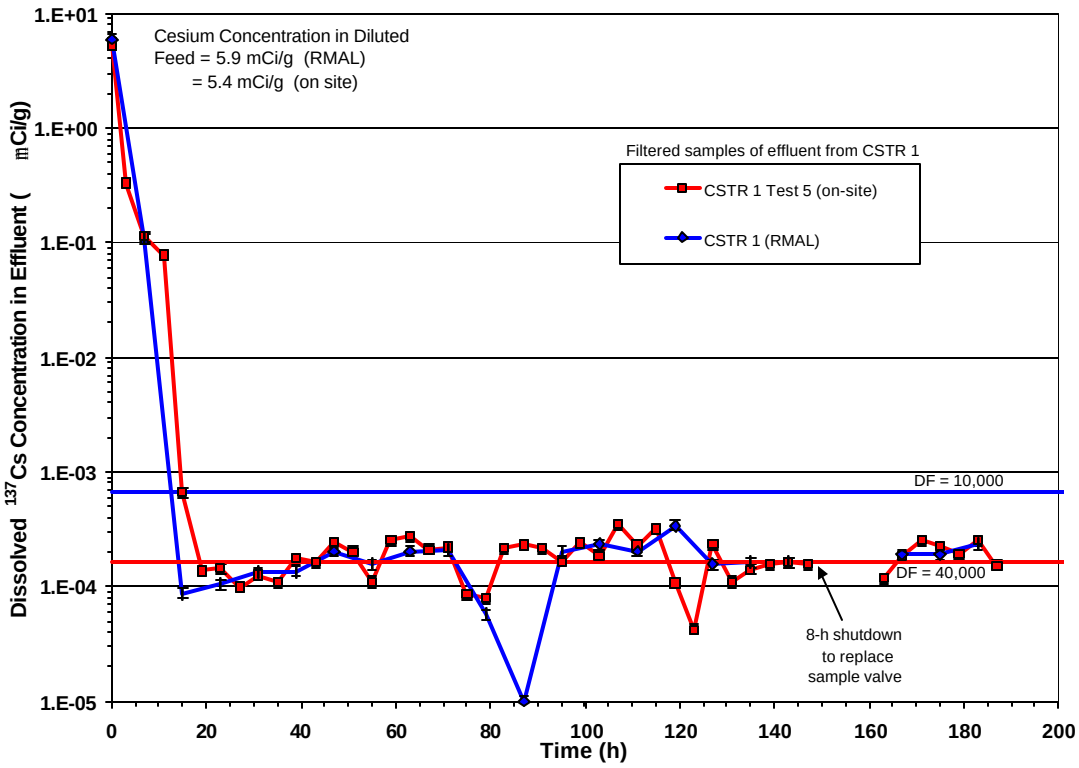

Fig. 16. Cesium removal results for CSTR 1 in Test 5: comparison of sample -analysis results for on-site and RMAL instruments.

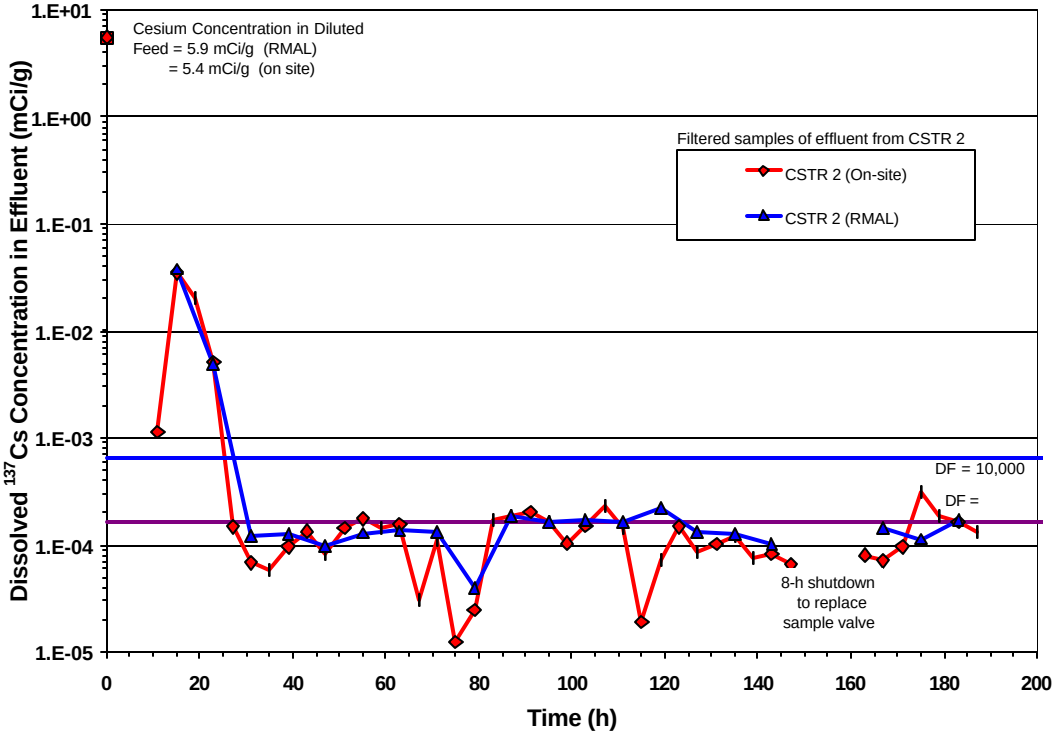

Fig. 17. Cesium removal results for CSTR 2 in Test 5: comparison of sample -analysis results for on-site and RMAL instruments.

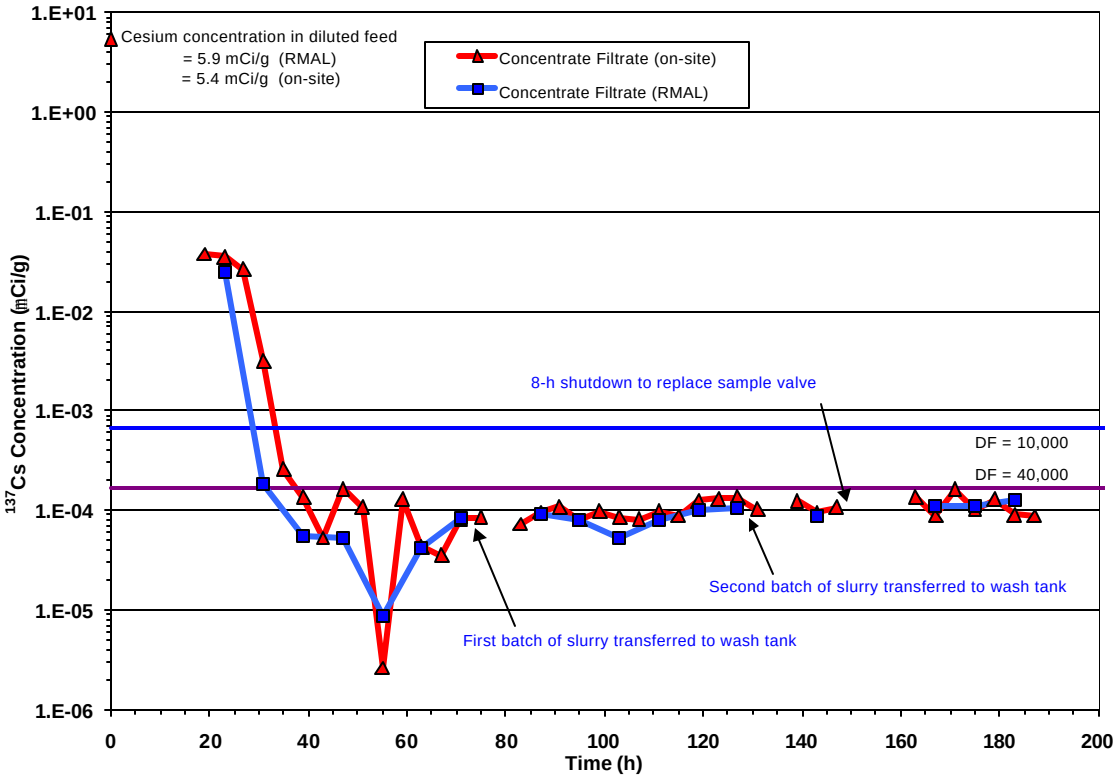

Fig. 18. cesium removal results for the SCT filtrate in Test 5: comparison of sample-analysis results for on-site and RMAL instruments.

4.2.2 Analysis of Recycle Wash-Water Feed

Samples of the recycle wash water that was fed to the CSTR were taken downstream from the location where NaTPB was added to the stream, before it entered the CSTR. The samples were analyzed for TPB and the 3PB decomposition product to verify that the correct quantity of excess TPB was being added to CSTR 1 and to determine the quantity of 3PB that was being recycled to the feed. The 3PB decomposition product is important in the determination of the TPB decomposition rate; thus, knowledge of the amount coming in with the wash water was essential in calculation of the CSTR 1 TPB decomposition rate. The results are shown in Table 5. The table indicates the actual percent excess NaTPB that was delivered to CSTR 1 and confirms that the NaTPB was delivered consistently at or slightly above the required 60% during most of the test. In addition, a significant quantity of 3PB was recycled with the wash water to CSTR 1. The ratio of wash water to total feed was about 6.8:31.5, or 0.215. This increased the concentration of 3PB in CSTR 1 by amounts ranging from 5.6 mg/L at the beginning of the test to 23.7 mg/L at the end of the test. These values of 3PB were subtracted from the total concentration of 3PB in CSTR 1 to accurately calculate the amount of benzene produced in CSTR 1 from TPB decomposition. Sample 19T5SP8-04 of the RWW feed produced from Test 4, 25ºC slurry wash, was analyzed for all phenylborates and reaction products. In addition to NaTPB and 3PB, it was found to contain 72 mg/L 1PB and 30 mg/L phenol. The presence of phenol indicated that the phenylborates in the wash water had undergone some additional decomposition while being held in the RWWT for the 15 weeks between Test 4 and Test 5. By calculation, this added about 6.5 mg/L phenol to CSTR 1; however, the total phenol concentration in CSTR 1 was always below the detection limit of 20 mg/L.

Table 5. Analysis of recycle wash water

Sample time (h)	RWW sample ID (washing at 15 mL/min)	NaTPB (mg/L)	3PB (mg/L)	Calculated contribution of RWW to 3PB in CSTR 1[a] (mg/L)	Excess TPB delivered to CSTR 1 (%)
19[b]	19T5SP8-04	10,400	26.2	5.6	65.5
27	27T5SP8-04F	11,100	50.1	10.8	69.9
55[c]	55T5SP8-07	10,400	79.7	17.2	65.5
59	59T5SP8-08	10,200	93.1	20.1	64.23
75	75T5SP8-10	9,580	85.9	18.6	60.33
83[d]	83T5SP8-11	9,810	99.4	21.5	61.78
91	91T5SP8-12	11,300	58.3	12.6	71.16
99	99T5SP8-13	10,400	84.4	18.3	65.5
107	107T5SP8-14	9,830	80.3	17.4	61.90
115	115T5SP8-15	10,300	89.2	19.3	64.86
123	123T5SP8-16	9,920	74.6	16.3	62.47
131	131T5SP8-17	9,930	80.3	17.4	62.53
139[e]	139T5SP8-18	9,500	93.3	20.2	59.82
147	147T5SP8-19	9,190	87.4	18.9	57.87
163	163T5SP8-20	9,560	84.6	18.3	60.20
171	171T5SP8-21	9,530	99.8	21.6	60.01
179	179T5SP8-22	10,100	81.3	17.6	63.60
187	187T5SP8-23	9,600	110.0	24.2	60.45

[a]Calculated on the basis of the ratio of RWW feed to total feed (6.8 mL/min ÷ 31.5 mL/min).
[b]Started Test 5 with wash water from Test 4 wash of 25ºC slurry.
[c]Refilled wash-water tank with wash water from Test 4 wash of 45ºC slurry at 47.5 h.
[d]Started refilling wash water tank with wash water from washing first Test 5 slurry batch at 77 h.
[e]Started refilling wash water tank with wash water from washing second Test 5 slurry batch at 134 h.

4.2.3 TPB Decomposition Data

Figures 19–23 summarize the results of the HPLC analyses performed by RMAL for filtered samples from the two CSTR overflows and the SCT filtrate. The concentrations of NaTPB, 3PB, 2PB, 1PB, and phenol were measured. Figure 19 shows the results of the analyses of CSTR 1 samples and includes the off-gas benzene concentration as measured by on-line FTIR. Figure 19 also includes a plot of the calculated 3PB concentration in the RWW fed to CSTR 1. At 48 h, the wash water from the second Test 4 slurry batch was added to the RWWT, slightly increasing the amount of 3PB being recycled. When the first batch of Test 5 slurry was being washed at 77 h, the 3PB level in the RWW rose to about 90 mg/L, increasing the 3PB concentration in CSTR 1 by about 20 mg/L. Figure 20 shows the 1PB that was intentionally fed to the CSTR 1 as part of the catalyst system. The trends for both CSTRs and the SCT show no increase in 1PB concentration above the amount fed to CSTR 1, indicating little or no decomposition of 2PB to 1PB in the process. This was expected because the RCS components do not decompose 2PB or 1PB. Figure 21 shows the potassium and soluble NaTPB concentrations in CSTRs 1 and 2; as observed, the soluble NaTPB was below the detection limit until the potassium concentration was reduced to less than about 100 ppm. The data for the CSTR 1 samples clearly indicate that TPB decomposition was in progress. The 3PB concentration began to increase in the CSTR filtrate at 75 h and exhibited a consistent trend, averaging about 60 mg/L in the 120- to 186-h time frame. If all the 3PB were generated in the decomposition of TPB, the equivalent benzene production rate would be about

2.4 mg/(L·h). The NaTPB concentration in CSTR 1 was too erratic to indicate a trend; however, it averaged 101 mg/L during the test.

The benzene concentration in the CSTR 1 off-gas was low at the beginning of the test but showed a significant increase at 40 h and remained above 70 ppm (parts per million, by volume) for the remainder of the test. The benzene concentration did not follow the 3PB concentration during the first half of the test but closely paralleled it during the last half. The relatively sudden increase in benzene concentration is consistent with observations in Test 4. It is speculated that a significant quantity of benzene can be retained by the TPB slurry; however, once the slurry is saturated, the benzene is released at a rate that is dependent on the rate of TPB decomposition. The benzene retention behavior of TPB slurry was also sensitive to temperature because the vapor pressure of benzene doubled, going from 99.7 to 200 mm Hg, when the temperature was increased from 25 to 42.2ºC. A few samples showed levels of 2PB near the start of the test. After the second batch of Test 4 wash water had been started, however, HPLC determination of the 2PB was impossible due to overlapping and masking 1PB peaks.

Figure 22 shows similar results for NaTPB 3PB, 2PB, and benzene in the off-gas in CSTR 2. In CSTR 2, the soluble NaTPB remained below the detection limit until the potassium concentration was reduced and then the potassium increased to 120 mg/L at about 40 h. As in the case of CSTR 1, the TPB data for CSTR 2 are widely scattered, but the range of concentrations is slightly lower than that for CSTR 1, averaging 85 mg/L, due to the precipitation and decomposition reactions taking place. Under the conditions in the CSTRs (4.7 *M* sodium at 25ºC), the solubility of NaTPB is about 175–450 mg/L (at 45ºC it is about 225–600 mg/L).[8–10] The soluble TPB concentration was never low enough to lose the cesium DF (the ITP process in SRS Tank 48H did not lose cesium DF at a soluble TPB concentration estimated at 7.4 mg/L). The 3PB concentrations and trend in CSTR 2 were very similar to those in CSTR 1. In the last 60 h of the test, the 3PB concentration was generally higher in CSTR 2 by about 10–20 mg/L. The 2PB concentration was also similar to that in CSTR 1 and could only be detected for about the first 50 h. The benzene in the CSTR 2 off-gas was constant at a low concentration of about 35 ppm until about 100 h, when it began to increase and averaged about 140 ppm over the last 60 h of the test. The overall increases in 3PB and benzene concentrations for CSTR 2 are indicative of the ongoing decomposition of TPB at an average rate of about 0.5 mg/(L·h) at the end of the test.

The TPB, 3PB, and 2PB analytical results for the SCT filtrate, along with the benzene monitoring results, are shown in Fig. 23. Again, the 2PB could not be detected after about 40 h, but some samples showed 2PB between 120 and 130 h and again at the end of the test. Unlike CSTRs 1 and 2, the TPB profile was less erratic and exhibited some well-defined trends. The soluble TPB began at a low concentration, as in CSTR 2, and then increased to a range of 130 to 160 mg/L until processing of the first batch of 10 wt % slurry was complete. This increase may have been the consequence of the increasing concentration of mixed TPB solids, including NaTPB, by the filtration system. Some NaTPB precipitate would be expected to dissolve if the associated liquid were not saturated. In addition, the circulation rate for the slurry concentrate was about 13 L/min, or about two tank turnovers each minute, allowing much better contact between precipitated NaTPB and the liquid. While the second batch of slurry was being processed, the TPB concentration indicated a clearly decreasing trend from about 150 to 90 mg/L. This trend corresponds with an increasing trend in 3PB concentration, indicating increased decomposition of soluble TPB. The TPB and 3PB processing during the third slurry batch did not exhibit the same trends as were observed for the second slurry batch. While the third batch of slurry was being processed, the TPB maintained a concentration in the 130- to 140-mg/L range for over 40 h;, then the last data point showed a decrease to 100 mg/L. The corresponding 3PB data showed a slightly decreasing trend from about 115 mg/L to 90 mg/L. Off-gas benzene concentrations for the second and third batches were also very different. This anomalous behavior may have been the result of mechanical and hydraulic difficulties during the processing of the third slurry batch. Regardless of the cause, the trends in TPB and decomposition product behavior were not similar, or even comparable, for the three batches of slurry. To establish that steady-state conditions existed, consistent trends in 3PB and TPB concentrations would

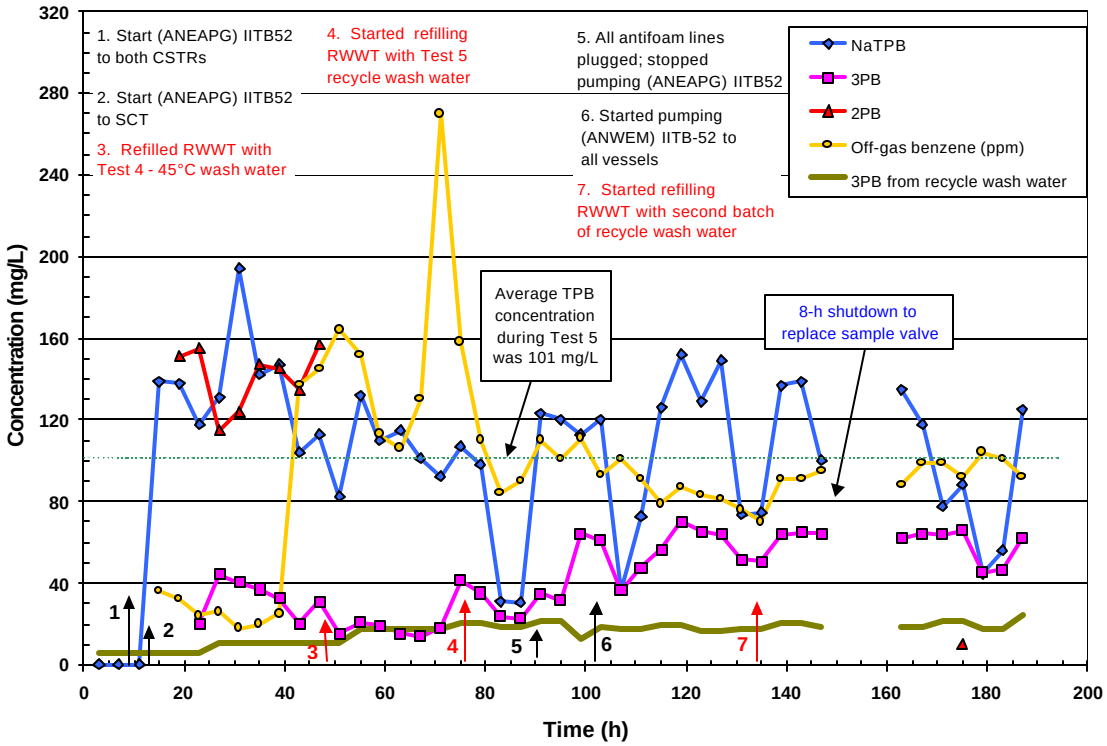

Fig. 19. HPLC results for CSTR 1 in Test 5.

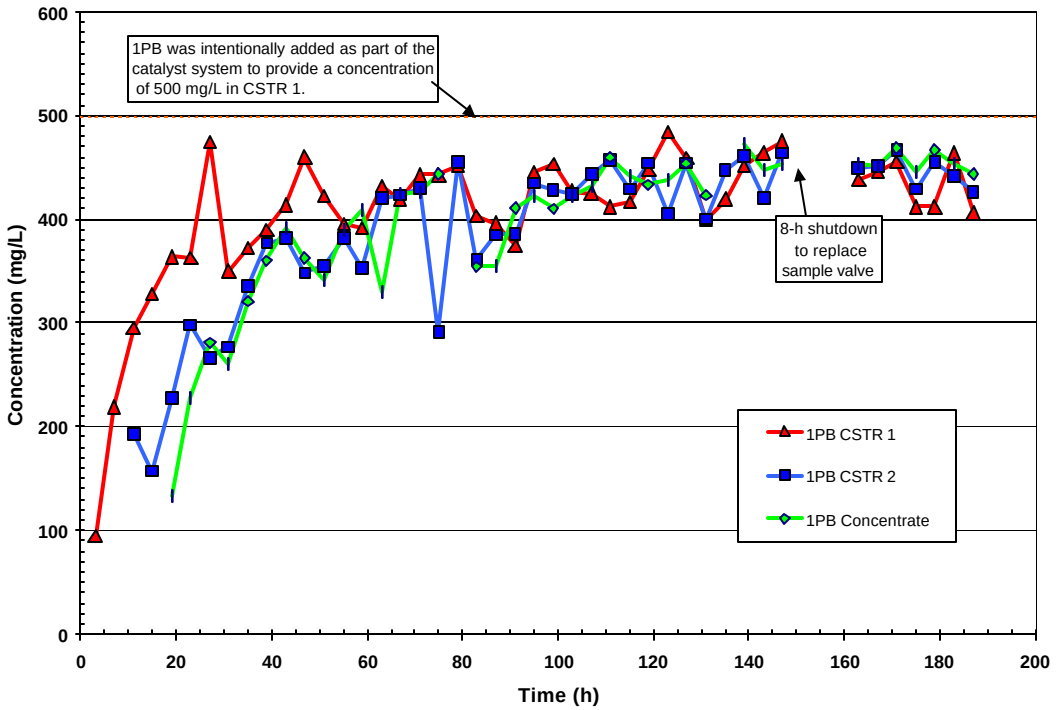

Fig. 20. 1PB HPLC results for CSTRs and SCT in Test 5.

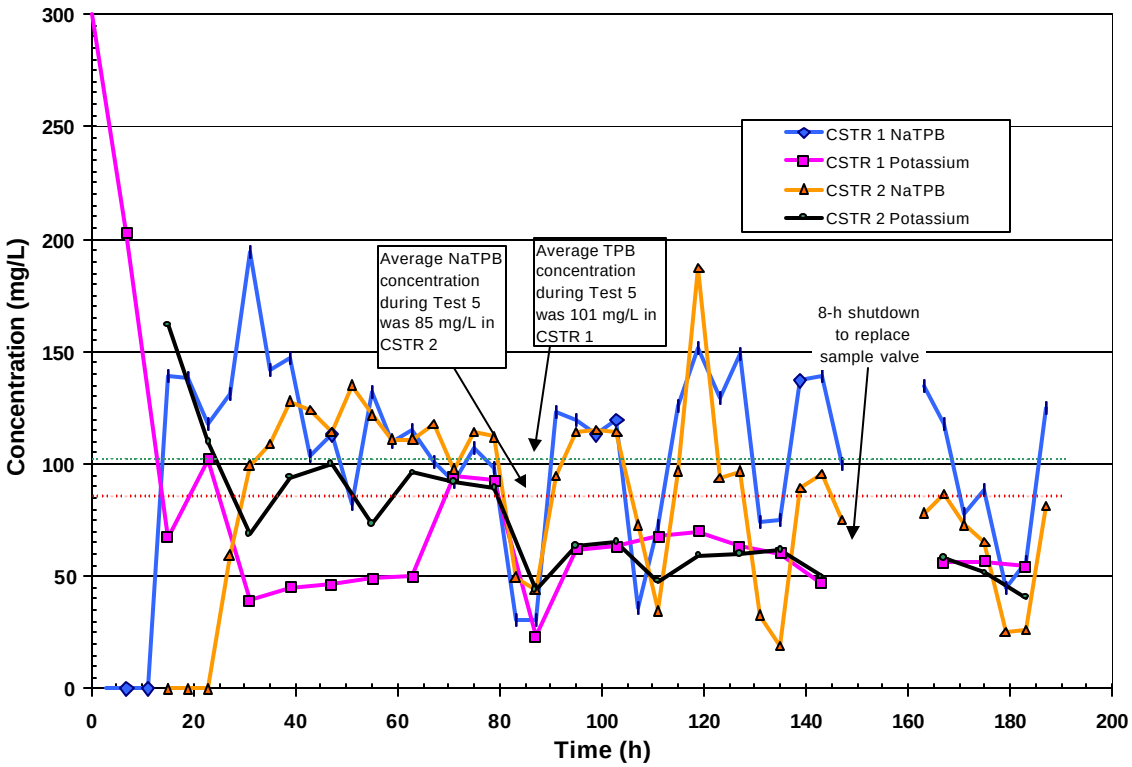

Fig. 21. Soluble NaTPB and potassium in CSTRs 1 and 2.

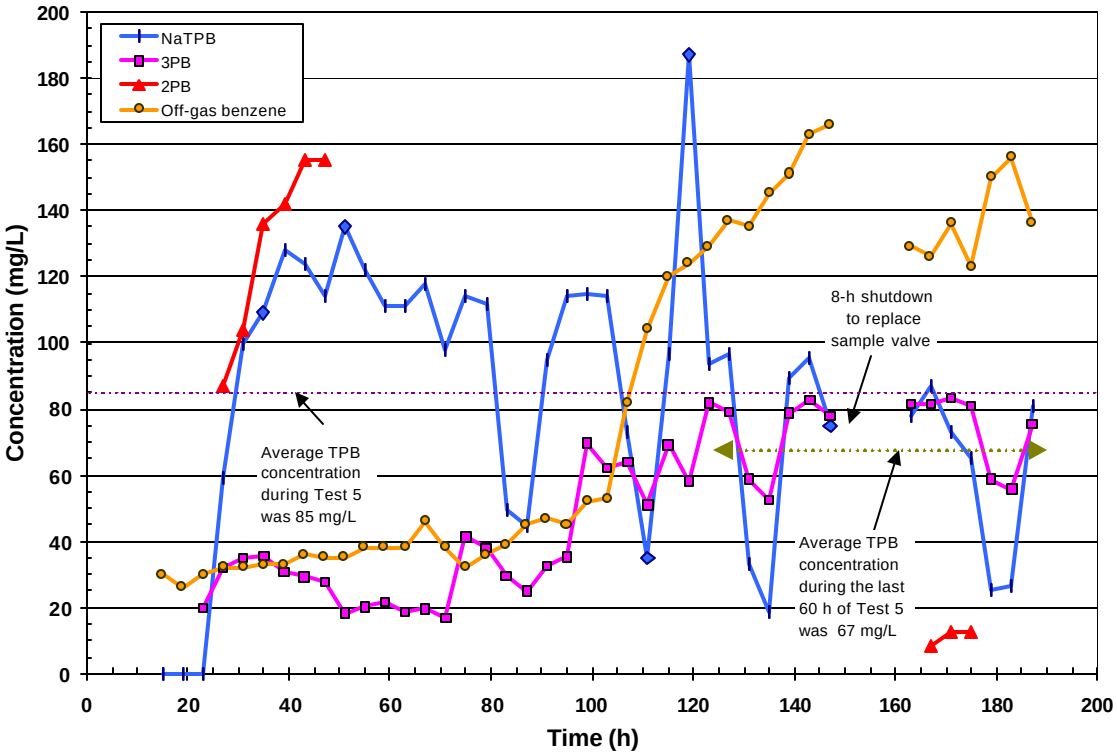

Fig. 22. HPLC results for CSTR 2 in Test 5.

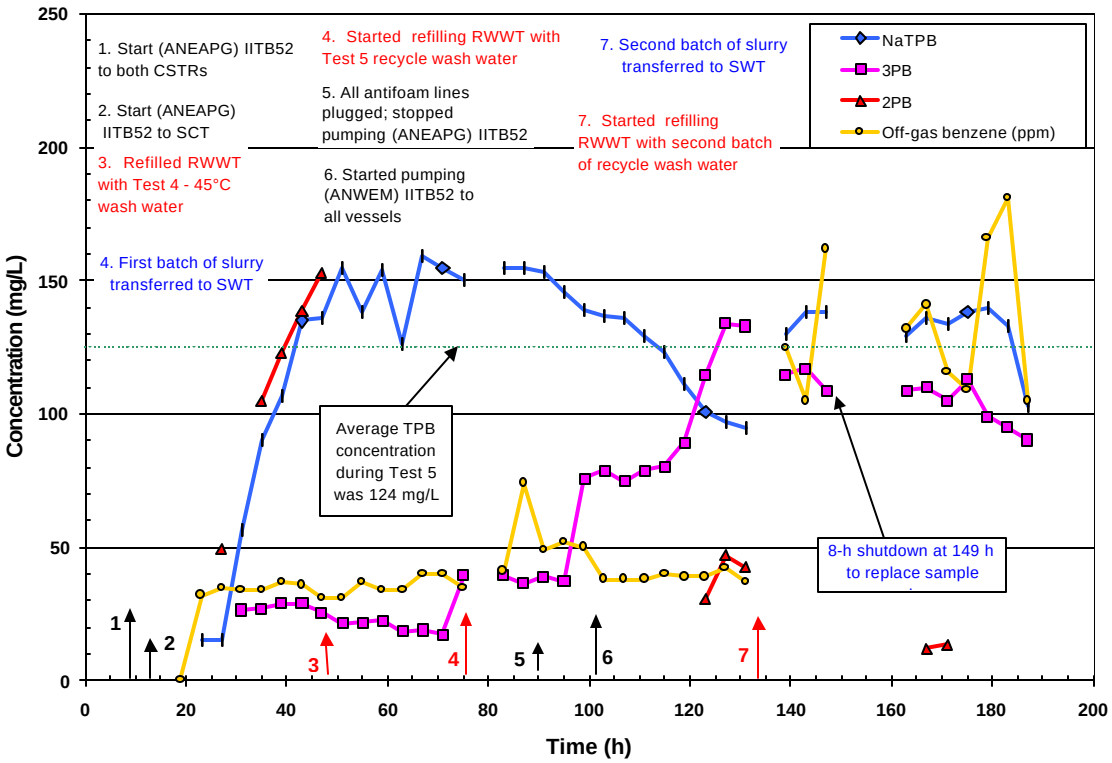

Fig. 23. HPLC results for SCT filtrate inTest 5.

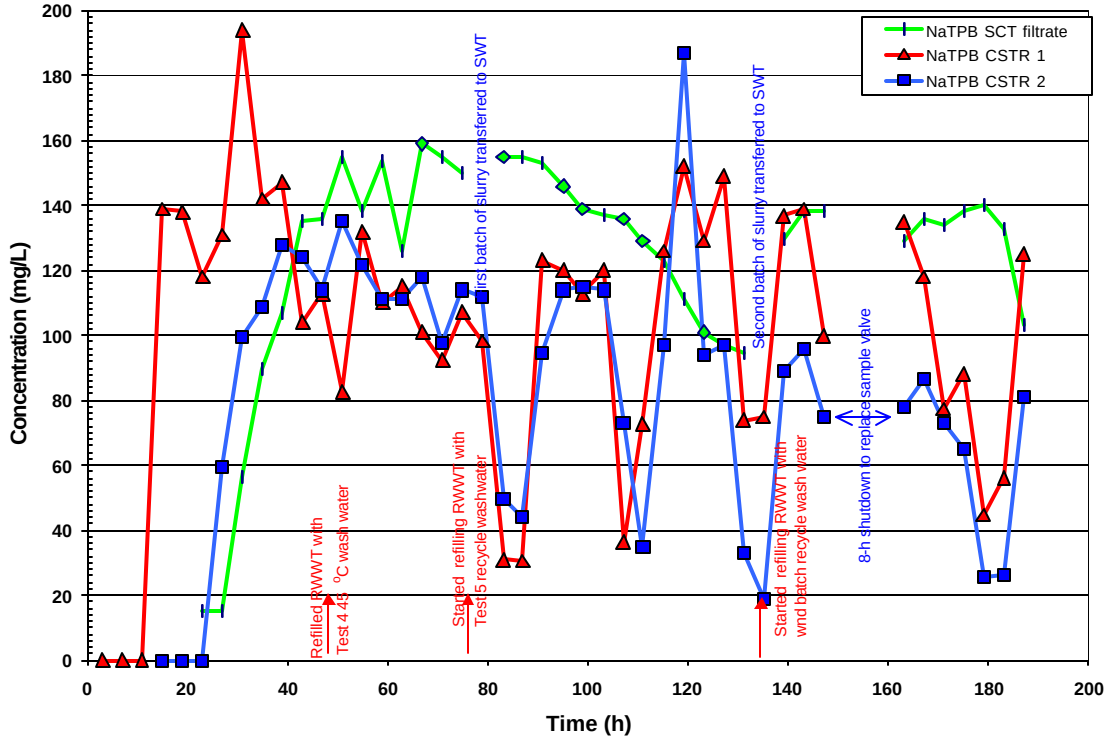

Fig. 24. HPLC results for TPB in CSTRs and SCT in Test 5.

have to be observed while processing several batches of slurry. (Such trends were not observed in this operation.) Although the TPB concentration was consistently above 90 mg/L (about 4% of the 60% excess TPB supplied to CSTR 1), it is not possible to predict similar performance in a longer-term operation.

A comparison of the soluble TPB concentrations in all three vessels is shown in Fig. 24. Significant events during the test are also noted. The graph shows that both CSTRs typically have similar soluble TPB concentrations, but the concentrate filtrate does not follow a similar trend because of the differing chemical conditions discussed above.

Figure 25, a plot of the 3PB concentrations for the three process vessels, also notes additional events that could have influenced the chemical behavior of the system. During the first 100 h of the test, the concentrations and trends of 3PB in each vessel were similar. After 100 h, however, the data for each vessel begin to separate and the 3PB in the SCT increases at a higher rate. At 160 h, the trends still appear to be similar, but the concentrations are widely separated. The increase in the SCT 3PB while the second batch of slurry was being processed may be due to the combined effect of the higher total fraction of TPB (soluble and insoluble) and the increased concentration of catalyst retained in the slurry. The notes on this plot also indicate the times during which the source and composition of the RWW was changing. There does not appear to be any significant trend or pattern in the decomposition behavior of the system that would indicate an immediate impact due to the change in RWW composition or antifoam batch. Additional discussions of wash water and antifoam effects are given in Sect. 4.2.5.

Because Test 5 was a test of catalytic decomposition of TPB and the ability of the system to cope with it, it is helpful to see how much of the TPB present was actually decomposed during the test. Figures 26 and 27 show the calculational results for CSTRs 1 and 2. Shown in the figures are the molar concentration of TPB fed to CSTR 1, the molarity of the measured soluble TPB, the molarity of the excess TPB, and the molarity of the TPB decomposed as calculated from the measured 3PB in the filtered samples. For Test 5, the average (potassium + cesium) molarity in the CSTR slurry was 0.0115 mol/L. The planned goal was to provide 60% more TPB than needed to precipitate the potassium and cesium, which means that the TPB molarity in the slurry needed to be 0.0069 *M* in excess of the 0.0115 *M* concentration. For CSTR 1, the decomposed TPB represents 2.47% of the excess TPB fed. The combination of CSTRs 1 and 2 is shown with an additional 1.44% of the excess TPB decomposed in CSTR 2. In Fig. 28, all three of the vessels are shown with the total displayed. The TPB decomposition of 0.00036 mol/L for the 62 mg 3PB/L represents a 5.2% loss of the excess TPB concentration. This small amount of decomposition would have no effect on the ability of the system to maintain the cesium DF.

4.2.4 ICP-AES Analyses for Potassium and Boron

Samples of the CSTR and SCT process fluids were analyzed for potassium to confirm the TPB reaction and the precipitation of potassium. Boron was also analyzed to confirm the total concentration of soluble phenylborate compounds. Figures 29–31 show the RMAL ICP results for potassium and boron for the filtered samples from CSTR 1 and CSTR 2 and the filtrate from the SCT. They also show the calculated amount of boron that would be present from the soluble TPB and decomposition products in solution. The potassium decreased from 210 mg/L at the first sample to 50 mg/L in CSTR 1 in about 30 h, but the potassium in CSTR 2 did not fall to this level for another 55 h. Potassium levels in the SCT filtrate followed the same trend as observed for CSTR 2. As compared with the cesium removal from the feed, the potassium decontamination was slower and not as complete.

The boron measured in CSTR 1 and that calculated from the soluble phenylborates present were very close until about 45 h, when the wash water from the Test 4 slurry batch produced at 45ºC was added to the RWWT. At approximately the same time, the analysis for 2PB in the samples failed due to increases in interfering substances in the HPLC analysis. Loss of 2PB from the calculation for boron present can explain most of the difference between the calculated and the measured boron. The differences between the calculated and measured boron values increased slightly in CSTR 2 and were even greater in the SCT filtrate, possibly indicating an increasing amount of 2PB generated.

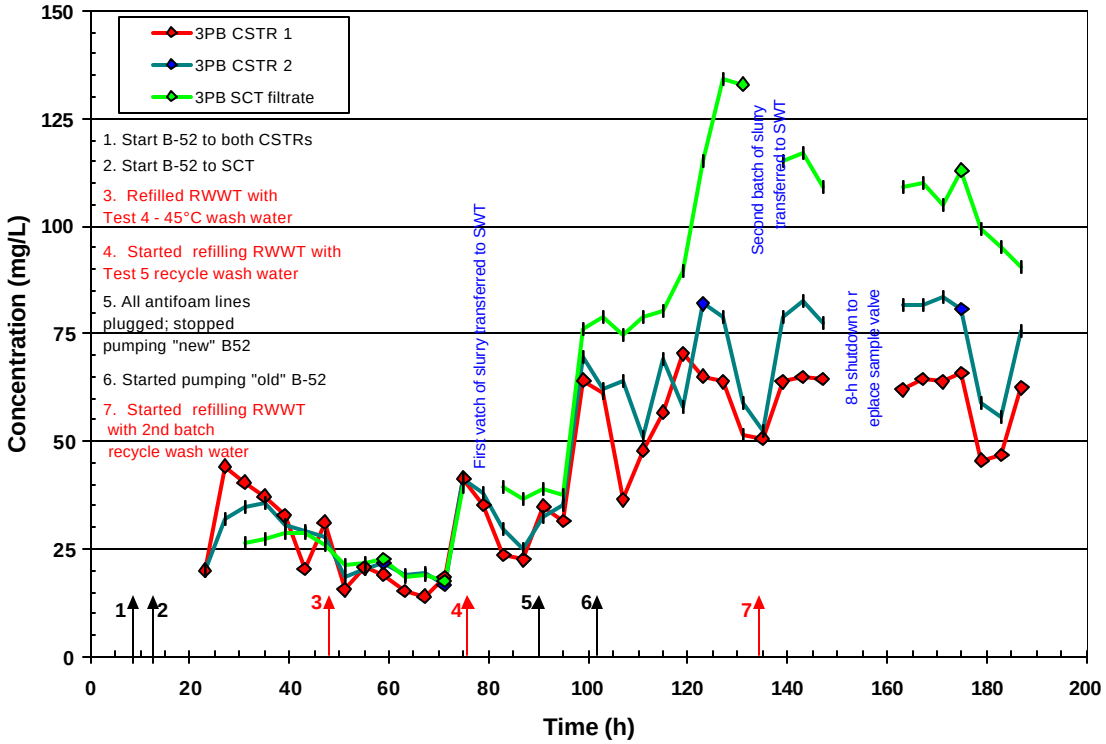

Fig. 25. HPLC results for 3PB concentrations in CSTRs and SCT in Test 5.

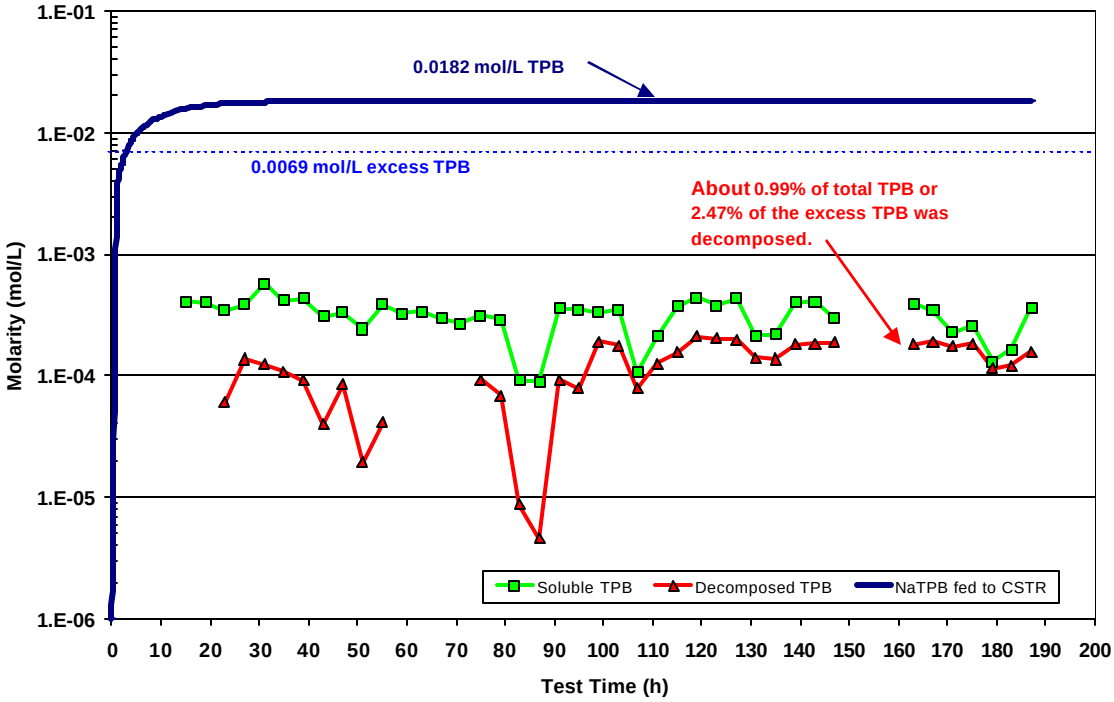

Fig. 26. NaTPB behavior in CSTR 1 during Test 5.

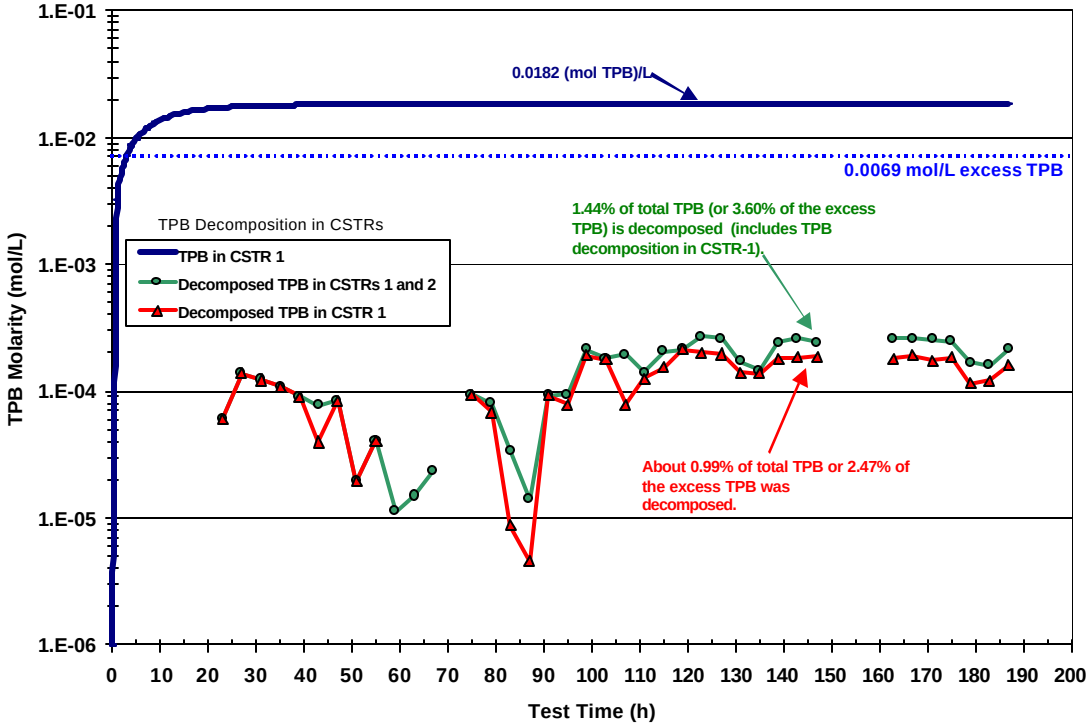

Fig. 27. NaTPB behavior in CSTR 2 during Test 5.

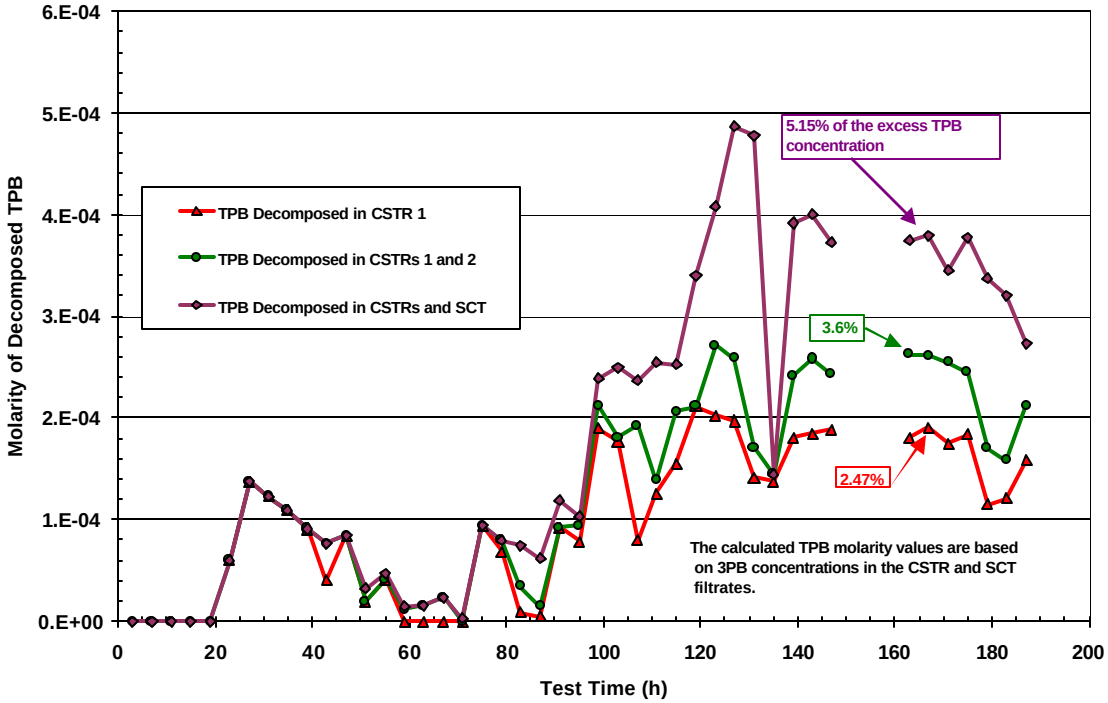

Fig. 28. NaTPB behavior in SCT during Test 5.

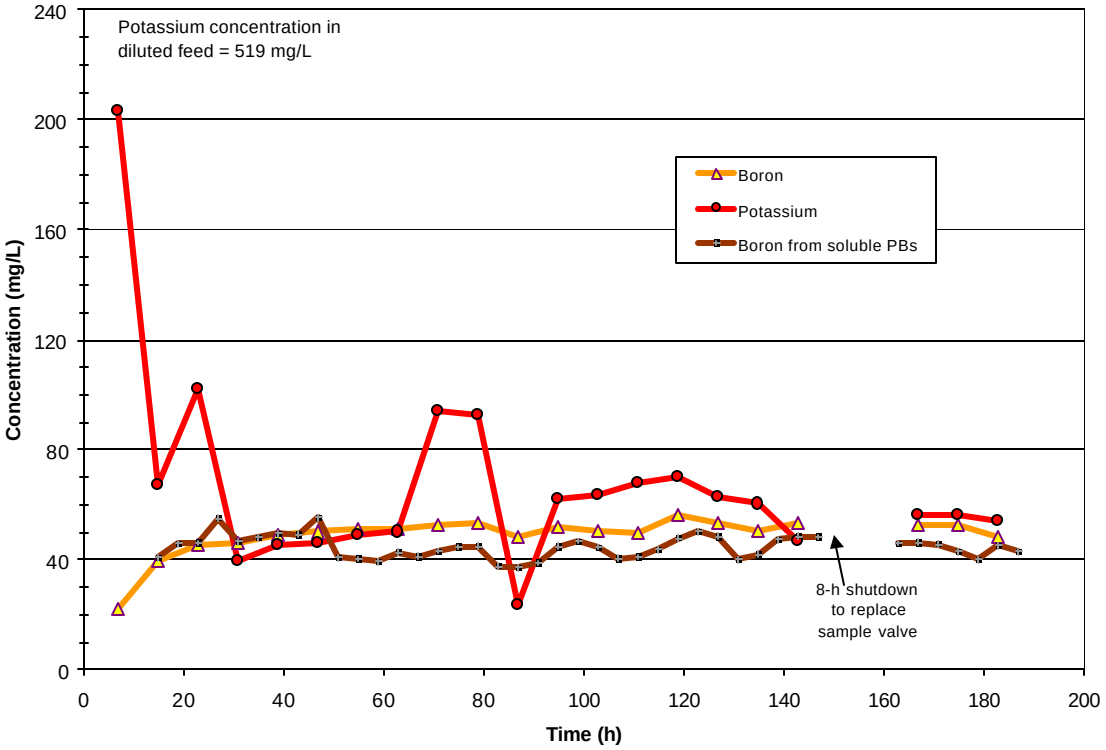

Fig. 29. CSTR 1 results for boron and potassium in Test 5.

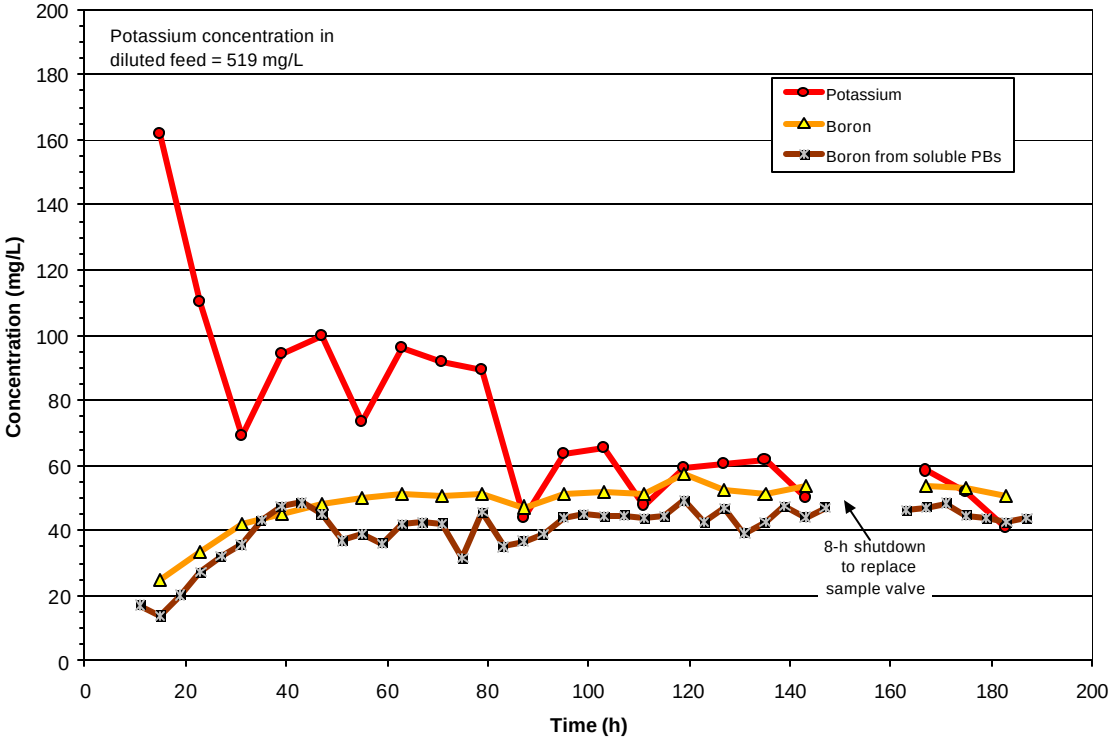

Fig. 30. CSTR 2 results for boron and potassium in Test 5.

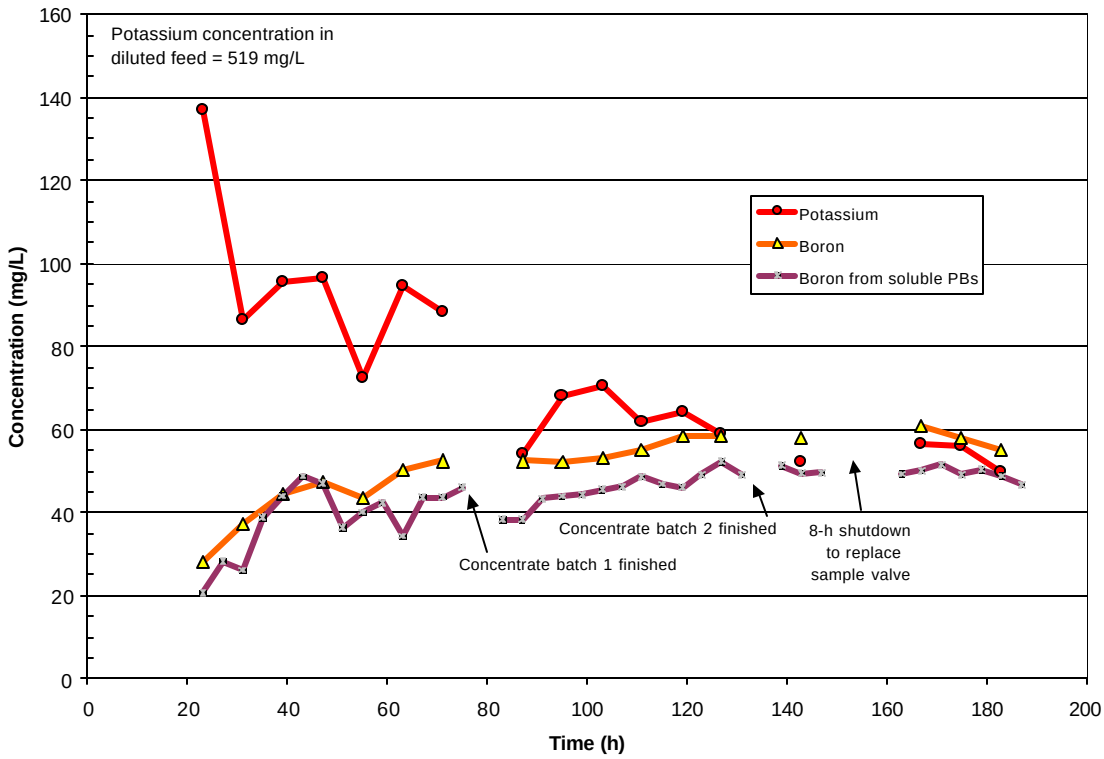

Fig. 31. SCT filtrate results for boron and potassium in Test 5.

4.2.5 Benzene Production Rate as a Measure of TPB Decomposition

Benzene is produced in the STTP by the catalytic decomposition of TPB and its decomposition products (3PB, 2PB, and 1PB). The four phenyl groups of the TPB molecule have the potential of forming four benzene molecules. The RCS catalyst system used in Tests 4 and 5 is known to decompose TPB to 3PB and benzene, and then further decompose 3PB to 2PB and benzene. Catalysts known to rapidly decompose 2PB and 1PB were not added. Palladium catalyst (5% on γ-alumina) and $Hg(NO_3)_2 \cdot H_2O$ were delivered in the MST/water to CSTR 1 at a rate that provided palladium and mercury concentrations of about 7.8 and 85 mg/L, respectively. The palladium concentration was equal to three times that used in the Enhanced Comprehensive Catalyst (ECC) system developed by the Savannah River Technology Center. The 1PB, also added as part of the catalyst system, was delivered in the NaTPB feed to CSTR 1 at a rate that provided a concentration in the slurry of 500 mg/L. The TPB decomposition goal, based on TPB decomposition to 3PB, was to obtain a benzene generation rate of ~2.5 mg/(L·h) in the SCT. The SCT would have the highest concentration of palladium catalyst because all of the solids and precipitates fed to and produced in the system are collected and concentrated in each batch of slurry in the SCT. A rate of 2.5 mg/(L·h) benzene would provide a benzene concentration of about 100 ppm in the purge gas (assuming no holdup of benzene in the process fluids).

For relevant Test 5 background information for this discussion, CSTR 1 was first filled with ~9 L of salt feed before Test 5 was initiated. At design conditions, it took about 36 h for the palladium concentration in the slurry to reach the 33 concentration of 7.8 mg/L. In Test 5, the initial catalyst feed rate was about 18% higher than the target rate, so the palladium concentration at 36 h was 3.653 (9.5 mg/L). The feed rate was reduced by 25% at 35 h to begin to bring the average rate more into line with the target rate. It took ~8 h for the TPB and potassium molar concentrations in the slurry to become equal. It also required about 36 h for the TPB and the potassium to reach steady state, at which point the

excess TPB (that TPB not precipitated as potassium and cesium) was maximized. The first filtrate sample to have a measurable amount of soluble TPB (139 mg/L) was that taken at 15 h. At that time, the calculated excess TPB (total as NaTPB) was 38%. The RWW TPB and 3PB contents are given in Table 5.

Benzene generation rates were calculated on the basis of the concentrations of 3PB in the CSTR filtered samples and the SCT filtrate samples during Test 5. The 3PB contributed by the wash water recycled to CSTR 1 was not included in the calculations for CSTR 1. It was assumed that for each mole of 3PB formed, a mole of benzene was generated. Benzene generation rates were also calculated on the basis of the benzene concentrations in the off-gas from each tank.* Comparisons of these rates of generation are given in Figs. 32–34. The concentrations of 3PB in the samples taken during the first 19 h of operation from all three tanks were below the HPLC detection limit. Considering the background information above, this is not surprising. The 3PB supplied in the recycle water would be below the HPLC detection limit when diluted in the CSTR 1 slurry. In addition, the excess TPB (precipitated as NaTPB), soluble TPB, and the palladium concentrations were low in the early stages of the run in all the vessels. Once the TPB decomposition reaction began at ~23 h, benzene generation, based on the concentration of 3PB, rose quickly to ~1.3 mg/(L•h) at 27 h (see Fig. 32). After dropping to a very low level at 65 h, the rate showed an unsteady climb to about 2 mg/(L•h) at 120 h. In the time frame between 120 and 187 h, the rate varied between 1.1 and 1.9 mg/(L•h). The benzene concentrations calculated from 3PB in the liquid phase and FTIR off-gas measurements for benzene do not show good agreement at any particular point. This might be explained by the strong evidence (observed in Test 4) that benzene is retained by the liquid or TPB slurry phase. If retained in the slurry, the benzene release into the gas phase could be delayed for an unknown time. In addition, variation in the off-gas benzene concentration was expected because the headspace above the liquid in the CSTR is not optimized for gas mixing. Good agreement, however, was obtained when the average concentration of benzene from the calculation was compared with the average concentration detected by the FTIR system. The averages for benzene calculated from the 3PB produced and for the benzene rate based on the FTIR analysis were 1.1 and 0.95 mg/(L•h), respectively.

Figure 33 shows the net increase in benzene concentration for CSTR 2 as a function of time. The data indicate that there was very little change in the benzene generation rate (based on the increase in 3PB concentration over that in CSTR 1) until 103 h, where it fluctuated between 0 and 0.35 mg/(L•h). The same was the case for benzene generation rates based upon the off-gas measurements, where the values increased only slightly from 0.3 to 0.5 mg/(L•h) in the 23- 103-h time frame. From 103 h to the end of the test, the values based on 3PB generally increased but fluctuated between 0 and 0.8 mg/(L•h), averaging about 0.4–0.5 mg/(L•h). The off-gas values rose steadily to 1.65 mg/(L•h) at 147 h and remained between 1.2 and 1.5 mg/(L•h) until the end of the test. In general, however, the benzene concentration indicated by the off-gas measurements (average, 0.8 mg/(L•h) was significantly greater than that given by the 3PB calculation [0.3 mg/(L•h)].

If CSTR 1 and CSTR 2 are considered together, the average total benzene generation rate based on 3PB production for the period after 103 h is about 1.6 + 0.5 = 2.1 mg/(L•h). The benzene generation rate based on the benzene in the off-gas for both vessels together was 0.9 + 1.3 = 2.2 mg/(L•h), indicating that there is good agreement in the two rates when both CSTRs are considered as a single unit. It also indicates that the possible delay in the release of benzene from the TPB slurry should be considered when evaluating benzene production as measured by the benzene in the off-gas of a single vessel. The lack of

*An example of a benzene generation rate calculation based on 200 ppm benzene in the off-gas (on-line FTIR measured) from a tank with a purge rate of 800 mL/min nitrogen [(800 mL/min)/(22.4 L/mol)]/(1000 mL/L) = 0.0357 mol/min N_2 (200 ppm benzene equates to a mol fraction of 0.0002) and [(0.0002) × (0.0357)]/0.9998 = 7.1E–6 mol/min. Therefore, [(7.1E–6 mol/min) × (78,000 mg/mol) × (60 min/h)]/(15.4 L) = 2.17 mg/(L•h) = the benzene generation rate for a CSTR; [(7.1E–6 mol/min) × (78,000mg/mol)×(60 min/h)]/(5.8 L) = 5.8 mg/(L•h) = the rate for the SCT.

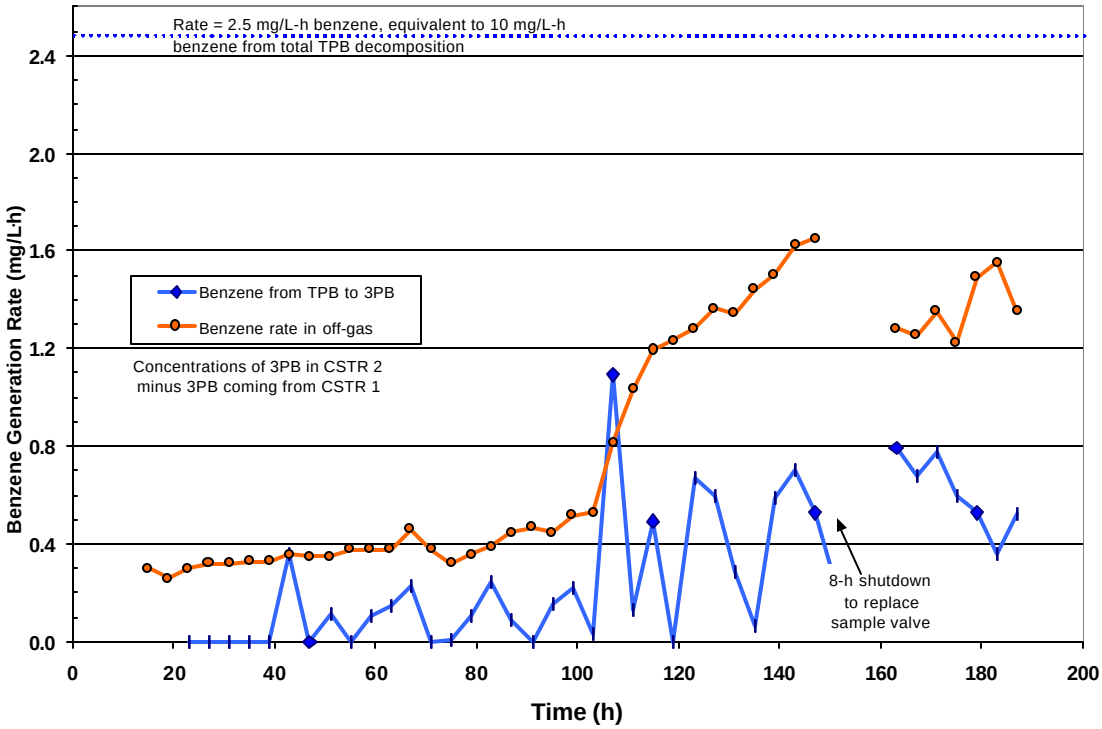

Fig. 32. Benzene generation results for CSTR 1.

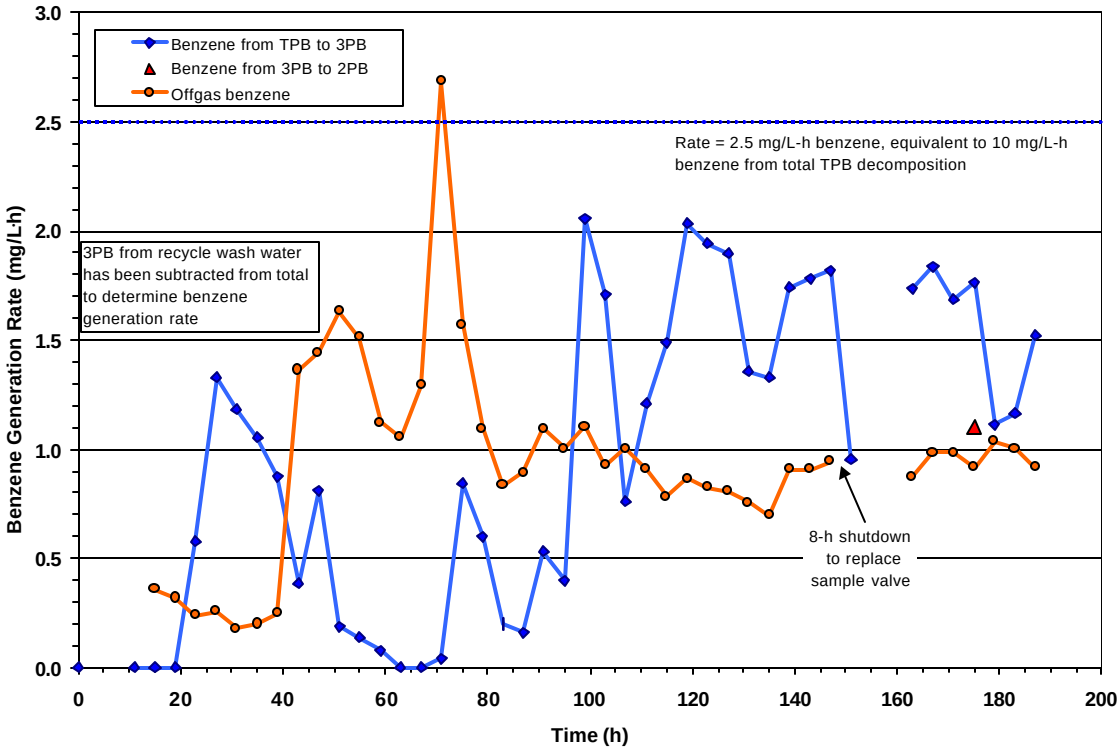

Fig. 33. Benzene generation results for CSTR 2.

additional 3PB in CSTR 2 may have been caused by a decreased amount of catalyst entering CSTR 2. It is possible that the palladium/alumina catalyst slurry, which had a much faster settling rate than the MST or TPB solid may not have transported to CSTR 2 from CSTR 1 as well as was intended. During CSTR sampling activities, a black solid material, assumed to be the palladium/alumina, was observed to have settled to the bottom of some of the sample bottles. Another possible explanation is that the palladium became coated by the TPB solids and was unavailable for reaction or became deactivated by oxidation with time.

A comparison of the calculated (TPB to 3PB) benzene generation with the off-gas concentrations in the SCT showed similar trends for most of the operation, as shown in Fig. 34. However, as in the CSTRs, the values were not in good agreement with the exception of a short period near the end of the operation. For the first 87 h of the test, there was also little or no additional 3PB formed in the SCT. The calculated off-gas benzene generation rate was very consistent with an average rate of ~1 mg/(L·h). The break in the curves at 75 h and 131 h indicates the times when batches of concentrated slurry were transferred out of the SCT for the washing operation. After the transfers, the mixing characteristics of the remaining slurry were changed due to the lower operating level, and the slurry solids content in the SCT was reduced as the tank was refilled with slurry from CSTR 2. The benzene generation rate based on 3PB increased to 2.9 mg/(L·h), exceeding the test goal of 2.5 mg/(L·h), as the second batch of slurry solids was concentrated to 10 wt % at 131 h. The lack of additional benzene release to the off-gas while the second batch of slurry was being concentrated indicates that benzene may have been retained in the process fluids. After the second batch of slurry concentrate was transferred to the SWT and the SCT was refilled with slurry from CSTR 2, the benzene rate as based on the decomposition of TPB to 3PB fluctuated from slightly a detectable level to about 6.5 mg/(L·h), with most values between 2 and 3.5 mg/(L·h). During the same period, the off-gas benzene generation increased to values in the range of 2.7 to 4.6 mg/(L·h). Figure 34 also gives benzene generation rates for 2PB measured in the SCT that ranged from 0.5 to 0.8 mg/(L·h) in the time frame between 163 and 187 h.

Figure 35 shows the benzene generation rate from the TPB decomposition to 3PB for each vessel, as well as the total for the system. After 101 h, the total benzene generation rate stayed in the range of 2.8 to 8.2 mg benzene/(L·h) and appeared to be in steady state in the two CSTRs during the last phase of the test while the third batch of slurry was being concentrated. Most of the benzene formed was produced, by very active decomposition of TPB in the SCT and CSTR 1. Benzene generation in the SCT, however, was not consistent for the three slurry batches processed.

Overall, the data indicate that TPB decomposition was successfully initiated and sustained during Test 5 operations, although a significant amount of time was required to achieve a sustained reaction. It is not clear that this can be attributed to the catalyst system alone. Several of the changes that occurred in the 0- to 100-h time frame for Test 5 were related to the RWW and antifoam feed systems. As shown in Fig. 25, the source of the RWW changed from the material provided from Test 4 to that which was generated from Test 5. As discussed in Sect. 4.2.2, the change in composition was gradual, rather than sudden. Recycle wash water from Test 4 [which contained IITB52 (ANWEM) and its degradation products] was used while the first batch of Test 5 slurry was being concentrated. At 55 h, the wash water produced from washing the Test 4 slurry during the 45ºC phase of the test was blended with wash water produced while washing Test 4 slurry at 25ºC. The decomposition activity at this time did not appear to respond to the change and continued a slight downward trend for an additional 20 h. Wash water from Test 5 became available at 76 h and began to be blended with the Test 4 wash water. At that time, the wash water holding tank (RWWT) was still filled to the 55% level with Test 4 wash water. Just prior to the addition of the Test 5 wash water at about 70 h, the 3PB content of CSTR 1 began to increase from about 20 to 42 mg/L. It appeared as though this increase was not related to the addition of Test 5 wash water. Over the next 17 h, the RWWT was refilled with batch 1 wash water that contained IITB52 (ANEAPG) and possible antifoam degradation products. Batch 2 slurry wash water from Test 5 started entering the RWWT at about 134 h. The washing operation for the second batch of slurry was not completed until the end of the test. If a step change in composition occurred in the RWWT, it would

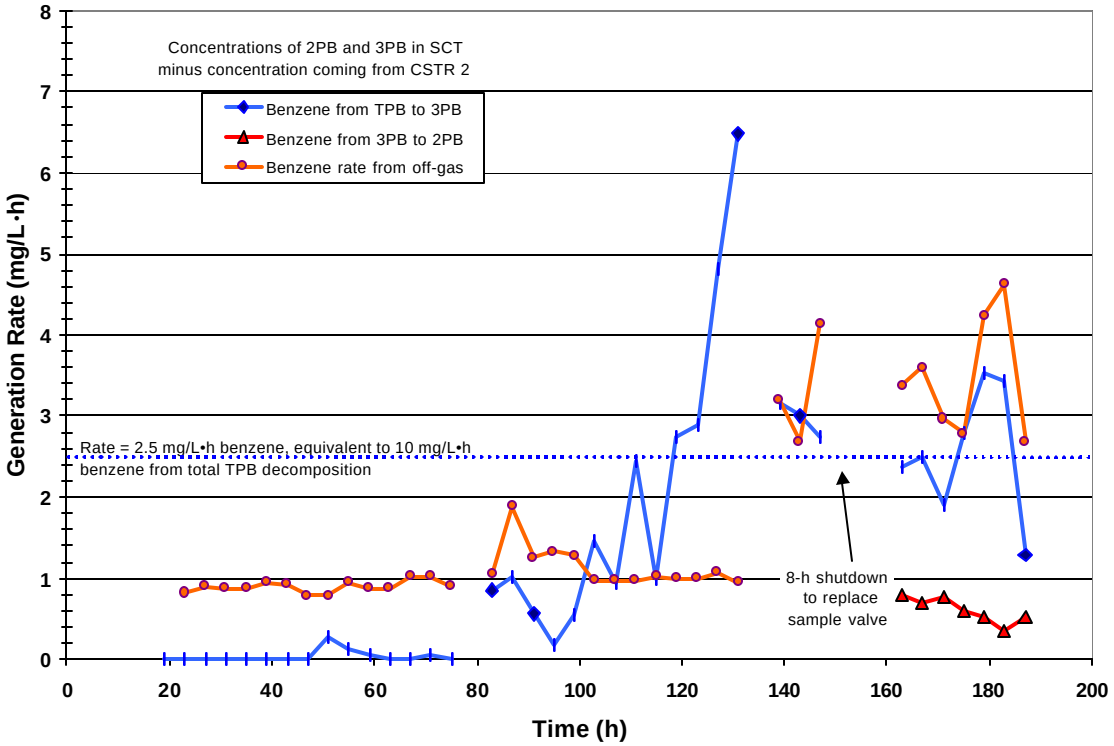

Fig. 34. Benzene generation results for the SCT.

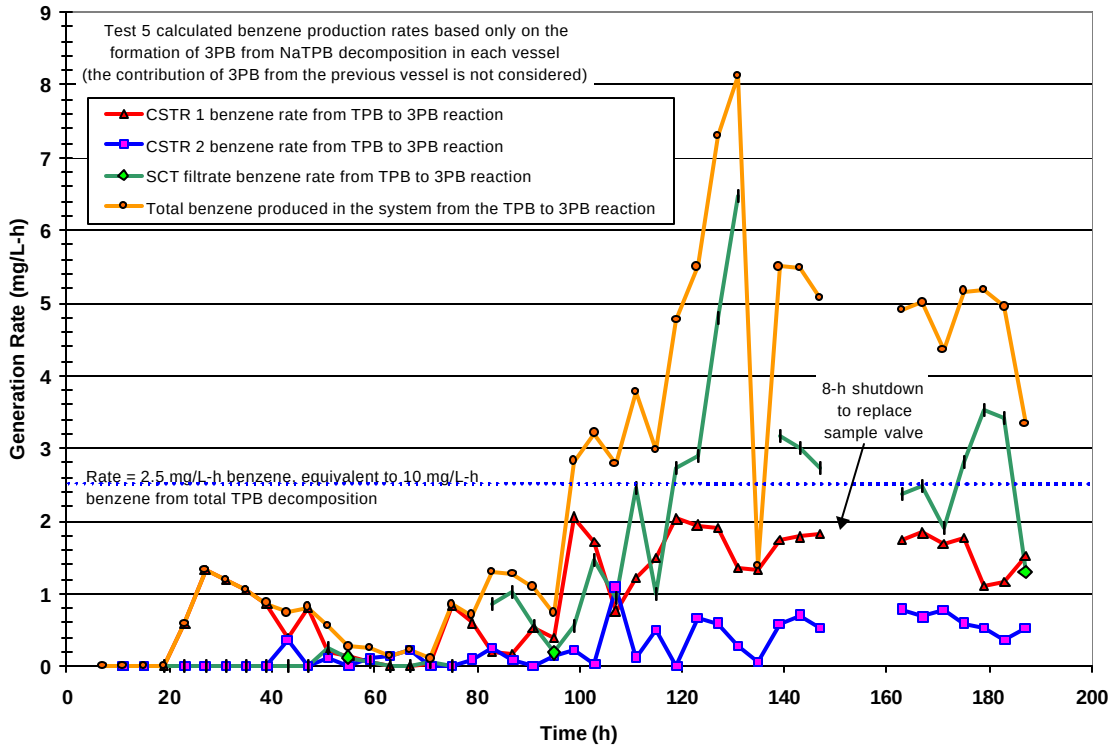

Fig. 35. Benzene generation results from conversion of TPB to 3PB in Test 5.

take about 24 h (three residence times) to reach 95% completion in CSTR 1 — and longer times in CSTR 2 and the SCT. As the fraction of Test 5 wash water increased, the CSTR 1 3PB concentration increased in an unsteady manner and appeared somewhat level for the two CSTRs. The erratic 25-mg/L changes made it difficult to distinguish a leveling trend. A far more significant increase in the 3PB concentration in the SCT began at about 95 h. This increase was very likely due to the concentrating operation and the associated increase in the concentration of the palladium catalyst, rather than possible effects from the wash water or antifoam.

4.3 SUBSYSTEMS OPERATION

4.3.1 Feed System Operations

The various feed streams to the CSTR are shown in Figs. 11 and 12 in terms of total mass delivered and flow rate as a function of time. The simulated salt feed system used a peristaltic pump to transfer the feed from the two 55-gal holding tanks to CSTR 1. The salt feed flow was monitored by level changes in the holding tanks and by periodically diverting the flow to a graduated cylinder for timed measurements. As shown by Fig. 11, the simulant flow was very steady throughout the test. The TPB and excess TPB feed systems presented no problems, and their flow rates were very stable, as was the RWW pump flow inside the hot cell. All three used Accu piston-type metering pumps, manufactured by Sci-Log, with FMI pump heads.

4.3.2 Antifoam Operations

Frequent problems occurred during the efforts to maintain a consistent flow of antifoam IITB52. The lines to the process vessels were initially filled with nondiluted IITB52 (Lot –10-05-2000, product index ANWEM) using 5-mL syringes in the syringe pumps. After the process fluids began overflowing from CSTR 2 into the SCT, the syringes were refilled and the syringe pumps started at the desired rates. After 2.5 days of acceptable operation, the pumps stopped operating and could not be restarted. Cleaning and replacing the syringes did not correct the problem. SPP antifoam development personnel recommended trying to reestablish flow using antifoam diluted with water at a ratio of 9:1. Smaller 1-mL glass syringes were used to apply greater pressure, and the lines were flushed with a solution consisting of water and antifoam mixed in a ratio of 9:1. Subsequently, the antifoam (9:1) was placed in 30-mL syringes and the pumps for CSTR1 and 2 were restarted. After about 4 h, the pumps failed again. The 1-mL syringes were then replaced with 5-mL syringes to provide greater pressure, and flow was reestablished. However, after operating for 18 h, all of the syringe pump lines became plugged. Visual inspection of the antifoam supply indicated that this particular batch appeared to be more viscous than the batch used in earlier testing. Diluting the antifoam 9:1 with water appeared to make the antifoam somewhat less viscous, but more gelatinous in nature. The SPP antifoam development personnel recommended the use of an earlier batch of antifoam, IITB52 (Lot 7-31-2000, ANAEPG), that had successfully been used in undiluted form for Tests 3 and 4. The use of the IITB52 (ANWEM) was discontinued.

The lines were cleared once again, and 5-mL syringes were used to pump the undiluted IITB52 (Lot 7-31-2000, ANAEPG). The antifoam feed pumps operated well for the remainder of the test. Despite the antifoam feed problems, there was no evidence of foam in the CSTRs or in the slurry concentrating or washing systems.

4.3.3 Problems with MST/Catalyst Feed Mixture

Problems were periodically experienced in maintaining a consistent flow of the feed mixture consisting of water, MST, palladium/alumina, and mercury nitrate. In a preliminary pumping test

conducted several weeks before Test 5, the catalyst feed mixture was prepared and pumped through a 0.03-in–ID line continuously for 9 days without the line becoming plugged. The preparation involved adding and mixing 4.54 mL of 15.8 *M* HNO_3, 28.28 g of $Hg(NO_3)_2 \cdot H_2O$, and 223.3 g of wet MST solids with 13.3 L of deionized water and sieving the entire mixture through a 200-mesh (70-µm pore opening) stainless steel sieve. The pH of the solution was slightly acidic (about 5.5). A few moments before conducting the pumping test, 28.3 g of palladium catalyst was slowly added to the solution.

Since the pumping test was successful, three similar solutions were prepared for Test 5, which contained no palladium catalyst. The palladium catalyst was received in bottles packed under argon. Three separate bottles, each containing 28.3 g of dry palladium/alumina catalyst, were prepared. Shortly before starting the test, one of the bottles of palladium catalyst powder was slowly added to a bottle of MST/mercury solution. This was done to minimize potential oxidation of the palladium by shortening the exposure time in the MST water.

At the start of the test, problems occurred in pumping the first bottle of MST/mercury/palladium catalyst mixture to CSTR 1. The (0.03-in.–ID) supply line plugged frequently and the flow could not be maintained. The tubing was sized to maintain the velocity necessary to keep the palladium catalyst in suspension during pumping. In an attempt to correct the problem, the first bottle was replaced with a freshly prepared MST/mercury/palladium catalyst feed mixture. This mixture was metered into the system successfully. The contents of the first bottle were then passed through the 200-mesh sieve; however, a small mass of clumpy material, most of which was palladium catalyst, was retained. These clumps were broken up with a rounded spatula and forced through the sieve. The specified particle size for the as-received palladium/alumina powder was 5µm, but the additional sieving indicated that larger and/or agglomerated particles were present.

The third bottle of MST/mercury/palladium catalyst mixture was prepared in the same manner as the second, but it too plugged the line (one line was irreversibly plugged). This batch of material was also removed for sieving. Again, a small amount of solids had to be forced through the sieve. After sieving, the third batch of material was metered successfully; only two short-term plugging problems were experienced. After the third bottle was used, the first bottle that had been sieved was used successfully.

It is recommended that the MST/dilution water, with or without the palladium catalyst and mercury, be wet-sieved after preparation. If mercuric nitrate is added, the solution should be made slightly acidic to prevent the precipitation of mercuric hydroxide, which can cause agglomeration of particles and lead to pumping problems.

4.3.4 Performance of the Slurry Concentration System

The process control and the performance of the concentrating and washing systems were excellent. As shown in Figs. 11 and 12, the flow of filtrate was very smooth and did not limit the process throughput capacity. The cross-flow filter element was adequately sized and required only occasional backpulsing to reduce transmembrane pressure. The results of filter operation are shown in Fig. 36. The filter flux and the normalized filter flux (permeance) [flux per unit psi of transmembrane pressure (TMP)] are shown as a function of test time. The permeance is plotted because the filter was operated by decreasing the TMP after a backpulse and then increasing the TMP during the times between backpulses to maintain the desired filtrate flow rate. The backpulses were then infrequent and did not disrupt the concentration operation very often. The filter was operated at an axial velocity of 5.5–6 ft/s and had an average TMP of 11.5 psi (2–25 psi) and an average flux of 0.03655 gpm/ft^2. Figure 37 shows that both the flux and permeance results agreed with results that were obtained in Tests 3 and 4 in which IITB52 was also used to prevent foam formation. These results also agreed with those obtained in similarly conducted tests at SRS.[11] Tests 1a and 2, which did not use antifoam, yielded very similar flux results. The flux in Test 1a averaged 0.031 gpm/ft^2; in Test 2, it averaged 0.0348 gpm/ft^2.

The backpulse system of the filter was very effective, as shown in Fig. 36, and operation of both the concentration and the wash system filtration systems was generally smooth and trouble free. During one short time period after the first slurry batch had been completed, the concentration filtrate flow

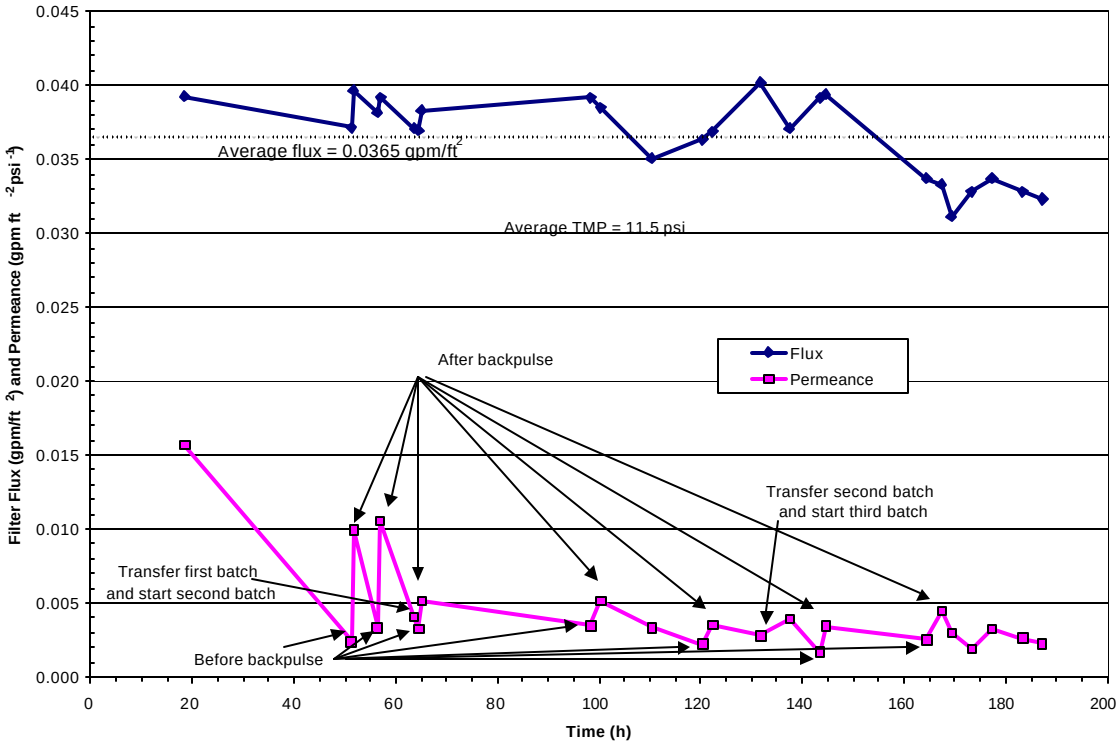

Fig. 36. Performance of SCT cross-flow filter in Test 5.

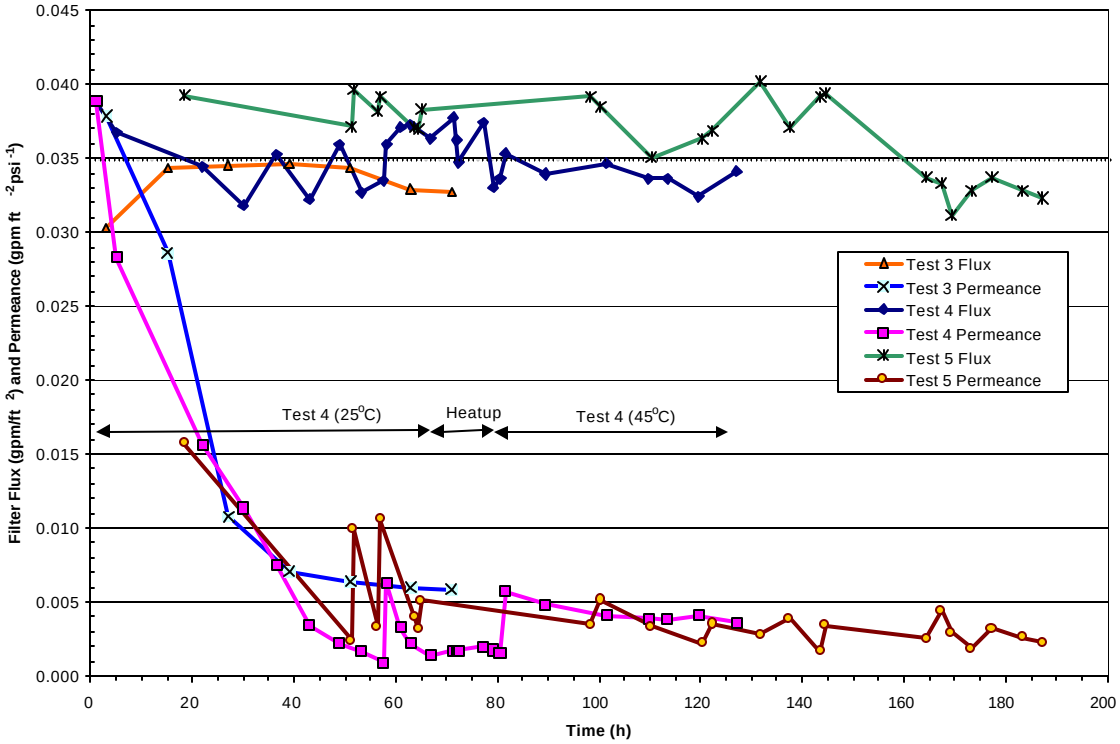

Fig. 37. Performance of SCT cross-flow filter in Tests 3, 4, and 5.

control valve malfunctioned and became fixed in the open position. To continue control of the filtrate flow, the backpressure control valve was used to control the filtrate flow by adjusting the TMP. After a few hours, the malfunctioning valve suddenly started operating properly again, and no further problems were experienced.

A more serious problem developed after 120 h of operation when the fluid seals for the Moyno pump in the concentration system began leaking. A similar problem had occurred previously during Test 4, in which the seal failure had led to a drive-bearing failure of the original Moyno pump and the pump had to be replaced. The Test 5 pump will be examined later to determine the cause of the seal failure.

4.3.5 Hydraulic Performance of the CSTR

Fluid transfer problems occurred in the overflow lines between the CSTR vessels due to accumulation of settled solids in or around the sampling valves installed in the lines. The slurry is transported by gravity flow between vessels, and it appeared that small, pea-size agglomerations ("globs") of antifoam/TPB/palladium tended to deposit at the openings to the transfer tubes, restricting flow. Sometimes these globs passed through the tube when the pressure from the rising slurry levels in the vessels became fairly high. Lightly tapping the overflow line with a manipulator tool often cleared the obstruction. The CSTR 2 outlet to the SCT eventually plugged and could not be remotely cleared. In this case, it was necessary for a trained radiation worker to enter the hot cell, remove the valve, and manually push a clean stainless steel rod through the overflow line into the CSTR. The valves themselves were not plugged; however, the material had accumulated had in the line at the entrance to the valve. A small deposit of the solids was removed with a spatula and put in a sample bottle for analysis. The valve was then replaced with an identical new one; and the old valve was removed from the cell and placed in a radiochemical fume hood for inspection. No deposits were subsequently found in the old valve, and tests showed that the valve was in good working condition. Plugging problems continued to occur during the test, but none were severe enough to cause further delays in the operation.

4.3.6 Performance of the Control and Data Acquisition System

Overall, the computer control and data acquisition system provided good control of process flows, gave adequate warnings when operating parameters were outside normal ranges, and collected the necessary data for evaluating system performance. The system consisted of a PC with dual P-III 650-Mhz processors, running Windows® NT SP3, contained two 20-Gbyte hard drives, and an add-in eight-port multiplexed serial port card. The system used control software by Intellution. Problems occurred intermittently with the calculation for the flow rates based on weigh-scale input when the associated serial port communication stopped unexplainably and had to be restarted. In addition, communication with the backup computer stopped without warning for about 10 h due to Ethernet problems in the building. The primary data collection system continued to operate properly; thus, no data were lost.

4.4 SLURRY WASHING

The slurry washing system was operated without difficulty throughout the test. The filter ran smoothly and did not require backpulse at any time. The filter flux averaged 0.0223 gpm/ft^2, and the permeance averaged 0.1334 gpm ft^{-2} psi^{-1}; the axial velocity was about 5.8 ft/s and the TMP was less than 1 psi.

Tables 6 and 7 and Fig. 38 give the water-washing results for the two batches of concentrated slurry generated in Test 5. The washing goal was to produce RWW with Na^+ and TPB concentrations of about 1.2 and 0.033 *M* (12,800 ppm), respectively. This concentration of TPB was designed to provide an

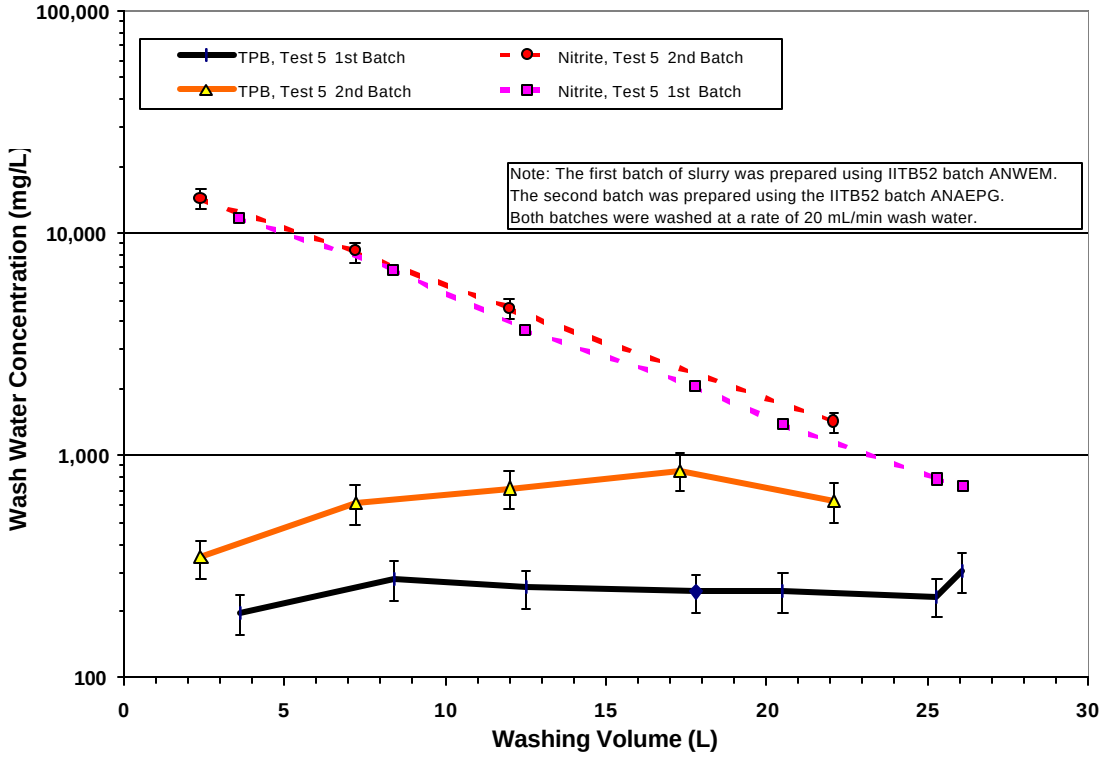

Fig. 38. Nitrite and NaTPB concentrations in wash water during slurry washing in Test 5.

Table 6. Wash-water results for batch 1 slurry washed at 20 mL/min in Test 5

Washing volume (L)	Washing time (h)	SWT filtrate sample ID	NO_2^- (mg/L)	NaTPB (mg/L)	3PB (mg/L)
3.6	2.5	79T5SP12-01	11,800	195	20.3
8.4	6.5	83T5SP12-02	6,910	278	
12.5	10.5	87T5SP12-03	3,700	255	
17.8	14.3	91T5SP12-04	2,040	244	
20.5	17.1	99T5SP12-05	1,390	245	5.2
25.3	21.1	103T5SP12-06	786	233	2.5
26.1	21.8	111T5SP12-07	735	301	3.0

Table 7. Results for batch 2 slurry washed at 20 mL/min in Test 5

Washing volume (L)	Washing time (h)	SWT filtrate sample ID	NO_2^- (mg/L)	NaTPB (mg/L)	3PB (mg/L)
2.4	2	B2T5SP12-00	14,300	347	113
7.2	6	B2T5SP12-01	8,240	613	99.3
12.0	10	B2T5SP12-02	4,610	714	90.1
17.3	14.5	175T5SP12-8		860	
25.2	18.5	179T5SP12-9	1,420	625	75.9

excess of 60% TPB above the amount added by the feed supply, which is separately pumped to CSTR 1. Based on the nitrite results for washing the two batches, the Na^+ concentration goal was obtained; however, the targeted quantity of TPB was not recovered.

After 77 h of operation in Test 5, the first batch of concentrated slurry (10 wt % TPB/MST solids) was completed in the SCT. A total of about 2.66 mol of TPB, 1.81 mol of K^+, and 0.023 mol of Cs^+ had been pumped to CSTR system. The SCT and cross-flow filtration system contained about 7 L of the concentrated slurry, which consisted of about 2.11 mol of TPB, 1.45 mol of K^+, and 0.018 mol of Cs^+. About 5 L was transferred to SWT. The transferred batch contained about 1.53 mol of TPB, 1.04 mol of K^+, and 0.013 mol of Cs^+. Therefore, ~0.48 mol of NaTPB was available for recovery. This batch was washed with water for 24 h at 20 mL/min, and only 0.055 mol TPB, or 11%, was removed. If all the available NaTPB had dissolved, the concentration of TPB in the 28.8 L of RWW would have been 0.016 mol/L. This is half the TPB concentration needed to provide 60% excess TPB.

The second batch of concentrated slurry was produced over the next 55 h of operation. The resulting 7 L of slurry contained about 2.51 mol of TPB and 1.64 mol of K^+ and included the slurry left in the system from the first batch. Again, about 5 L was transferred to SWT. This batch contained 1.79 mol of TPB, 1.13 mol of K^+, and 0.011 mol of Cs^+ (or 0.65 mol of available NaTPB). It, too, was washed for 24 h at 20 mL/min. Only about 0.021 mol of the available NaTPB, or 3.2%, was removed,. If all the available NaTPB had dissolved, the concentration of TPB in the RWW would have been 0.022 mol/L, or 67% of the NaTPB concentration needed to provide 60% excess NaTPB.

Under ideal conditions and assuming complete solubility of the NaTPB with water washing, the available moles of NaTPB for batches 1 and 2 would have been limited to 14.4 and 18.7 L of water in order to obtain recycle water with the desired TPB concentration of 0.033 *M*.

Water washing of both batches of slurry concentrate in Test 5 was extremely ineffective. The TPB recoveries achieved from earlier tests are comparable or superior to the Test 5 washing results. These results are compared in detail in Sect. 5.5, and several factors that appear to influence TPB recovery efficiency are discussed.

5. EVALUATION OF 20-L CSTR SYSTEM PERFORMANCE

5.1 CESIUM REMOVAL

Since the bounding separation goal for ^{137}Cs was to obtain decontamination factors (DFs) of 40,000 (99.998% removal), it was important in conducting the five 20-L CSTR system tests to obtain accurate cesium analyses. The amount of ^{137}Cs needed to provide a DF of >40,000 for these tests was based on the assumption that 1000 counts are needed for a 30-min count of 10-mL samples of filtrate for the needed counting accuracy. In each test, enough ^{137}Cs/L (~9 mCi of ^{137}Cs/L) was added to the salt feed to provide a concentration of ~6 mCi of ^{137}Cs/L in the CSTR slurry. Before being added to the salt feed, the tracer was mixed thoroughly with a small volume of water containing the needed mass of stable cesium to provide a total cesium molarity of 0.00016 in the salt feed. Even though these tests were conducted with simulant salt feed, the salt feeds had high radioactivity levels. For example, 4 Ci of ^{137}Cs were added to the salt feed in Test 5.

The TPB was very effective in the five tests in meeting or exceeding the required DF of 40,000. Figure 39 shows the slurry concentrating system product filtrate DFs for all five tests. Tests 1a, 2, and 3 all began with the first two CSTRs initially filled with the salt feed solution diluted to 4.7 *M* Na^+ with water, creating initially high concentrations of potassium and cesium in the tanks as compared with steady state operation. The SCT was also initially filled with about 3 L of salt feed, significantly delaying the attainment of cesium DF in the concentrate filtrate because several CSTR residence times were required for the TPB concentration to reach steady-state in the SCT. Test 4 started with both CSTRs filled with

the slurry left from Test 3; however, the SCT was cleaned, and the cesium DF was reached very quickly compared with the previous tests. Test 5 began with all vessels empty, but CSTR 1 was filled only to 60% with salt feed before all normal flows were established. The TPB reactions were ongoing for slurry that initially reached the SCT; thus, the DF for the SCT filtrate was achieved rapidly (filtration started about 15 h after the start of the test). In all cases, once the DF had been attained in the concentrating system, it remained consistently at or greater than the requirement, except in Test 2. A slight process upset for Test 2 caused slurry to overflow from the SCT to the overflow sump that contained a small amount of untreated salt feed. When the overflowed material was added directly back to the SCT, the cesium DF declined; however, the increasing trend was reestablished within a few hours. The precipitated hydrous metal oxides in the sludge and catalyst used in Test 2 had no apparent impact on cesium removal.

Figures 40 and 41 show similar DF plots for the cesium removal in CSTR 1 and 2. In both plots, it is evident that the cesium DF for Test 4 is greater than 40,000 at the start of the test, indicating no loss of DF for the process fluids from Test 3 left in the vessels during the 2-month interval between the end of Test 3 and the start of Test 4. During Test 4, the DF remained between 40,000 and 100,000 during the testing at 45ºC in each CSTR. The cesium DF results in Test 5 were similar to those in Test 4 for both CSTRs. Both tests used the RCS to initiate TPB decomposition, and in each case, the cesium DF was relatively unaffected during TPB decomposition. Variations in the DF results in each test were greater than the overall variations between separate tests both in the CSTRs and in the SCT.

The data comparison indicates that the antifoam had no effect on cesium removal. The CSTR DF profiles for Test 3, which included antifoam, were almost identical to those shown for Test 1a, where no antifoam was used.

Overall, there were no chemistry, TPB decomposition, antifoam, or operational difficulties during the five tests that prevented the system from attaining the desired DF in the slurry concentration filtrate product, or in either of the two CSTRs.

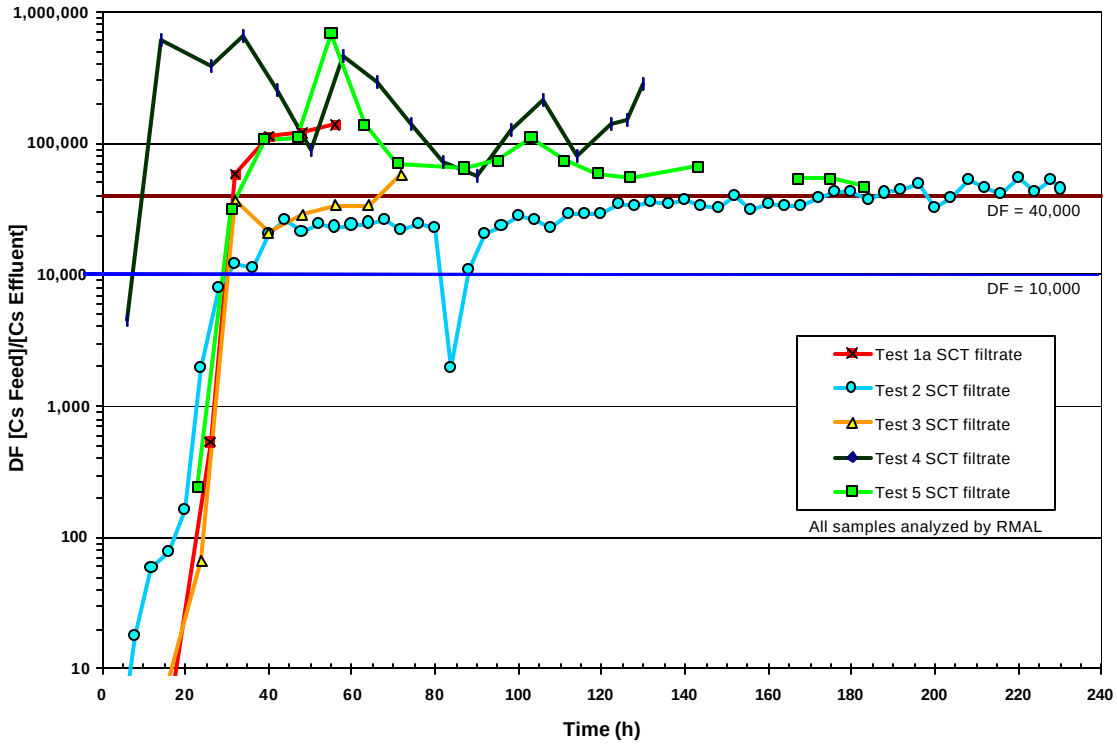

Fig. 39. Comparison of cesium DFs for all CSTR tests.

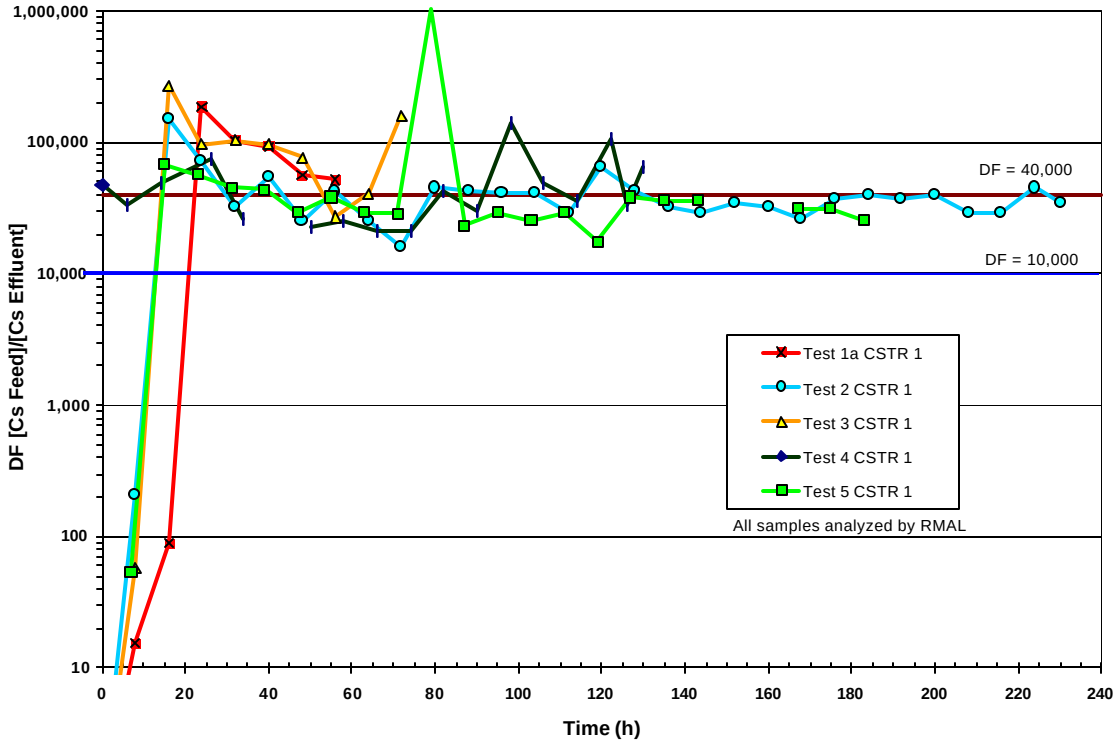

Fig. 40. Comparison of cesium DFs for all CSTR tests (CSTR 1).

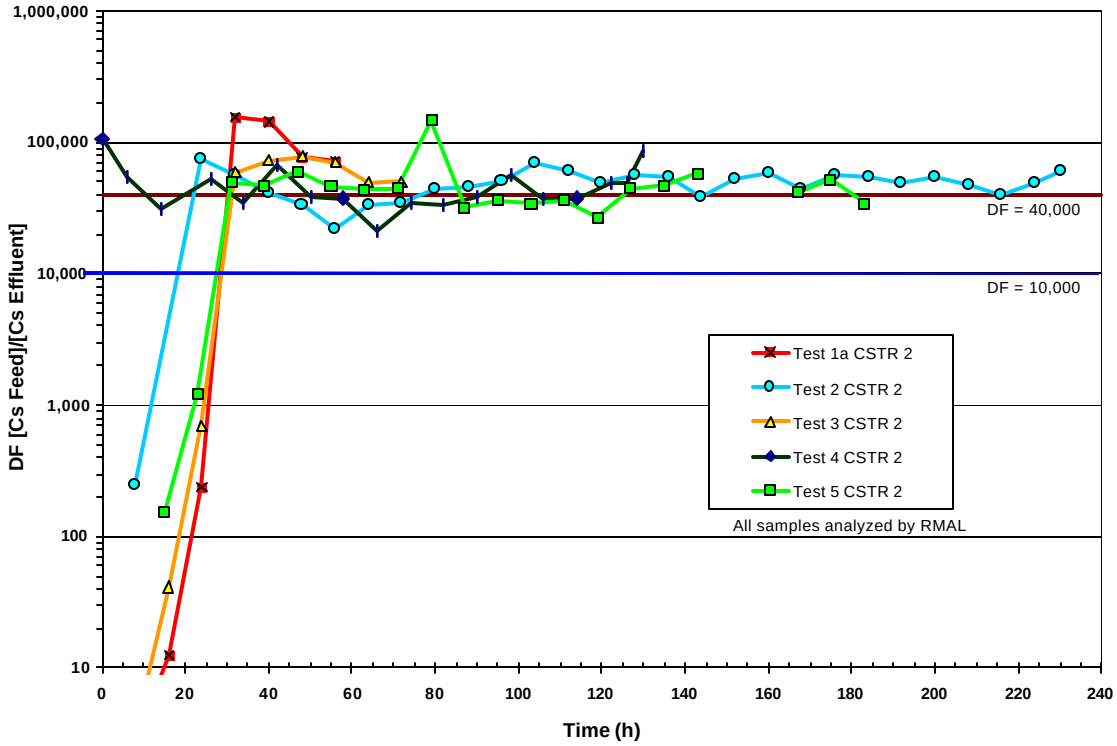

Fig. 41. Comparison of cesium DFs for all CSTR tests (CSTR 2).

5.2 STRONTIUM REMOVAL

Monosodium titanate (MST) is the sorbent employed in the STTP system for removing strontium and actinides (Pu, Np, and U) from the SRS high-salt alkaline waste at the SRS. The WAC goal for saltstone for ^{90}Sr is <40 nCi/g. The bounding separation goal for ^{90}Sr is to obtain a decontamination factor (DF) of 26 (96.15% removal).

Normal strontium traced with ^{85}Sr ($t_{1/2}$ = 64.8 days) was added to salt feeds in Tests 1a, 2, and 3, providing concentrations of 0.045, 0.046, and 0.047 mg/L, respectively. The ^{85}Sr concentrations in the salt feeds were 66, 84.5, and 68 µCi/L. In Test 2, sludge and catalyst (modified ECC system) were added to the salt feed. The sludge contained ~400 mg of normal strontium as $SrCO_3$, which increased the strontium concentration in the salt feed by 1.1 mg/L. To minimize repartitioning of ^{85}Sr between the strontium in the sludge and liquid phases, the ^{85}Sr and normal strontium should have been isotopically mixed before being added to the salt feed. However, the rate of isotopic mixing between the traced strontium and the sludge strontium was not known. Another problem in Test 2 was that both the sludge and the ECC system contained constituents that formed hydrous metal oxides when added to the salt feed that sorbed the strontium. The key constituents, known to sorb strontium in alkaline solution, were the hydrous metal oxides of iron, zirconium, neodymium, and manganese. When Test 2 was initiated, much of the strontium had already been removed by these sorbents in the feed tanks. This was confirmed by analyzing both filtered and unfiltered samples of salt feed. The strontium concentration for Test 2 remained almost constant in the filtrates from all three vessels during the test. The DF ranged between 30 and 40. Sludge and the ECC system were not used in Tests 1a and 3, and the total strontium was directly related to ^{85}Sr. The calculated effective specific activities were 1.47 and 1.84 mCi/mg, respectively.

The results of Tests 1a and 3 showed that the MST was very effective in removing the strontium. The strontium removal results for all the vessels are compared in Fig. 42, which gives RMAL (official) gamma-counting data. The shapes of the curves in the CSTRs for the two tests show good agreement, but the percentage and rate of strontium removal in Test 3 were greater. An increase in the strontium concentration occurred during the last two sample periods of Test 3 in both CSTRs due to the loss of MST feed. The staging effect of the CSTR vessels in the last 24 h of each test is apparent; the strontium concentration is higher in CSTR 1 than in CSTR 2. It took about 60 h in Test 3 to reach steady state for strontium removal in the SCT, but steady-state strontium removal was not quite achieved in the Test 1a SCT. The extended time necessary to reach steady state was necessary because both tests were started with process tanks inventoried with untreated process fluids.

Figure 43 shows the DFs obtained for ^{85}Sr strontium removal in the CSTRs and SCT in Tests 1a and 3. It took ~24 h to obtain a DF of 30 for strontium in the SCT in Test 3, and the DF_{Sr} slowly increased to about 60 at the end of the test. A DF_{Sr} of 26 was needed to reach the WAC standard for saltstone. Based on the data shown below, IITB52 antifoam did not appear to impede the sorption of strontium by the MST. It is speculated that the improved rate of strontium removal shown in Test 3 is the consequence of the improved mass transfer caused by increased mixer speed (from 600 rpm to 1200 rpm) used in all three of the process vessels for this test. The higher speed was used to evaluate the performance of the antifoam under more challenging conditions.

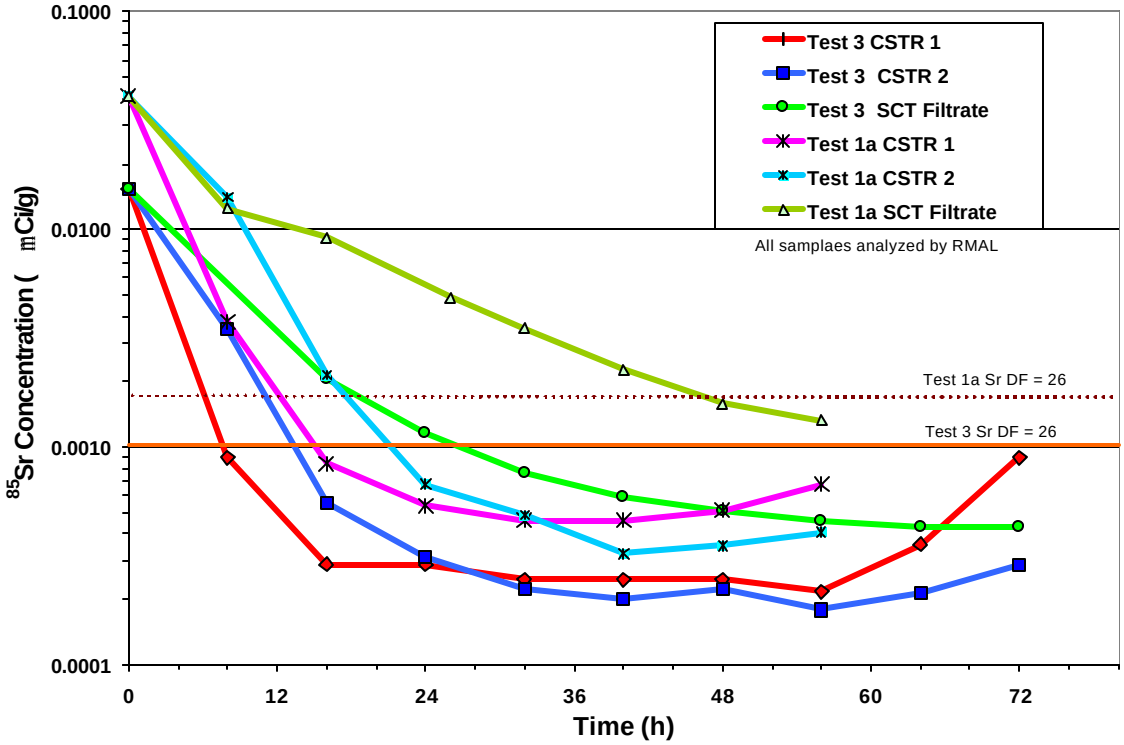

Fig. 42. Strontium concentrations during Tests 1a and 3.

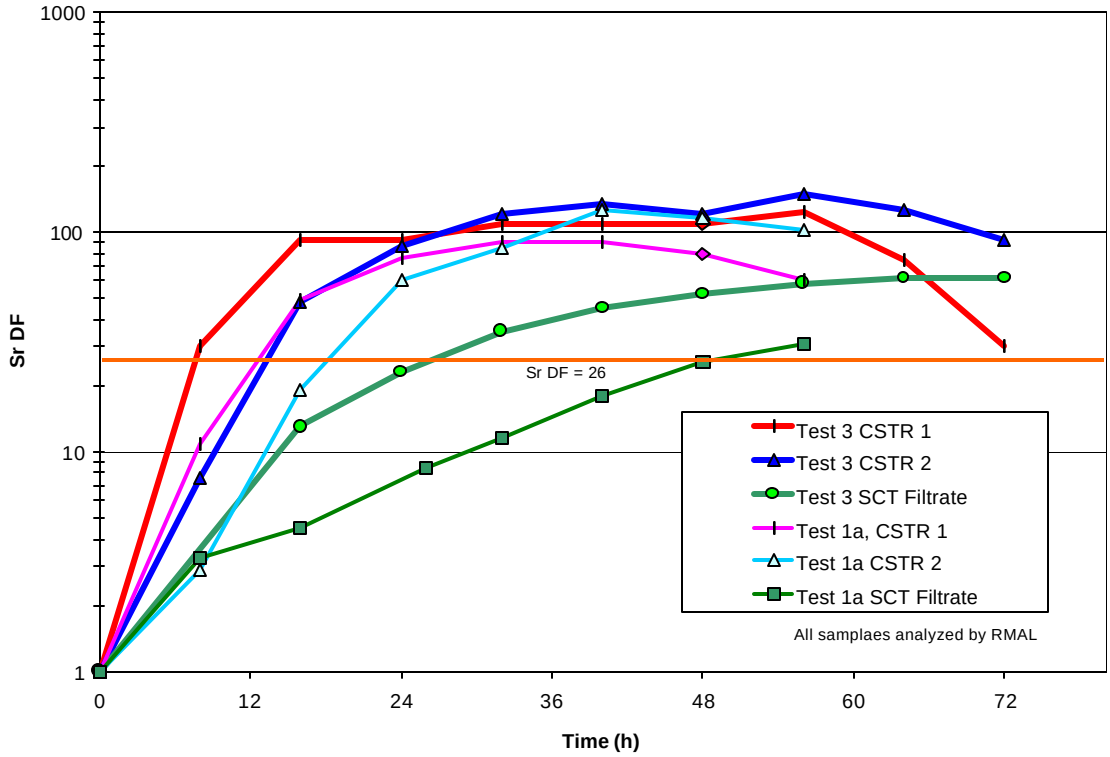

Fig. 43. Strontium DFs in system vessels during Tests 1a and 3.

5.3 URANIUM REMOVAL

The STTP system used MST to remove actinides (Pu, Np, and U) and strontium from the SRS salt waste. MST was supplied to CSTR 1 in each of the tests at a rate that provided a concentration in the slurry of about 500 mg /L. Uranium was added to the salt feeds in Tests 1a, 2, and 3 but was not used in Tests 4 and 5. The concentrations of uranium in the salt feed in Test 1a, 2, and 3 were 0.925, 1.01, and 0.99 mg/L, respectively, and the concentrations in the combined process fluid were 0.63, 0.70, and 0.68 mg/L. The vessel filtrate samples were analyzed by delayed-neutron counting of the ^{235}U content in the uranium.

As was pointed out in Sect. 5.2, sludge and catalyst (modified ECC system), were added to the salt feed in Test 2. Both the sludge and the ECC system contained constituents that formed hydrous metal oxides when added to the salt feed that sorbed the uranium. The key constituents were the hydrous metal oxides of Fe, Zr, Nd, and Mn. As with strontium, when Test 2 was initiated, most of the uranium had already been removed by these sorbents. This was confirmed by analyzing filtered and unfiltered samples of salt feed. The uranium concentration remained almost constant in the filtrates from all three vessels during the test. The DF ranged from 1.5 to 2.5.

Figure 44 compares the uranium results obtained in Tests 3 and 1a. Operating conditions for these two tests were similar except for the use of IITB52 antifoam and higher mixing speeds in Test 3. After 60 h of testing, the Test 3 DFs were 5 in the SCT, 3.5 in CSTR 2, and 2.3 in CSTR 1 as compared with DFs of 3, 2.5, and 2.3 for Test 1a. The superior uranium removal performance in Test 3 may be attributed to the higher mixing speed for the process vessels. There is no evidence that the presence of IITB52 had any effect on uranium removal performance.

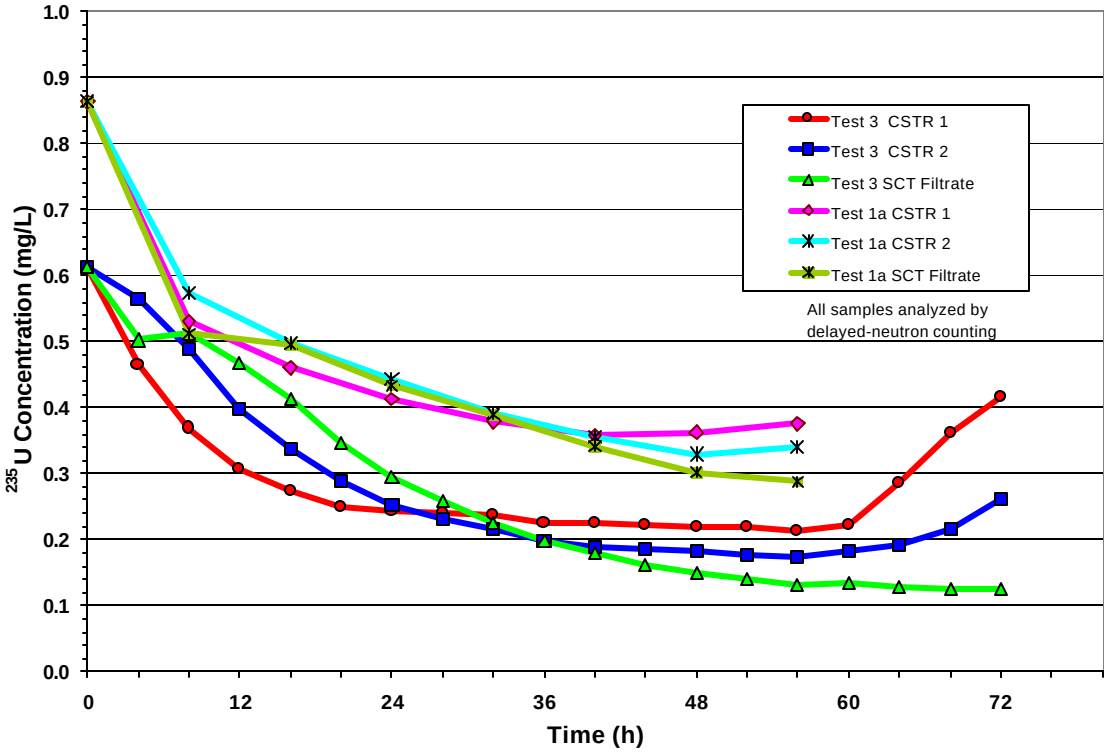

Fig. 44. Uranium concentrations during Tests 1a and 3.

A DF (RMAL) of 5 for uranium in the SCT was obtained at the end of Test 3, as shown in Fig. 45. This is indicative that if the other actinides (Np and Pu) had been present in the salt feed, they probably would have been removed to meet WAC standards. A DF_U of 2 was reached after 12, 18, and 22 h in CSTR 1, CSTR 2, and the SCT, respectively. Later in the test, as steady-state conditions were approached, the concentrations of uranium in the three process vessels were aligned in accordance with the expected stagewise behavior of the process; the concentration in CSTR 1 was greater than CSTR 2, and the lowest uranium concentration was in the SCT. The data demonstrate the importance of residence time in the sorption of uranium by the MST. As with strontium, there was a reduction in the uranium DF for CSTR 1 in the 64- to 72-h samples, and for CSTR 2 in the 68- and 72-h samples, due to the loss of MST flow to CSTR 1.

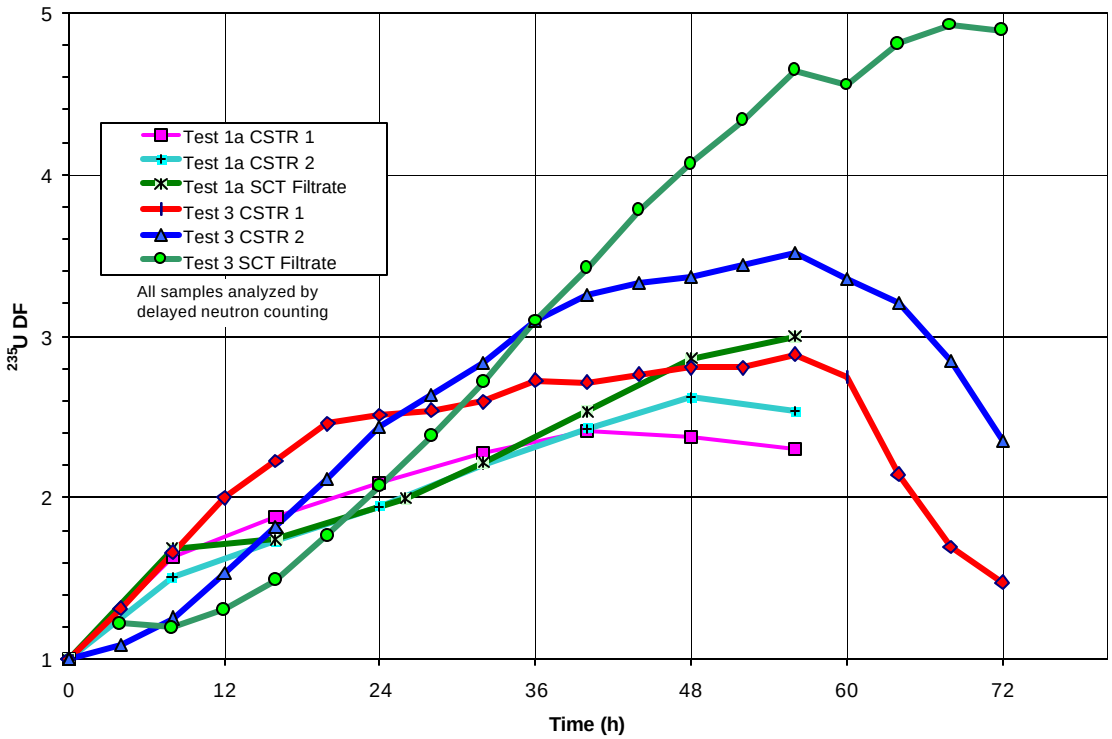

Fig. 45. Uranium DFs in system vessels during Test 1a and 3.

5.4 BEHAVIOR OF SOLUBLE TPB DURING DECOMPOSITION

A measurable level of soluble TPB was maintained for the duration of all 20-L CSTR tests. In addition, a similar level was maintained during Tests 4 and 5 under conditions of active TPB decomposition. Figures 46–48 show the soluble TPB concentrations in CSTR 1, CSTR 2, and the SCT filtrate for Tests 1a–5. The soluble TPB represents only a small fraction of the total amount of available TPB. Most of the available TPB is precipitated as NaTPB and mixed crystals of NaTPB-KTPB, both of which have limited solubility and are sources of the soluble TPB. Antifoam IITB52 was not added in Tests 1a and 2, but was used in Tests 3-5. Test 3 did not include the catalyst system for TPB decomposition, and there was no evidence of decomposition in the analysis of the filtrate samples. Test 3 data serve as a benchmark against which to compare soluble TPB concentrations under conditions where

TPB is not decomposing. It is apparent that very large swings can occur in the soluble TPB concentration in relatively short periods (60–100 ppm in 4 h) that cannot be explained. Figure 46 shows nondetectable levels of soluble TPB at the beginning of Tests 1a, 2, 3, and 5 because the CSTR 1 was initially filled with untreated salt solution. Shortly after startup, Test 1a, 2, 3, and 5 had measurable TPB levels. However, the Test 3 TPB concentrations were generally lower than the others for unknown reasons, but they could possibly be affected by the increased stirrer speed during the test. At about 60 h, the Test 3 concentration increased sharply to a level that was within the range of the Test 5 data. Results of Test 4 indicate measurable TPB at the beginning of the test because CSTR 1 was initially filled with process fluid (containing soluble TPB) from Test 3. Both Fig. 46 and Fig. 47 show measurable levels of soluble TPB throughout the test for CSTR 1 and CSTR 2; however, neither plot displays any well-defined trends. These data are all within the soluble NaTPB ranges (100–200 mg/L) reported by SRTC for similar concentrations and ratios of potassium to tetraphenylborate.[9]

Figure 48 shows the trends in soluble TPB for the tests conducted using the slurry concentration system. All but Test 4 exhibited an increase in soluble TPB from zero during the first 40–60 h, which is reflective of the startup conditions for these tests. From 80 h to the end of the tests, the soluble TPB generally remained in the 70- to 150-mg/L range for Tests 4 and 5. The Test 5 data showed a well-defined declining trend while processing the second batch of slurry in the 80- to 130-h time frame but did not follow a similar trend during the processing of the third and final batch. The Test 4 data did not show a particular trend in the 70- to 130-h time frame but remained consistently above 70 mg/L. The greatest difference was between the two tests without antifoam and the three tests with antifoam. In the two CSTRs, there was nothing to differentiate the various tests; however, in the SCT, Tests 1a and 2 showed a higher soluble TPB concentration than the other three, indicating that the antifoam may have an effect when the concentration of the insoluble TPB is taking place. This finding may be related to the problems with dissolving the NaTPB during water washing when the slurry contains the IITB52 antifoam.

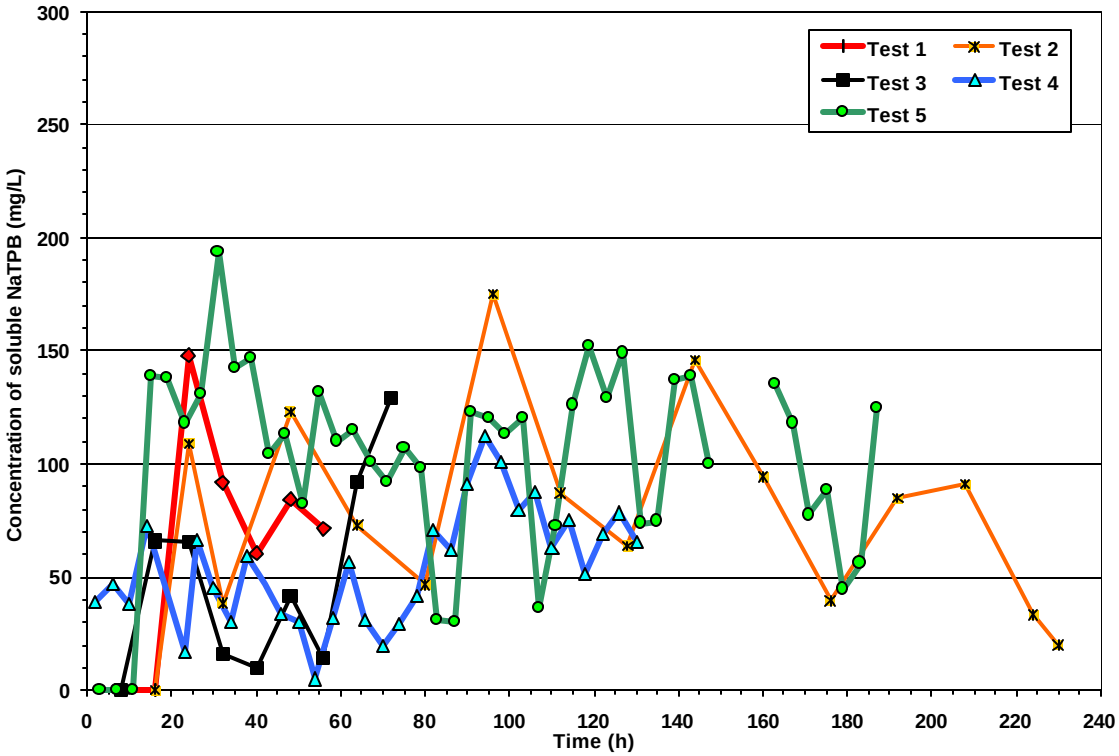

Fig. 46. Soluble TPB results for CSTR 1 in Tests 1–5.

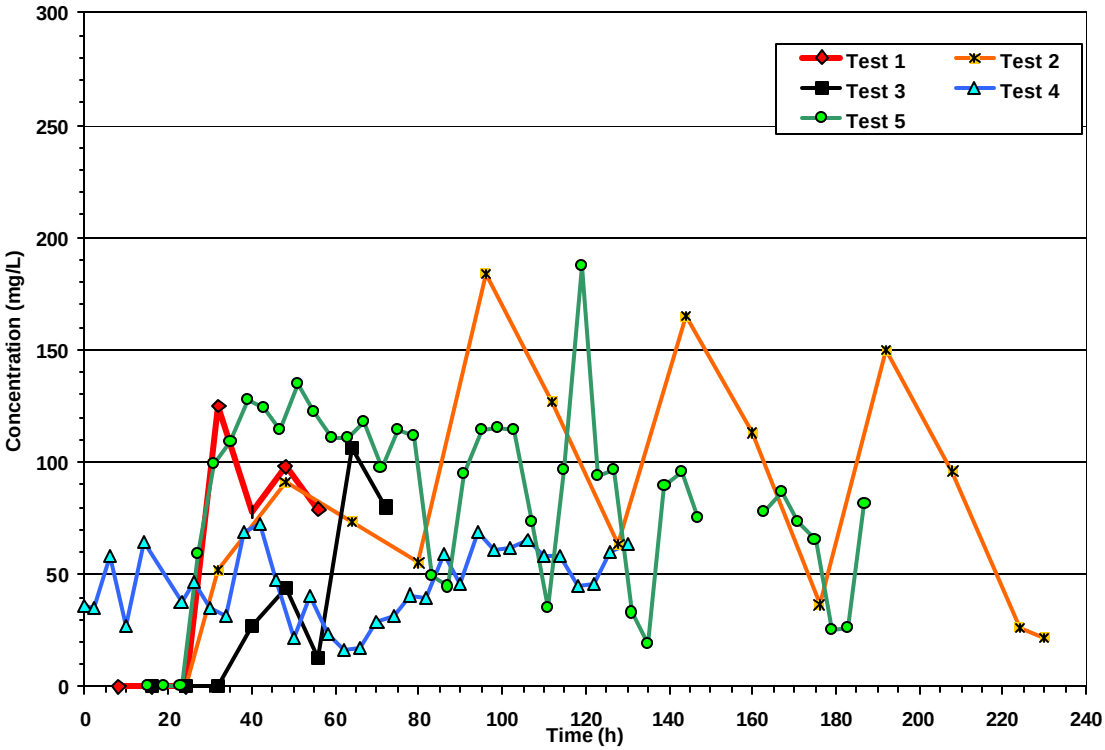

Fig. 47. Soluble TPB results for CSTR 2 in Tests 1–5.

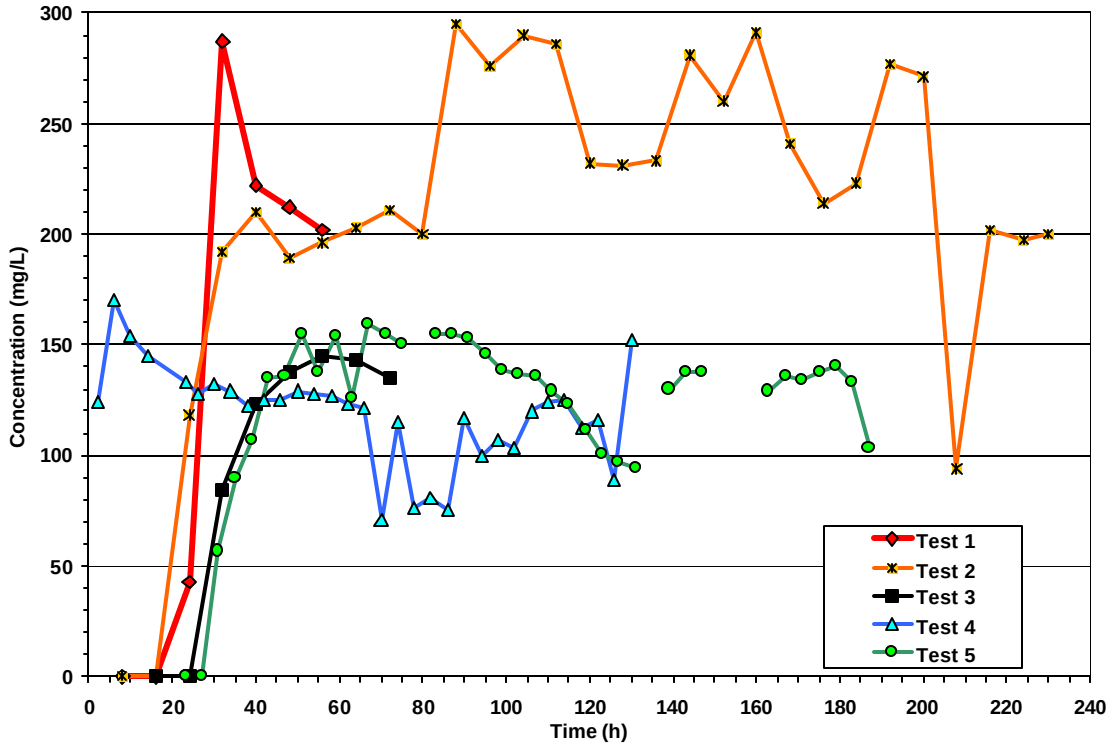

Fig. 48. Soluble TPB results for SCT filtrate in Tests 1–5.

5.5 TPB DECOMPOSITION AND BENZENE PRODUCTION

Benzene is produced in the STTP by catalytic decomposition of TPB and its decomposition products (3PB, 2PB, and 1PB). The four phenyl groups of the TPB molecule have the potential of forming four benzene molecules if TPB and all of its decomposition products decompose. Since 1PB was added intentionally and 2PB could not be detected due to HPLC interferences, the rate of TPB decomposition was determined principally by monitoring the concentration of soluble 3PB in the process fluids. The experimental goal for Tests 4 and 5 was to force TPB to decompose at a rate that would generate 2.5 mg/(L· h) benzene based on the generation of 3PB, which is equivalent
decomposes completely to benzene and boron products. The rates achieved in this testing were conservatively low due to limitations in the HPLC analysis. The 2PB concentrations could not be quantified, making it impossible to quantify the 2PB concentration and to account for the 3PB lost by decomposition to 2PB, although the 2PB concentration could be inferred from the boron analysis.

It has been reported that acceptable cesium removal (DF >10,000) is attainable using an excess TPB molarity of 30%.[12] Due to the potential for TPB decomposition, 60% molar excess of TPB is needed to ensure the required DF_{Cs} during plant operation.[13] The amount of TPB being decomposed at 2.5 mg/(L· h) benzene in the CSTRs is equivalent to a 5.2% loss of the excess TPB (balance of 54.8% total excess TPB).

5.5.1 Test Conditions for Catalyst Activation

In Tests 2, 4, and 5, a catalyst mixture was added to stimulate TPB decomposition and evaluate the impact of TPB loss on process performance. In Test 2, a modified ECC system and simulated sludge were added to the salt feed to encourage TPB decomposition. The active components of this catalyst system were Pd, Cu, tetraphenylborate decomposition product intermediates, Hg, and benzene. In addition, a number of other inorganic and organic species were added. The test, which was conducted at 25ºC, showed little evidence of TPB decomposition. However, there was evidence of decomposition of 3PB, 2PB, and 1PB, which were added in the salt feed as part of the catalyst system. For Tests 4 and 5, a simplified catalyst system (RCS) was designed using reduced palladium on alumina, that provided a 3× ECC concentration of palladium (3×2.60 = 7.8 mg/L) in the CSTR slurry in conjunction with $Hg(NO_3)_2$, benzene, and 1PB. The new catalyst system successfully initiated and sustained the TPB decomposition reactions during these two tests.

The components of the RCS catalyst system were added in conjunction with various other feeds to achieve the targeted rate of TPB decomposition. Palladium catalyst (5% on γ-alumina) and $Hg(NO_3)_2 \cdot H_2O$ were mixed with the MST/water slurry for delivery to CSTR 1, and 1PB was delivered in the NaTPB feed to CSTR 1. Benzene was added in Test 4 (but not in Test 5) via the NaTPB feed line to CSTR 1 during the 23- to 68-h time frame; however, it was then discontinued for the remainder of the test.

Startup and operating conditions for Tests 4 and 5 were significantly different. Test 4 was started with both CSTRs inventoried with process fluids remaining from Test 3. All the potassium and cesium were in the TPB precipitated forms, and there was an excess of 60% TPB as NaTPB. Recycle wash water from Test 3 was used at the start of Test 4, followed by the use of simulated wash water. The temperature of each of the slurries in the system vessels was maintained at 25ºC for the first 76 h of operation and was then "ramped" to 45ºC over the next 13 h and maintained at that temperature for the remainder of the test (~43 h). For the first 57 h of the test, the average slurry concentration for the palladium catalyst system was ~2.6× (6.8 mg/L); for the remainder of the test, the average was lower, ~1.9× (4.9 mg/L).

In Test 5, CSTR 1 was first filled with ~9 L of salt feed diluted with water to 4.7 *M* Na^+ before starting the test. The initial catalyst feed rate for Test 5 was about 18% higher than the target rate, and a level of 3.65× was reached after 36 h. The MST/catalyst feed rate was reduced by 25% at 35 h to reduce the catalyst level to 3×. At the reduced catalyst feed rate, it took about 60 h to lower the concentration to

3× in the CSTR process fluids. The TPB and the potassium reached equilibrium at about 36 h, and the excess TPB was maximized. The first filtrate sample for Test 5 to have a measurable amount of soluble TPB (139 mg/L) was the 15-h sample. At that time, the calculated excess TPB (total of insoluble and soluble NaTPB) was 38%. The RWW for Test 5 can be reviewed in Table 5 of this report.

5.5.2 Benzene Production in CSTR 1: Tests 4 and 5

Table 8 provides a summary of the notable benzene generation rates for Tests 4 and 5 process vessels and the percentages of TPB decomposition to 3PB at the peak benzene generation rates. The data show that (1) for the SCT, the targeted benzene generation rate based on the TPB to 3PB reaction was reached; and (2) the highest fraction of excess TPB being decomposed was 10.5% in CSTR 1. The conditions used for the tests significantly influenced the rate of decomposition. Figure 49 compares the CSTR 1 benzene generation rates for Tests 4 and 5, based on the TPB to 3PB reaction only. The data indicate that the benzene generation for Test 4 in the first 76 h was higher than for Test 5 in the same time frame. The higher decomposition activity for Test 4 may have been due to the addition of benzene as a component of the catalyst system. The indication of 3PB content very early in the Test 4 operation suggests the presence of decomposition products in the Test 3 fluids that were left in the vessels for nearly 2 months. Although no catalyst was added in Test 3, a small amount of TPB may have decomposed with time, possibly because of the ^{137}Cs activity. The effect of temperature on decomposition of TPB is very apparent in Test 4. After the temperature had been elevated in stepwise fashion to 45ºC, the catalyst system became more reactive and the rate increased sharply. The rate peaked at 5.9 mg/(L·h) at the end of the test, which is equivalent to ~10.5 % decomposition of the excess TPB. In contrast, the benzene generation rate for Test 5 in CSTR 1 increased only slightly and stayed in the range of 1.1 to 2.1 mg/(L·h), which is equivalent to 1.5–3% decomposition of the excess TPB. The 3PB analysis clearly showed that TPB decomposition in CSTR 1 was more rapid at 45ºC than at 25ºC.

Table 8. Summary of benzene generation for Tests 4 and 5

Test	Vessel	Temperature (°C)	Palladium concentration (mg/L)	Benzene generation rate range [mg/(L·h)]	Average benzene generation rate [mg/(L·h)]	Maximum excess TPB decomposed (%)
4	CSTR 1	25	2.6×	0.6–1.9	1.04	3.4
4	CSTR 1	45	1.9×	1.1–5.9	3.94	10.5
5	CSTR 1	25	3.0–3.65×	0.0–2.1	1.01	3.0
4	CSTR 2	25	2.6×	0.0–1.3	0.29	0.4
4	CSTR 2	45	1.9×	0.0–1.1	0.30	2.1
5	CSTR 2	25	3.0–3.65×	0.0–0.8	0.29	1.1
4	SCT	25	2.6-26×	0.0–4.0	1.86	0.15
4	SCT	45	7–22×	0.0–3.0	2.04	0.29
5	SCT	25	3.6–35×	0.0–6.5	1.40	0.24

While the increase in temperature was clearly the cause of the increased activity in CSTR 1 for Test 4, it is not clear what initiated the increased decomposition activity in Test 5. Several changes occurred in the 0- to 100-h time frame for Test 5 that were related to the RWW and antifoam feed systems (shown in Fig. 25). The source of the RWW changed during the test from that which was provided from Test 4 to that which was generated from Test 5; however, as discussed in Sect. 4.2.2, the change in composition was gradual rather than sudden. Recycle wash water from Test 4 [all of which contained IITB52 (ANWEM) and its degradation products] was used throughout the concentration of the first batch

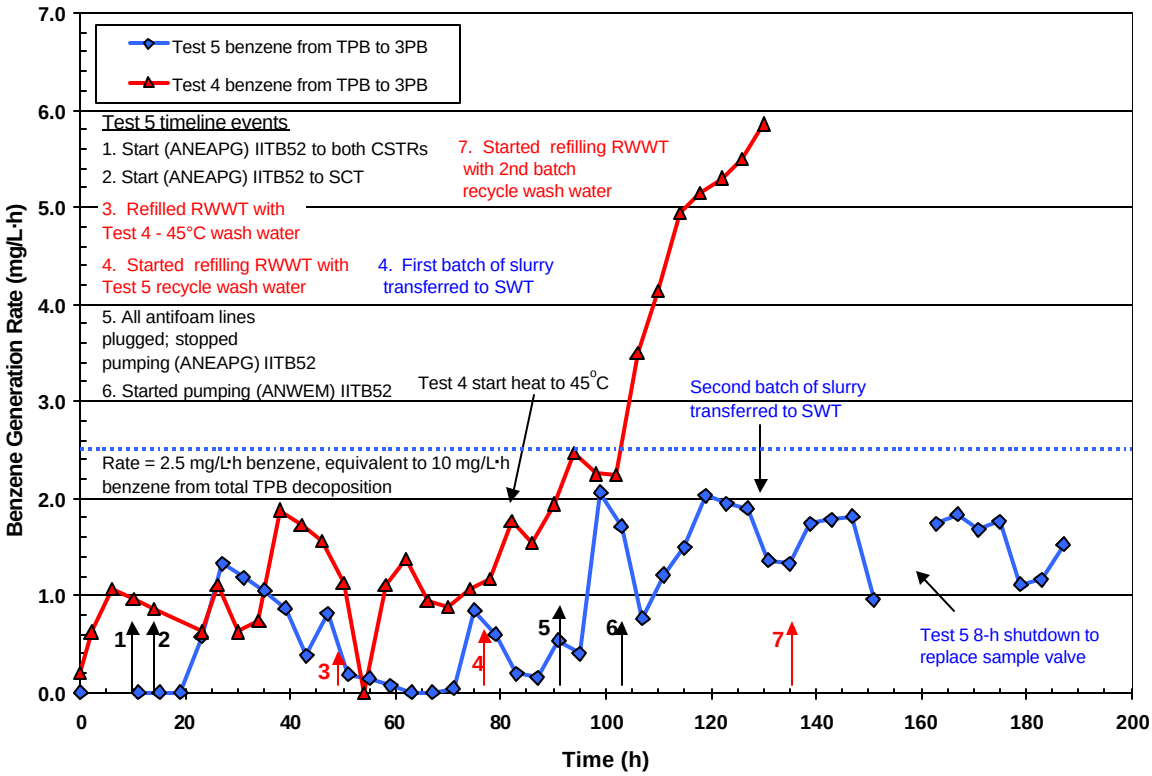

Fig. 49. Benzene generation in CSTR 1 in Tests 4 and 5.

of Test 5 slurry (while IITB52 antifoam, batch ANEAPG, was being added directly to CSTR 1). At 48 h, the wash water generated during the 45ºC phase of Test 4 was blended with the 25ºC wash water. The decomposition activity did not respond to this change and continued a slight downward trend for an additional 20 h into the test. The addition of wash water from Test 5 to the Test 4 wash water began about 76 h into the test. At that time, the wash-water holding tank (RWWT) still contained 55% of the Test 4 wash water. Just prior to the Test 5 wash-water addition, the 3PB content of CSTR1 increased from about 20 to 42 mg/L, making it appear as though this increase was not related to the change in RWW source. Over the next 17 h, Test 5 batch 1 wash water (containing IITB52 (ANEAPG) and possible degradation products) refilled the RWWT. Batch 2 slurry wash-water started entering the RWWT at about 134 h, and the batch 2 wash was not completed until the end of the test. If a step change in composition occurred in the RWWT, it would take about 24 h (three residence times) to reach 95% completion in CSTR 1 — and even longer times in CSTR 2 and the SCT. As the fraction of Test 5 washwater increased, the 3PB concentration increased in an unsteady manner but appeared somewhat level for the two CSTRs, albeit with erratic 25-mg/L changes, until the test ended. There was a far more significant increase in the 3PB concentration in the SCT that began at about 95 h; however, this is likely the consequence of the concentrating operation and the associated increase in palladium concentration.

IITB52 antifoam, batch ANEAPG, was used for the first 76 h of the test, although the feed rate was erratic due to plugging difficulties. The data indicate that the initial increase in 3PB concentration occurred prior to the change from batch ANEAPG to batch ANWEM of the antifoam. During a short time period while trying to reestablish the feed of antifoam, the 3PB concentration indicated a short-lived increase of about 25 mg/L. Shortly after the flow of a different batch of antifoam had been established at 98 h, the 3PB level for the CSTRs showed a short-lived decreasing trend followed by a slightly increasing, but fluctuating, trend.

The fluctuating concentration of 3PB made it difficult to determine the response to the changes described above. It can only be concluded that the gradual increase in the fraction of Test 5 wash water and the change from one batch to another batch of antifoam seemed to correspond with an overall unsteady increase in 3PB generation in the CSTRs. The increased decomposition activity could just as likely be the effect of the catalyst system with a lengthy activation period.

5.5.3 Benzene Production in CSTR 2: Tests 4 and 5

In Tests 4 and 5, the decomposition activity in CSTR 2 generally appeared to be lower than that obtained in CSTR 1. In Test 4 (Fig. 50), virtually no additional 3PB formation (or benzene generation) occurred in CSTR 2 during the first 90 h. This was followed by a slight rise in decomposition activity when the temperature was elevated and a subsequent fall in the concentration for the rest of the test. Similarly, in Test 5, very little additional benzene was generated in CSTR 2 during the first 90 h, followed by a small increase in decomposition activity for the remainder of the test. As discussed in Sect. 5.5.2, the slight increase in decomposition activity in CSTR 2 may have been the result of the catalyst system, the changing composition of the RWW, the change in antifoam batch source, or a combination of these three factors. In both tests, the data indicate that the TPB decomposition rate dropped off significantly in CSTR 2, indicating several possible conditions: (1) increased rate of decomposition of 3PB to 2PB in CSTR 2, (2) decreased catalyst concentration due to poor transport of palladium/alumina slurry to CSTR 2, or (3) deactivation of the catalyst system due to possible palladium oxidation at elevated temperatures. An examination of Fig. 30 shows that the rate of 3PB decomposition to 2PB did not increase, because the gap between the boron concentration and the calculation of the expected boron from soluble TPB, 3PB, 1PB and phenol did not increase during this time.

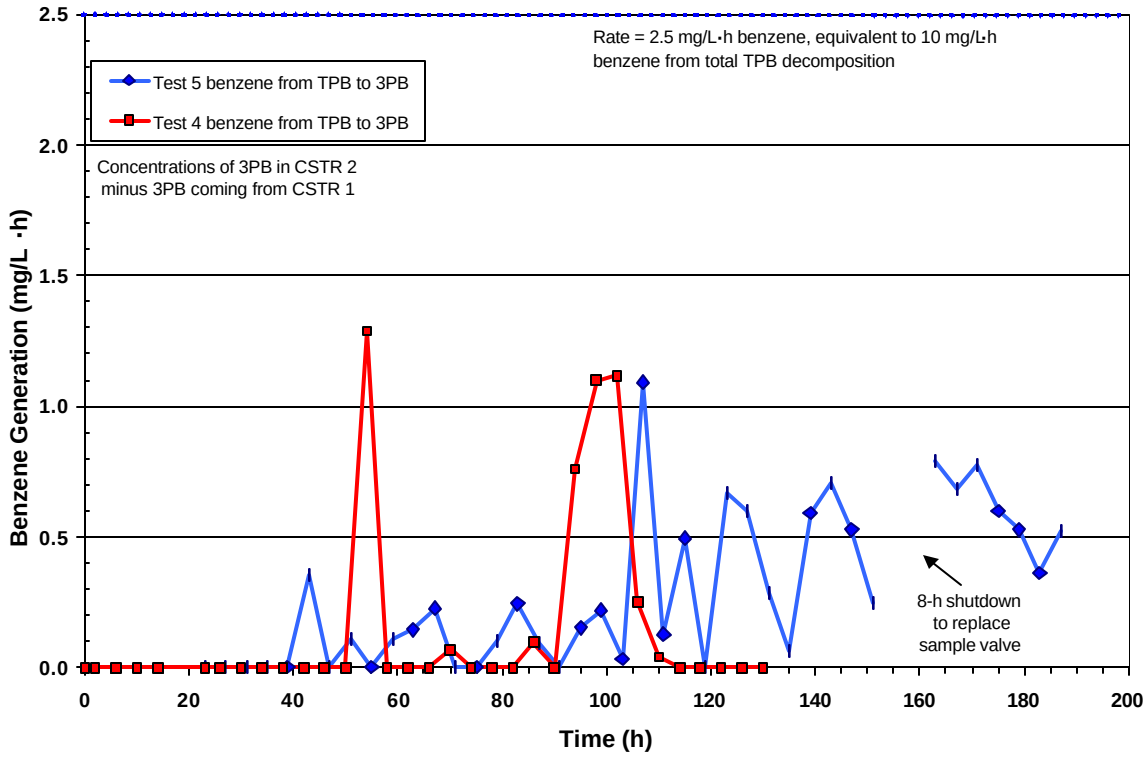

Fig. 50. Benzene generation in CSTR 2 in Tests 4 and 5.

5.5.4 Benzene Production in the SCT and the Combined System: Tests 4 and 5

TPB decomposition activity in the SCT appeared to be significant in both Test 4 and Test 5. It is speculated that the increased activity was at least partially due to the increase in the concentrations of insoluble components of the catalyst system. In the SCT in each test, the palladium concentrations increased to the range of 10 to 35× ECC as the sludge solids were concentrated to 10 wt % (assuming uniform slurry composition and no holdup of palladium in the CSTRs). Figure 51 shows that in Test 5 little or no additional benzene was generated in the SCT during the first 87 h of the test. As the second batch of slurry solids for Test 5 was concentrated, the benzene generation rate increased to 6.5 mg/(L· h), easily surpassing the test goal of 2.5 mg/(L· h). The amount of excess NaTPB in the SCT slurry being decomposed at the benzene generation peak was only 0.24% (see Table 8). After the second batch of slurry concentrate had been transferred to the SWT, the decomposition rate dropped to 1.3 and 3.5 mg/(L· h) while the third batch of slurry was being processed. Any influence on the decomposition rate by the changing composition of the RWW would probably be overwhelmed by the increased palladium concentration. The initial increase in decomposition activity while processing the second batch of slurry precedes the change in antifoam batch (at 98 h) by only a few hours. However, even if the antifoam batch change coincided exactly, such an immediate impact by the antifoam would not be expected.

In Test 4, the intentional addition of benzene as a component of the catalyst system and the presence of decomposition products in the Test 3 fluids could also have influenced TPB decomposition activity during the processing of the first batch of slurry. The benzene generation rate in the SCT was only slightly detectable until 26 h. Afterward, the plot showed an unsteady increase in benzene generation while the first batch of slurry was being concentrated. The rate subsequently fluctuated at a relatively high level for the next 20 h. At 75 h, about 70% of the Test 4 SCT slurry was transferred to the SWT. The benzene generation rate for the more dilute slurry in the SCT in the 80- to 94-h time frame

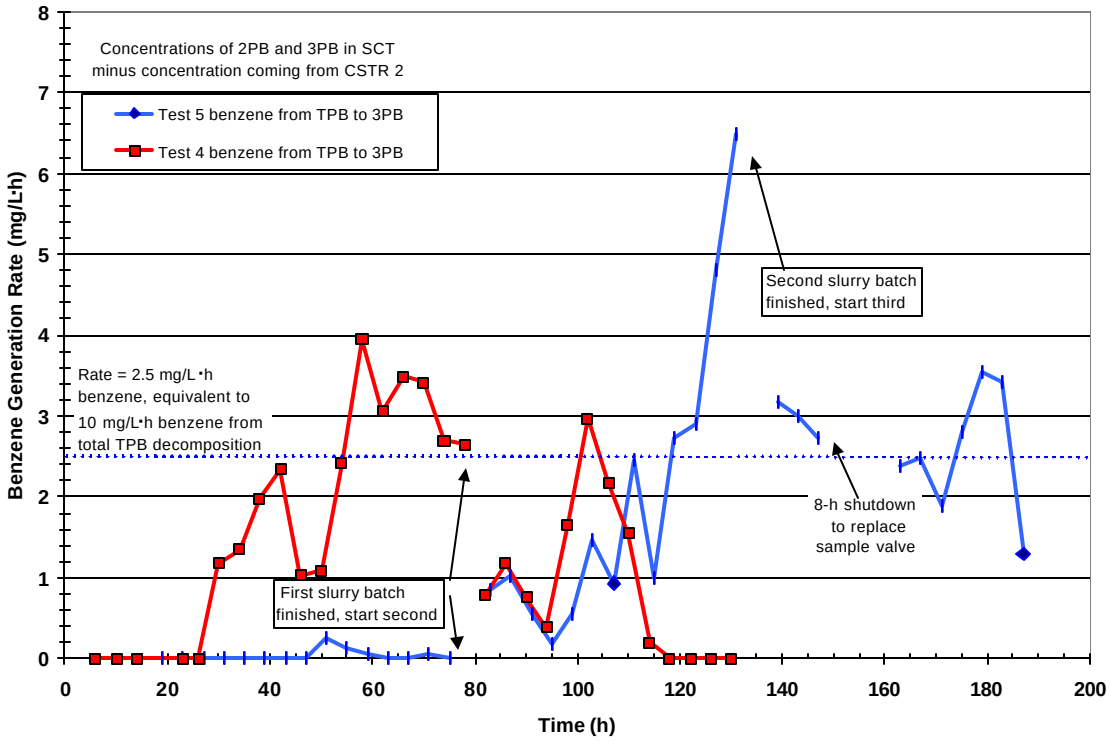

Fig. 51. Benzene generation in concentration system in Tests 4 and 5.

decreased despite the fact that the temperature of the tank had already reached 45ºC. The rate then increased slightly and subsequently dropped to a low level where it remained until the test ended. The decrease in 3PB concentration may have been due to the increasing decomposition of 3PB to 2PB. This could not be verified due to the limitations in 2PB analysis, although indications from the difference between the boron analysis and calculations of the expected boron concentration from soluble TPB, 3PB, 1PB, and phenol measurements suggest that this was not the case. Another possible reason for the decreased decomposition activity in this case would be the possible deactivation of the catalyst system caused by palladium oxidation at increased temperature. The percentage of the excess NaTPB in the SCT slurry being decomposed at the benzene generation peak for Test 4 was only 0.15% (see Table 8).

Figure 52 shows the cumulative benzene generation (based only on 3PB generation) for Tests 4 and 5 with the CSTRs and SCT taken as a whole. As is evident, the minimum benzene generation rate of 2.5 mg/(L· h) was met or exceeded for a major fraction of the operating time for both tests. Although the peak benzene generation rate for Test 5 was higher than that for Test 4 near the end of the test, the average rate appears to be significantly greater for Test 4.

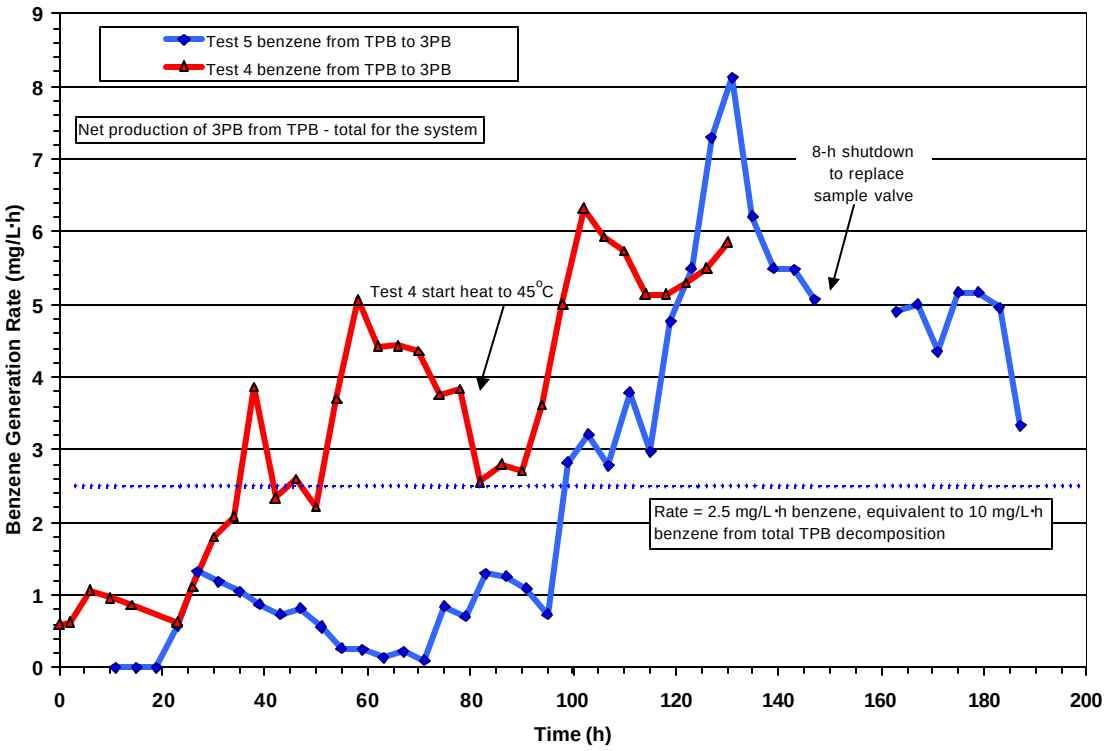

Fig. 52. Cumulative benzene generation for CSTR system in Tests 4 and 5.

5.5.5 Comparison with 1-L CSTR Test Results

A series of 1-L CSTR tests were conducted by Barnes at SRTC[14] to evaluate TPB decomposition reactions under varying experimental conditions and to define the catalyst system to be used in Tests 4 and 5 described in the present report. The decomposition behavior experienced in Tests 4 and 5 was comparable to smaller-scale CSTR results. Although significant differences existed in equipment design and size, Test 5 by Barnes et al. was conducted under conditions similar to those used for the 25°C portion of Tests 4 and Test 5 of the 20-L system. A notable difference in the tests was the consistent use of benzene as a component of the catalyst system for the 1-L test by Barnes et al. Benzene was not added

during Test 5 of the 20-L system and was used for only a short duration of Test 4. The 3PB concentration profile for the 1-L CSTR indicated a maximum concentration of about 60 mg/L, as compared with about 50 mg/L and 80 mg/L for CSTR 2 in Tests 4 and 5, respectively. The peak 3PB level was reached sooner for the 1-L test possibly due to the additional benzene used continuously as a component of the catalyst system. Similar behavior was noted in the comparison of Test 4 and 5 results, where increased 3PB generation for Test 4 was observed during the time that benzene was being added. The concentrate tank for the 1-L system reached a maximum 3PB concentration of about 190 mg/L at 80 h. The SCT for Test 5 of the 20-L system reached about 135 mg/L 3PB while processing the second batch of slurry in the 76- to133-h time frame. Calculated benzene generation rates for the 1-L system included benzene from the 3PB and 2PB formation, while the 20-L results were calculated using the 3PB formation only. Therefore, the estimated benzene generation rates for the 20-L system were consistently lower than those for the 1-L system. For example, the maximum benzene generation rate for the concentration tank in the Barnes et al. test was about 11 mg/(L· h), while the maximum rate for the SCT in Test 5 of the 20-L system was 6.5 mg/(L· h). If the Barnes et al. test had not included the 2PB in the estimate, the calculated benzene generation rate would have been about 30% lower, or about 7.8 mg/(L· h). With the capability to quantify 2PB, the benzene generation results for the 20-L system would have been significantly higher and in better agreement with the 1-L CSTR results. This is supported by the plots in Sect. 4.2.4, showing dissolved boron as compared with calculated boron levels based on TPB, 3PB, and 1PB. The separation in these profiles (Figs. 29, 30, and 31) indicates the presence of a significant level of 2PB.

5.5.6 Summary of Findings from Decomposition Studies

It is apparent from the 3PB results for Tests 4 and 5 and the SRTC batch tests that the TPB decomposition process is complicated and is sensitive to the palladium and benzene concentrations, time, and temperature, and possibly also to antifoam and the decomposition products of antifoam and TPB. In Test 4, which was performed at 25ºC, the use of aged process fluids from Test 3 and the addition of benzene as a component of the RCS catalyst system seemed to enhance the decomposition of TPB, especially in the SCT. Increasing the slurry temperature to 45ºC accelerated the decomposition in CSTR 1. However, in Test 4 there was very little additional 3PB generation in CSTR 2 and the SCT, indicating possible deactivation of the catalyst or increased decomposition of 3PB to 2PB, although the analytical data for boron suggest that this was not the case. In Test 5, most of the decomposition activity occurred in CSTR 1 and the SCT, but the additional residence time in CSTR 2 allowed for a small amount of additional decomposition activity. The increase in decomposition activity in the CSTRs for Test 5 could have been related to the changes in RWW composition, the change in antifoam batch source, and/or a prolonged activation period for the catalyst system. The fluctuation in the data and the time relationship of these changes complicated the ability to narrow the cause to a single factor. In the SCT for Test 5, a significant amount of additional TPB decomposition occurred, possibly due to the increased concentration of the palladium component of the catalyst system.

Reasonable agreement was obtained between the results of the 1-L CSTR testing conducted by SRTC and the 20-L CSTR results, although the comparison was limited by the inability to quantify 2PB concentrations in the 20-L testing. Certainly, in considering additional tests, more data are needed to evaluate the effect of operating conditions on TPB decomposition, with special emphasis on the generation of 2PB. A key goal of Tests 4 and 5 was to maintain the cesium DF while the palladium catalyst system was actively decomposing TPB to 3PB at the rate of 2.5 mg/(L· h). Both tests were very successful from this perspective.

5.6 SLURRY WASHING AND TPB RECOVERY

The goal of water washing the concentrated slurries in the five CSTR tests was to evaluate the ability to recover unreacted NaTPB from the slurry for recycle. NaTPB is soluble under dilute conditions, while KTPB and CsTPB are insoluble. In the closed-loop CSTR tests, the RWW containing the recovered TPB was returned to CSTR 1 for enhanced TPB utilization. The most successful effort in recovering the TPB by water washing provided only ~30% of the needed TPB concentration of 0.033 mol/L in the wash water.

An accountability analysis of potassium, cesium, and TPB for all the CSTR tests was conducted to determine the available moles of TPB in each batch of concentrated slurry that was washed (see Table 9). The analyses accounted for the moles of potassium, cesium, and TPB in the CSTRs and SCT before each test and, subsequently, the moles of each constituent added during each test. The analysis also accounted for the moles of constituents that were transferred to the SWT and the moles left in the SCT and associated cross-flow filtration system. In Test 1a, for example, all of the slurry in the SCT and its cross-flow filtration system and in both CSTRs was transferred to the SWT and washed. In Test 1a, as well as in Tests 2 and 3, the method of starting the test was to first fill the CSTRs with the 4.7 *M* Na^+ salt feed (an additional 3 L was added to the SCT). Consequently, the initial batches of concentrated slurry had TPB/(potassium + cesium) mole ratios that were much lower than any subsequent batches prepared, as in Tests 2 and 4. As a result, the initial batches of concentrated slurry for these tests had relatively low amounts of available TPB. Mole accounting for Test 1a revealed that the concentrated slurry contained 1.677 mol potassium, 0.0124 mol cesium, and 2.173 mol TPB. The total quantity of available TPB was 0.484 mol. The concentration of TPB in the slurry wash water was analytically determined by HPLC to be 0.0047 mol/L. The 12.3 L of wash water contained 0.058 mol TPB, or 12% of the available TPB in the slurry concentrate. If all the available TPB had been recovered in the Test 1a slurry batch, its concentration in the wash water would have been 0.039 mol/L.

Table 9. NaTPB recovery in slurry washing process in CSTR tests

Test	Wash cycle	Time (h)	Wash rate (mL/min)	Available TPB[a] (mol)	RWW[b] (L)	TPB Recovered (mol)	TPB[c] (mol/L)	Recovery[d] (%)
1a	1[e]	16	10	0.48	12.3	0.058	0.0047	12
2	1	31	10	0.86	18.6	0.072	0.0039	9
2	2	28	15	0.63	25	0.115	0.0046	18
2	3	43	8	0.76	20.6	0.148	0.0072	19
2	4	44	5	0.69	13.2	0.138	0.0105	20
3	1[f]	32	15	0.33	28.8	0.095	0.0033	29
4	1[g]	30	20	1.09	35.4	0.117	0.0033	11
4	2[g]	29	20	1.11	34.6	0.111	0.0032	10
5	1	24	20	0.48	28.8	0.055	0.0019	11
5	2	24	20	0.64	28.8	0.021	0.0007	3

[a]Moles of excess TPB as NaTPB in batch available to be dissolved by water washing.
[b]RWW = recycle wash water.
[c]Testing goal was to obtain enough TBP in RWW to provide a 60% excess (~0.033 mol/L).
[d](mol TPB recovered)/(mol available TPB in batch).
[e]Recycle wash water used in Test 2.
[f]Recycle wash water used in Test 4.
[g]Recycle wash water used in Test 5.

The initial batch of slurry concentrate that was water washed in Test 2 contained ~0.86 mol of available TPB. This quantity was higher because more TPB was added to CSTR 1 in this test than in Test 1a. The water-washing rate used for the initial batch of Test 2 slurry was 10 mL/min, and 18.6 L of RWW was collected with a TPB concentration of only 0.0039 mol/L. Only 9% (0.072 mol) was recovered. Similar analyses indicated that 18, 19, and 20% of the available TPB were recovered in the next three batches, respectively. These washes were twice as effective in removing the TPB, but the recoveries for Test 2 were ineffective overall. Slightly better recovery was obtained in Test 3. The mixing speed (1300 ± 100 rpm) used in Test 3 was about twice that used in Tests 1a and 2; IITB52 was used to control foam in Tests 1a and 2. Analyses showed that 0.33 mol of TPB were available for dissolution and ~29% (0.095 mol) was recovered.

The analyses of the washed batches in Test 4 found that the recoveries of TPB were also inefficient, with only 10 and 11% recovered. As in Test 3, antifoam IITB53 was used in Test 4. As compared with Test 3, the TPB recovery in Test 4 was significantly lower, probably due to using a lower mixing speed (650 ± 50 rpm) than that used in Test 3. The recoveries in Test 4 were similar to those obtained in the first batch of Test 2, but lower than those achieved for the other three batches in Test 2. Much lower wash rates and greater residence times were used in two of the four Test 2 batches than were used in Test 4, which may have enhanced efficiency of TPB recovery in Test 2. Of the washing tests performed, the washing conditions for the two batches of slurry in Test 4 were more comparable to those employed in the second wash cycle in Test 2 from the standpoint of available TPB (0.63 vs 1.09 mol), washing time (28 vs 30 h), washing rate (15 vs 20 mL/min), and mixing speed (both 650 ± 50 rpm). Although the volume of RWW collected in Test 4 (~35 L) was larger than that collected from the second batch of slurry in Test 2, the same amounts of TPB were recovered. Figure 53 indicates that for an equivalent washing volume, all the TPB concentrations for the second wash cycle in Test 2 were much higher than those obtained for the Test 4 batches. This indicates that the addition of IITB52 in Test 4 may have interfered with the TPB recovery.

Three batches of concentrated slurry were produced in Test 5, but only the first two were water washed. Again, the recoveries were ineffective; about 11% of the available TPB was recovered from the first batch and ~3% from the second. Table 10 shows that the washing conditions for Test 5 closely resemble those used in Test 4 and the second batch in Test 2. IITB52 was used in Tests 4 and 5. The results for the first batch in Test 5 and the two batches in Test 4 indicate very similar washing efficiencies—in the range of 10 to 12%. Although the washing conditions for the second slurry batch in Test 5 were also very similar, the results showed the poorest TPB recovery (i.e., 3%). TPB recovery for Test 2 second batch, at 18%, was significantly higher than the recoveries achieved in Test 4 and 5 slurry washes. These results reinforce the likelihood that IITB52 interfered with the TPB recovery.

The concentrations of NaTPB in the wash water during the slurry washings are compared in Fig. 53. Although the recovery was generally low in every case, the trends of these data show the importance of the washing parameters. The low concentrations of NaTPB in the wash water may be indicative of inefficient mixing, which in turn caused poor mass transfer and NaTPB dissolution rates. Several tests of TPB dissolution were conducted at SRS[15] in which slurries that had been produced by precipitation of a standard 4.7 *M* sodium simulant with 0.0125 *M* potassium were concentrated to 10 wt % using a cross-flow filter system. Laboratory batch-mixing tests were performed for one slurry without antifoam, while three other tests were performed with three different antifoams—one of which was IITB52. The results showed that about 60% of the excess TPB was recovered and the maximum concentration of NaTPB in the wash water was 0.041 *M*. When IITB52 was used, only 12.7% of the excess NaTPB was removed and the maximum NaTPB concentration was 0.0058 *M*. These large differences between the tests with and without antifoam were not observed in the 20-L system tests. The reason for the differences probably relate to the less than ideal mixing in the SWT, as evidenced by the increased recovery in Test 3 when the agitation was increased. From the plots in Fig.53, it is also notable that the NaTPB wash water concentrations in Test 2 increased from the first to the fourth batch of concentrated slurry washed. The higher TPB concentrations resulted from lower wash rates and longer mixing times. About 16 to 51%, more NaTPB was recovered in the third and fourth batch washes than

was removed from the first two batches where the wash rate was higher and the wash time was shorter. This is also indicative of poor mass transfer in the RWWT.

Further insight can be gained by plotting the nitrite concentration in the wash water versus the washing volume. As Fig. 54 shows, the slurry washings with and without antifoam were different. The nitrite was removed by dilution, so the plot should be linear on a semilog plot. Table 10 gives a listing of the slopes for the nitrite removal in the slurry washings. The calculated starting nitrite concentrations are all about the same for the slurries of Test 2, Test 3, and the first Test 4 wash. The starting nitrite concentrations for the two Test 5 washes and the second Test 4 wash were somewhat higher. The slopes of the curves for Test 2 versus those for Tests 3–5 indicate a difference in the conditions for the washes. Tests 3-5, all of which used the IITB52 antifoam, had similar slopes. It is possible that the antifoam caused a change in the properties of the slurry that made it difficult to wash out the nitrite and recover the TPB. The lower wash rates and higher residence times used in Tests 1a and 2 may have enhanced nitrite removal. Rheology testing of the slurries at SRS[14] showed that the addition of IITB52 to a washed 10 wt % slurry reduced the yield stress, based on a Bingham model, by a factor of 5. This indicates that the slurry is easier to pump or stir than one that contains no IITB52; however, it is not known whether the rheology difference could have influenced TPB recovery.

Overall, recovery of TPB from the concentrated slurry batches for all the tests was not as efficient as expected. None of the collected RWW approached the 0.033 *M* TPB needed to provide a 60% excess. The batch washing results for all the tests indicated that three conditions seem to enhance TPB recovery: (1) lower wash rates, providing longer residence times; (2) higher mixing speed; and (3) absence of IITB52. However, if a higher mixing speed is used, antifoam must be used.

Table 10. Nitrite removal wash results for slurry washing in Tests 2–5

Test	Wash cycle	Wash rate (mL/min)	Washing volume (L)	Starting nitrite concentration[a] (mg/L)	Slope of exponential curve
2	1	10	18.6	15,219	–0.1734
2	2	15	25.0	12,893	–0.1317
2	3	8	20.6	15,070	–0.1454
2	4	5	13.2	15,455	–0.1582
3	1	15	28.8	15,070	–0.1227
4	1	20	35.4	16,250	–0.1094
4	2	20	34.6	21,302	–0.1158
5	1	20	28.8	18,659	–0.1251
5	2	20	28.8	19,019	–0.1175

[a]Calculated from the equation for best-fit line for each wash.

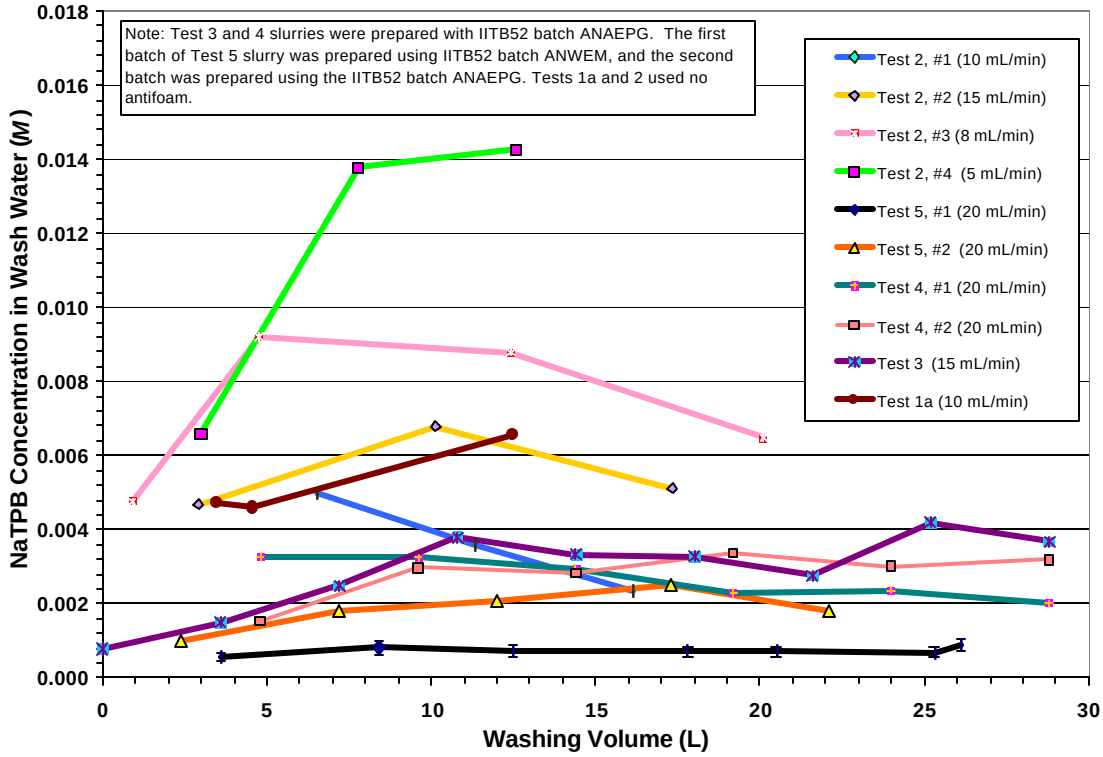

Fig. 53. NaTPB concentrations in slurry wash water during slurry washing in Tests 1–5.

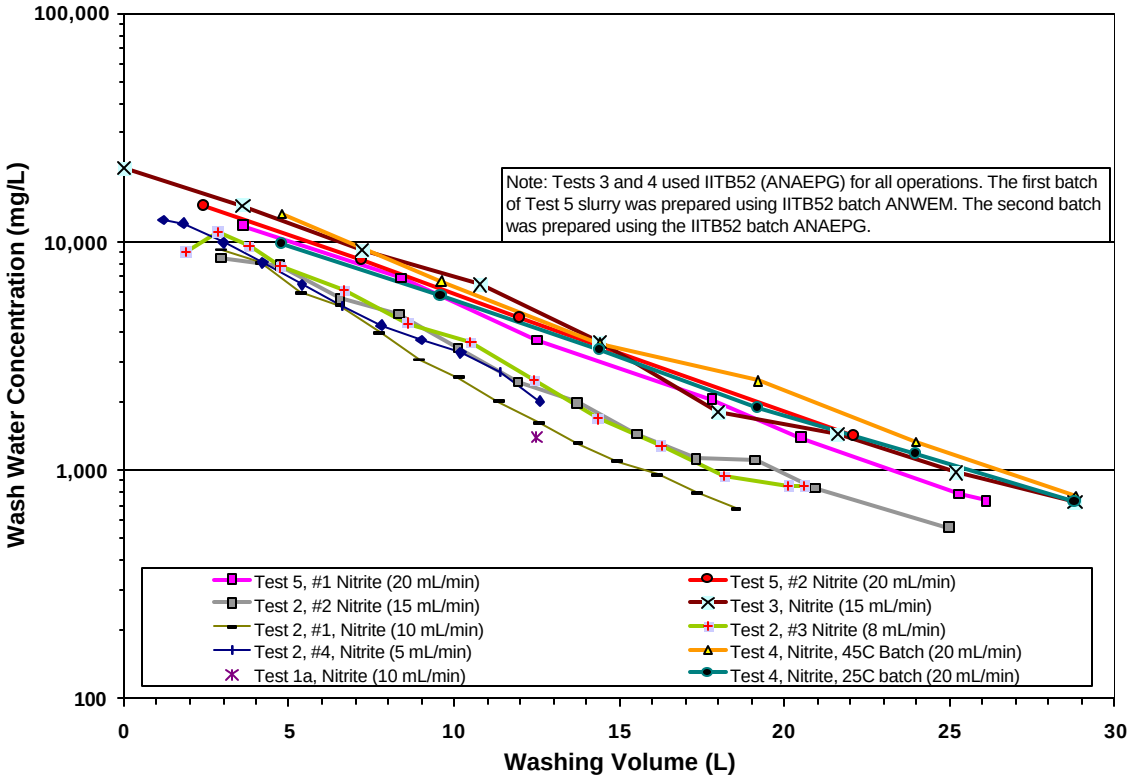

Fig. 54. Nitrite concentrations in slurry wash water during slurry washing in Tests 1–5.

6. CONCLUSIONS AND RECOMMENDATIONS FOR THE 20-L CSTR TEST PROGRAM

Overall, during the five tests there were no difficulties associated with the chemistry, TPB decomposition, antifoam, or operation that prevented the system from attaining the required DF in the slurry concentration filtrate product, or in either of the two CSTRs. System shutdowns for equipment replacement lasting up to 8–10 h caused no loss in DF. Shutdowns of up to 2 months with the CSTRs remaining inventoried with TPB slurry between Test 3 and Test 4 resulted in no loss of DF. These and other upset conditions that occurred during operations did not cause loss of DF, indicating a robustness needed to ensure success in large-scale operations.

Data comparison for all of the tests indicated that the antifoam had no effect on radionuclide removal. In each test, the required DF for cesium was achieved. For Test 3, which included antifoam, the CSTR DF profiles were almost identical to those for Test 1a, where no antifoam was used. The DFs obtained for ^{85}Sr removal in the CSTRs and SCT in Tests 1a and 3 exceeded the strontium DF of 26 needed to reach the WAC standard for saltstone. The uranium results obtained in Tests 1a and. 3 were similar, with both tests meeting the removal requirements for saltstone. The data also indicated that the improved rate of strontium and uranium removal shown in Test 3 was the consequence of the improved mass transfer caused by increased mixer speed (600 to 1200 rpm) used in all three of the process vessels for this test. The higher speed was used to evaluate the performance of the antifoam under more challenging conditions. When the antifoam agent was used, the agitation speeds in the CSTRs could be increased without foam production, improving mass transfer between the solution and MST and allowing for enhanced strontium and uranium removal.

A key goal of Tests 4 and 5 was to maintain the cesium DF while the palladium catalyst system was actively decomposing TPB to 3PB at the rate of 2.5 mg/(L·h). Both tests were very successful from this perspective. It is apparent from the 3PB results that the TPB decomposition process is complicated and is sensitive to the palladium concentration, reaction time, temperature, TPB decomposition products, and possibly antifoam decomposition products and RWW composition. In Test 4, at 25ºC, the use of aged process fluids from Test 3 and the addition of benzene seemed to enhance the decomposition of TPB to 3PB. Increasing the slurry temperature to 45ºC appeared to accelerate the decomposition in CSTR 1. The data indicated a reduction in decomposition activity in CSTR 2, possibly due to poor catalyst transfer from CSTR 1 to CSTR 2. A similar reduction in decomposition activity was observed in the SCT in Test 4, which could have been caused by deactivation of the palladium catalyst by possible oxidation at elevated temperature. Further decomposition of 3PB to 2PB could make it appear as though decomposition activity was declining in the SCT; however, boron analytical data suggest that 2PB formation was not increasing. In Test 5, most of the decomposition activity occurred in CSTR 1 and the SCT. The increase in decomposition activity in CSTR 1 could be related to the changes in RWW composition, the change in antifoam batch source, and/or a prolonged activation period for the catalyst system. The fluctuation in the data and the time relationship of these changes complicated the ability to narrow the cause to a single factor. The additional residence time in CSTR 2 allowed for a small amount of additional decomposition activity. A significant amount of additional TPB decomposition occurred in the SCT in Test 5, possibly due to the increased concentration of the palladium component of the catalyst system.

For Tests 4 and 5, the TPB decomposition did not appear to reach steady state. To establish that steady-state conditions exist, consistent 3PB and TPB trends should be observed while processing several batches of concentrated slurry. Although the system performance was acceptable throughout the operation, it was not possible to predict similar performance in a longer operation without observing consistent TPB decomposition behavior in all vessels. As such, it was recommended that an additional 20-L CSTR test be performed in order to verify acceptable performance for a longer-term operation. In addition, more data are needed to evaluate the effect of operating conditions on TPB decomposition, with special emphasis on the monitoring of 2PB generation. In conjunction with this testing, a more-detailed analysis of the RWW should be conducted to determine which components of the catalyst system are being recycled to the feed. The analysis should include, at a minimum, TPB, all TPB decomposition products, palladium, mercury, and possibly antifoam decomposition products.

Benzene monitoring of the vessel off-gas can be used to indicate that decomposition is occurring; however, it cannot be used to quantify the amount of TPB decomposed. The ability of the TPB slurry to hold benzene and prevent its immediate release from the liquid phase complicates the process analysis. This behavior was observed when the benzene that was fed to CSTR 1 during Test 4 did not immediately appear in the off-gas at the expected concentration. In addition, benzene was produced not only as a consequence of the initial TPB to 3PB reaction but was also formed as the initial decomposition products (3PB, 2PB, and 1PB) continued to decompose further. This made it impossible to determine the rate of TPB loss without also knowing the extent of other phenylborate reactions. A quantification of the rate of decomposition must be made on the basis of the production of 3PB from TPB, taking into account the reactions that follow in the decomposition chain to 2PB, 1PB, and phenol/benzene.

The goal of water washing the concentrated slurries in these tests was to evaluate the ability to recover unreacted NaTPB from the slurry for recycle to the process. In the most successful effort of all of the tests, only 29% of the available TPB was recovered. The results of the tests strongly suggest that the presence of IITB52 antifoam inhibits both dissolution and recovery of TPB as well as the removal of nitrite during the slurry washing process. The best recovery of total TPB occurred in a test where antifoam was used, but the washing was performed at a higher mixing speed than that used in the other tests; thus, the results cannot be directly compared with those from tests without antifoam. The other tests, where washing conditions were similar (but not identical), the amount of TPB recovered was greater for tests where IITB52 was not used. In future tests, it is suggested that improved design and chemical features suggested for the washing process be evaluated in carefully designed experiments on the 20-L scale.

The manner in which the simulant was prepared in Test 2 limited the ability to evaluate the effectiveness of MST for removal of strontium and uranium. Both the sludge and the ECC system used in Test 2 contained constituents that formed hydrous metal oxides when added to the salt feed. These oxides sorbed strontium and uranium, and by the time the test was initiated, most of the strontium and uranium had already been removed by these oxides. For this reason, any further tests that may involve addition of the sludge or ECC components should not include an evaluation of strontium or uranium removal in the scope of the test. Alternatively, the experimental plan must use special procedures for preparing the sludge simulants and ECC components to ensure that strontium and uranium tracers are added in amounts that will result in soluble excess of the tracers at equilibrium.

Noticeable operational hydraulic difficulties were experienced during the tests using antifoam and the catalyst system. These occurred in the transfer tubes connecting the CSTRs and the SCT when agglomerated material blocked the opening of the transfer tubes, causing the fluid level in the vessel to increase to a level that required shutdown and recovery actions. It is not known whether this was caused by inadequate mixing and transport of the palladium/alumina component of the catalyst or by interactions between the catalyst, antifoam, and other insoluble components of the system (TPB reaction products, MST, etc.). It is recommended that the mechanism of formation of agglomerated solids be further examined prior to additional CSTR testing.

In each test using the catalyst system, the progressive-cavity slurry pump in the concentration system developed a seal leak. In Test 4, it occurred after normal shutdown of the CSTR system, while the second batch of slurry was being washed to provide recycle feed for Test 5. The pump was replaced after Test 4 but began to fail after about 150 h of operation during Test 5, forcing early termination of the test. It appears that the failure may have been due to the abrasive action of the alumina used as a support for the palladium. It is recommended that an improved fluid seal be used for the progressive-cavity pump in future tests. Problems were also encountered in metering of the diluted slurry mixture of MST, palladium/alumina, and mercury. The small-diameter transfer tubing tended to plug, despite efforts to maintain uniform mixing and sufficient fluid velocity in the tubing. It was found that solid particles in the mixture, assumed to be palladium/alumina, were larger than expected and tended to settle during transfer. It is recommended that the MST slurry, with or without the palladium/alumina and mercury components, be wet-sieved after preparation. If mercuric nitrate is used in the mixture, the solution should be made slightly acidic to prevent the precipitation of mercuric hydroxide, which can cause agglomeration of particles and pumping problems.

7. REFERENCES

1. D. D. Lee and J. L. Collins, *Continuous-Flow Stirred-Tank Reactor 20-L Demonstration Test: Final Report*, ORNL/TM-1999/234, Oak Ridge National Laboratory, Oak Ridge, Tennessee, February 2000.

2. D. D. Lee and J. L. Collins, *Test Results for CSTR Test 3*, ORNL/TM-2000/300, Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 2000.

3. D. D. Lee and J. L. Collins, *Test Results for CSTR Test 4*, ORNL/TM-2001/8, Oak Ridge National Laboratory, Oak Ridge, Tennessee, April 2000.

4. D. D. Lee, *Test Plan for CSTR Test 5*, CERS/SR/TPB/013, January 18, 2001.

5. J. L. Collins and D. D. Lee, *Preparation of Simulated Waste Solutions for CSTR Tests*, CERS/SR/TPB/005, Rev. 5, March 29, 2001.

6. J. L. Collins, *Sampling Plan and Procedure (CSTR Test 5)*, CERS/SR/TPB/006, Rev. 3, January 29, 2001.

7. T. R. Tipton, *Instrumentation Data Sheets and Loop IO Database*, CERS/SRS/TPB/009, Rev. 2, August 4, 2000.

8. S. M. Serkiz, J. D. Ginn, and A. R. Jurgensen, *Tetraphenylborate Solubility in High Ionic Strength Salt Solutions*, WSRC-TR98-00103, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina, April 3, 1998.

9. R. A. Peterson and J. O. Burgess, *Co-precipitation and Solubility Studies of Cesium, Potassium, and Sodium Tetraphenylborate*, WSRC-TR-99-00216, Westinghouse Savannah River Company, Aiken, South Carolina, June 24, 1999.

10. D. J. McCabe, *Cesium, Potassium, and Sodium Tetraphenylborate Solubility in Salt Solution*, WSRC-TR-96-0384, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina, December 16, 1996.

11. M. R. Poirier and J. L. Siler, *Continuous Concentration and Constant Volume Washing of Tetraphenylborate Slurries*, WSRC-TR-99-00243, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina, August 5, 1999.

12. L. L. Kilpatrick, *Cesium Decontamination Versus Sodium, Potassium, and Sodium Tetraphenylborate Molarities in Supernate (U)*, WSRC-RP-96-346, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina, July 22, 1996.

13. J. L. Collins, ORNL, communication with S. D. Fink, Savannah River Technology Center, April 16, 2001.

14 M. J. Barnes, L. N. Oji, T. B. Peters, and F. F. Fondeur, *Tetraphenylborate Catalyst Development for the Oak Ridge National Laboratory 20-L Continuously Stirred Tank Reactor Demonstration*, WSRC-TR-2000-00457, Rev. 0.0, Westinghouse Savannah River Company, Aiken, South Carolina, November 29, 2000.

15. M. A. Baich, D. P. Lambert, and P. R. Monson, *Laboratory Scale Antifoam Studies for the STTPB Process (U)*, WSRC-TR-2000-00261, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina, October 24, 2000.

INTERNAL DISTRIBUTION

1. K. K. Anderson
2. P. V. Bonnesen
3. D. A. Bostick
4–8. J. L. Collins
9. B. S. Evans
10. R. D. Hunt
11. H. L. Jennings
12. R. T. Jubin
13–15. T. E. Kent
16. L. Klatt
17–22. D. D. Lee
23. C. P. McGinnis
24. L. E. McNeese
25. S. A. Richardson
26. P. A. Taylor
27. J. R. Travis
28–30. J. F. Walker
31. T. D. Welch
32. ORNL Central Research Library
33. Laboratory Records, RC
34. Laboratory Records, OSTI

EXTERNAL DISTRIBUTION

35. M. J. Barnes, Westinghouse Savannah River Company, P.O. Box 616, 773-A, Room B112, Aiken, SC 29808

36. J. M. Boncella, Dept. of Chemistry and Center for Catalysis, University of Florida, Gainesville, FL 32611-7200

37. J. T. Carter, Westinghouse Savannah River Company, P.O. Box 616, 704-3N, Room S151, Aiken, SC 29808

38. N. F. Chapman, Westinghouse Savannah River Company, Building 706-S, Room 103, Aiken, SC 29808

39. E. Damerow, West Valley Nuclear Services, P.O. Box 191, West Valley, NY 14171

40. I. L. Drake, Jr., U.S. Department of Energy, 10282 Rock Springs Road, West Valley, NY 14171

41. M. C. Duff, Savannah River Ecology Laboratory, University of Georgia, Aiken, SC 29802

42. Herbert H. Elder, Westinghouse Savannah River Company, P.O. Box 616, 704-3N, Room S151, Aiken, SC 29808

43. Samuel D. Fink, Westinghouse Savannah River Company, P.O. Box 616, 773-A, Room B112, Aiken, SC 29808

44. Kurt Gerdes, TFA Headquarters Program Lead, DOE Office of Science and Technology, 19901 Germantown Rd., 1154 Cloverleaf Building., Germantown, MD 20874-1290

45. Roger L Gilchrist, Pacific Northwest National Laboratory, P.O. Box 999, MS: K9-91, Richland, WA 99352

46. H. D. Harmon, Tanks Focus Area Salt Processing Program, P.O. Box 616, 704-3N, Room S151, Aiken, SC 29808

47. R. A. Jacobs, Westinghouse Savannah River Company, Building 704-3N, Room S252, Aiken, SC 29808

48. Jim Jewett, Numatec Hanford Corporation, P.O. Box 1970, Richland, WA 99352

49. R. T. Jones, Westinghouse Savannah River Company, P.O. Box 616, 704-3N, Room S122, Aiken, SC 29808.

50. R. B. King, Dept. of Chemistry, University of Georgia, Athens, Georgia 30602-2556

51. R. A. Kirkbride, Numatec Hanford Corporation, P.O. Box 1970, MS: H5-27, Richland, WA 99352

52. K. A. Lockie, U.S. Department of Energy, Idaho Operations Office, 750 DOE Place MS: 1145, Idaho Falls, ID 83402

53. C. S. Louie, U.S. Department of Energy, Richland Operations Office, P.O. Box 550, MSIN: B4-55, Richland, WA 99352

54. C. L. Leung, Westinghouse Savannah River Company, P.O. Box 616, 704-3N, Room S151, Aiken, SC 29808

55. J. W. McCullough, Jr., U.S. Department of Energy, Savannah River Operations Office, P.O. Box A, Building 704-196N, Room S431, Aiken, SC 29802

56. Lynn Nelson, Westinghouse Savannah River Company, P.O. Box 616, 773-A, Room-B-112, Aiken, SC 29808

57. Arlin Olson, Idaho National Engineering and Environmental Laboratory, Building 637, MS-5218, Idaho Falls, ID 83415-5218

58. L. M. Papouchado, Westinghouse Savannah River Company, P.O. Box 616, 773-A, Room A-263, Aiken, SC 29808

59. S. F. Piccolo, Westinghouse Savannah River Company, Building 703-H, Room: 118, Aiken, SC 29808

60. J. M. Reynolds II, U.S. Department of Energy, Savannah River Operations Office, P.O. Box A, Building 704-196N, Room S441, Aiken, SC 29802

61. Jim Rindfleisch, Idaho National Engineering and Environmental Laboratory, Building 637, MS: 5218, Idaho Falls, ID 83415-5218

62. W. W. Schulz, 12704 Sandia Ridge Place NE, Albuquerque, NM 87111

63. Patricia C. Suggs, U.S. Department of Energy, Savannah River Operations Office, P.O. Box A, Building 704-196N, Room S431, Aiken, SC 29802

64. S. N. Schlahta, Tanks Focus Area Salt Processing Program, P.O. Box 616, 704-3N, Room S151, Aiken, SC 29808

65. J. L. Swanson, 1318 Cottonwood, Richland, WA 99352

66. W. L. Tamosaitis, Westinghouse Savannah River Company, P.O. Box 616, 773-A, Room A-231, Aiken, SC 29808

67. Larry Tavlarides, Syracuse University, Dept. of Chemical Engineering & Materials Science, 334 Hinds Hall, Syracuse, NY 13244-1190

68. T. A. Todd, Idaho National Engineering and Environmental Laboratory, Building 637, MS-5218, Idaho Falls, ID 83415-5218

69. George Vandegrift, Argonne National Laboratory, Building 205, 9700 South Cass Avenue, Argonne, IL 60439

70. J. H. Westsik, Pacific Northwest National Laboratory, P.O. Box 999, MS: K9-91, Richland, WA 99352

71. W. R. Wilmarth, Westinghouse Savannah River Company, P.O. Box 616, 773-42A, Room 153, Aiken, SC 29808

72. P. E. Woodall, U.S. Department of Energy, Idaho Operations Office, 750 DOE Place (MS: 1145), Idaho Falls, ID 83402

73. Tanks Focus Area Technical Team, c/o B. J. Williams, Pacific Northwest National Laboratory, P.O. Box 999, MSIN: K9-69, Richland, WA 99352

74. Tanks Focus Area Field Lead, c/o T. P. Pietrok, U.S. Department of Energy, Richland Operations Office, P.O. Box 550, MS: K8-50, Richland, WA 99352