DESTRUCTION OF TETRAPHENYLBORATE IN TANK 48H USING WET AIR OXIDATION: BATCH BENCH-SCALE AUTOCLAVE TESTING WITH ACTUAL (RADIOACTIVE) TANK 48H WASTE

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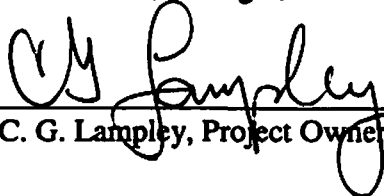
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LIST OF ACRONYMS

1PB	phenylboronic acid
2PB	diphenylborinic acid
3PB	triphenylborane
AAS	Atomic Absorption Spectroscopy
AD	Analytical Development
CsTPB	cesium tetraphenylborate $\{Cs(C_6H_5)_4B\}$
E&CPT	Environmental & Chemical Process Technology
FBSR	Fluidized Bed Steam Reforming
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectroscopy
HEPA	high efficiency particulate air
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ID	inside diameter
ICP-ES	Inductively Coupled Plasma-Emissions Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
KTPB	potassium tetraphenylborate $\{KB(C_6H_5)_4\}$
LFL	lower flammability limit
LSC	Liquid Scintillation Counting
LWO	Liquid Waste Organization
MST	monosodium titanate
NaTPB	sodium tetraphenylborate $\{NaB(C_6H_5)_4\}$
OD	outside diameter
PUREX	plutonium uranium extraction
PUTTA	Plutonium by Thenoyltrifluoroacetone
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SVOA	semi-volatile organic analyses
SVOC	semi-volatile organic compounds
SWT	Siemens Water Technologies Corporation
TIC	total inorganic carbon
TPB	tetraphenylborate ion $\{B(C_6H_5)_4^-\}$
TOC	total organic carbon
XRD	X-ray diffraction
VOA	volatile organic analyses
VOC	volatile organic compounds
WAO	wet air oxidation
WSRC	Washington Savannah River Company

SUMMARY

Wet Air Oxidation (WAO) is one of the two technologies being considered for the destruction of Tetraphenylborate (TPB) in Tank 48H. Batch bench-scale autoclave testing with radioactive (actual) Tank 48H waste is among the tests required in the WAO Technology Maturation Plan. The goal of the autoclave testing is to validate that the simulant being used for extensive WAO vendor testing adequately represents the Tank 48H waste. The test objective was to demonstrate comparable test results when running simulated waste and real waste under similar test conditions. Specifically: (i) Confirm the TPB destruction efficiency and rate (same reaction times) obtained from comparable simulant tests, (ii) Determine the destruction efficiency of other organics including biphenyl, (iii) Identify and quantify the reaction byproducts, and (iv) Determine off-gas composition.

Batch bench-scale stirred autoclave tests were conducted with simulated and actual Tank 48H wastes at SRNL. Experimental conditions were chosen based on continuous-flow pilot-scale simulant testing performed at Siemens Water Technologies Corporation (SWT) in Rothschild, Wisconsin. The following items were demonstrated as a result of this testing.

1) Tetraphenylborate was destroyed to below detection limits during the 1-hour reaction time at 280 $^{\circ}$C. Destruction efficiency of TPB was > 99.997%.

2) Other organics (TPB associated compounds), except biphenyl, were destroyed to below their respective detection limits. Biphenyl was partially destroyed in the process, mainly due to its propensity to reside in the vapor phase during the WAO reaction. Biphenyl is expected to be removed in the gas phase during the actual process, which is a continuous-flow system.

3) Reaction byproducts, remnants of MST, and the PUREX sludge, were characterized in this work. Radioactive species, such as Pu, Sr-90 and Cs-137 were quantified in the filtrate and slurry samples. Notably, Cs-137, boron and potassium were shown as soluble as a result of the WAO reaction.

4) Off-gas composition was measured in the resulting gas phase from the reaction. Benzene and hydrogen were formed during the reaction, but they were reasonably low in the off-gas at 0.096 and 0.0063 vol% respectively.

Considering the consistency in replicating similar test results with simulated waste and Tank 48H waste under similar test conditions, the results confirm the validity of the simulant for other WAO test conditions.

1.0 INTRODUCTION

Tank 48H currently holds legacy material containing organic tetraphenylborate (TPB) compounds from the operation of the In-Tank Precipitation process. This material is not compatible with the waste treatment processes at Savannah River Site (SRS) and must be removed or undergo treatment to destroy the organic compounds before the tank can be returned to Tank Farm service. In addition, the material can decompose to benzene and lead to potentially flammable concentrations in the tank headspace. Tank 48H currently holds approximately 240,000 gallons of alkaline slurry containing 21,800 kg of potassium and cesium tetraphenylborate (KTPB and CsTPB) solids. The tank has been isolated from Tank Farm service, and its return to service is a high priority to the Department of Energy.

Wet Air Oxidation (WAO) is one of the two technologies currently under consideration for the treatment of TPB in Tank 48H. The other technology is Fluidized Bed Steam Reforming (FBSR). WAO is an aqueous phase process in which soluble and/or suspended waste components are oxidized using oxygen or oxygen in air. In general, the process operates at elevated temperatures and pressures ranging from about 150 to 320 °C and 7 to 210 atmospheres, respectively. The products of the reaction are carbon dioxide, water, and low molecular weight oxygenated organics (e.g. acetate, oxalate, etc.).[1-5]

Batch bench-scale autoclave testing with actual (radioactive) Tank 48H waste is among the tests required in the WAO Technology Maturation Plan.[6-10] The objective of the testing is to confirm the ability of the WAO process to destroy TPB and its associated compounds using actual (radioactive) Tank 48H waste. Specifically:

(i)   Confirm the TPB destruction efficiency and rate (same reaction times) obtained from comparable simulant tests.
(ii) Determine the destruction efficiency of other organics including biphenyl.
(iii) Identify and quantify the reaction byproducts.
(iv) Determine off-gas composition.

The work was performed according to the "Task Technical and Quality Assurance Plan for Destruction of Tetraphenylborate in Tank 48H Using Wet Air Oxidation: Batch Bench-Scale Autoclave Testing With Actual (Radioactive) Tank 48H Waste".[7]

2.0 EXPERIMENTAL

2.1 MATERIALS

2.1.1 Tank 48H Simulant

Tank 48H simulant was used for the non radioactive portion of the testing. The Tank 48H simulant was prepared using the recipe[11] developed in 2004. A total of 500 mL of simulant was prepared in two batches (i.e., 250 mL per batch). About 100 mL of the first 250-mL batch was used prior to the start of this work. Therefore, another 100 mL was prepared to bring the total back to 250 mL. The target or nominal concentrations of the major constituents, trace metals/other compounds, and the PUREX sludge in the slurry simulant.[11] are given in Appendix A.

Characterization of the first batch of simulant was performed prior to the testing. The second batch of simulant was not characterized, but it is expected to be essentially the same as the first batch.

2.1.2 Radioactive (Actual) Tank 48H Waste

A portion (about 100 mL) of the actual Tank 48H waste (batch ID #: HTF-E-05-021) that was sampled and received at SRNL in March 2005, was used for the radioactive portion of the testing. Comprehensive analytical data for the untreated radioactive Tank 48H waste are available.[12-16] Hence, the radioactive waste was not re-characterized.

2.1.3 Chemicals

Chemicals described in this section are those dealing directly with the WAO tests. Chemicals used in the preparation of the Tank 48H simulant are left out for brevity.

All the chemicals were reagent grade. Sodium hydroxide pellets (NaOH, Fisher Chemicals, New Jersey) were used to prepare the 2M NaOH solution used as diluent for the Tank 48H material (simulant or actual waste). Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, Fisher Chemicals, New Jersey) was used to prepare the 0.785M $CuSO_4 \cdot 5H_2O$) solution used as catalyst for the oxidation reaction. Antifoam agent (IIT B52, Illinois Institute of Technology, Chicago, Illinois) was used as a foam-suppression chemical for the Tank 48H simulant. Deionized water was used in all preparations requiring water.

2.2 TEST APPARATUS

Parr Instrument Company's (Moline, Illinois) Model 4575A autoclave and its associated equipment (support stand, heater, baffle, and controller) were used for the testing (see Figure 2-1[17]). The picture is for Parr Model 4570 Series autoclaves. Hence, it is a little different from Model 4575 Series. The major difference is that the Model 4575 Series does not have the bottom retainer, the autoclave mount, and the pneumatic lift attachment. The other units added to complement the Parr system included two cooling systems, compressed air

cylinder/pressure regulator assembly, off-gas sampling cylinder and accessories, and a data acquisition computer.

The autoclave is essentially a 500-mL pressure vessel. It consists of a cylinder (body), a head (cover), and a removable baffle. The head has several attachments above and beneath it (see Figure 2-2[17]). The picture is for Parr Model 4570 Series autoclaves. Hence, it is a little different from Model 4575 Series. The major difference is that the Model 4575 Series cooling loop is U-shaped.

The autoclave is made of Inconel® alloy 600. All the attachments on the underside of the head (e.g., magnetic stirrer, thermowell, and cooling loop) are made of Inconel® alloy 600. The attachments on top of the head (e.g., external valves and adapters) are made of T316 stainless steel. Inconel® alloy 600 was chosen because of its high strength and corrosion resistance at high temperatures. The autoclave has a pressure and temperature rating of 5,000 and 500 ^{o}C respectively.

The heater, pressure transducer, stirrer, and thermocouples all connect to the back of the controller (Parr Instrument Company Model 4843) through electrical cables (see Figure 2-3[18]). The thermowell on the underside of the autoclave head has two Type J thermocouples as a safety precaution. The front panel of the controller has displays for the two temperature readings from the thermocouples, pressure, and stirrer speed (see Figure 2-4[18]). The controller has safety interlocks that allow the heater to shut off once a preset temperature and/or pressure is reached.

Two additional controllers (Model CNi3253, Omega Engineering, Inc., Stamford, Connecticut) were connected to the Parr controller and to the data acquisition computer for real time recording (every 15 seconds) of the autoclave temperature and pressure as well as saving of the data to a file. The data acquisition computer was a Dell laptop (Model Inspiron 9400, Round Rock, Texas).

The first cooling system comprised a recirculating chiller, water bath, pump, tubings/hoses, valves, pressure regulator, purge air supply line, and water addition line. The recirculating chiller (Model NESLAB RTE 7, Thermo Fisher Scientific, Newington, New Hampshire for the simulant tests and Model 100AC, Dimplex Thermal Solutions, Kalamazoo, Michigan for the radioactive tests) was used to cool water in a 4.2-liter stainless steel cylinder (referred to as cooling water bath) equipped with stainless steel coils. The recirculating chiller was connected to the cooling coils via braided Tygon® hoses (1/4-inch ID & 3/8-inch OD).

The pressure transducer and the magnetic drive motor of the stirrer require cooling throughout the duration of a test run. The description of the configuration for supplying cooling water to pressure transducer and the stirrer motor is as follows.

Overarm Plate

Universal Coupling

Top Retainer

Controller

Split Ring

Controller Mount

Bottom Retainer

Autoclave Cylinder

Back Plate

Pneumatic Lift Attachment

Left Support Rod

Right Support Rod

Heater

Cylinder Holder

Base Plate
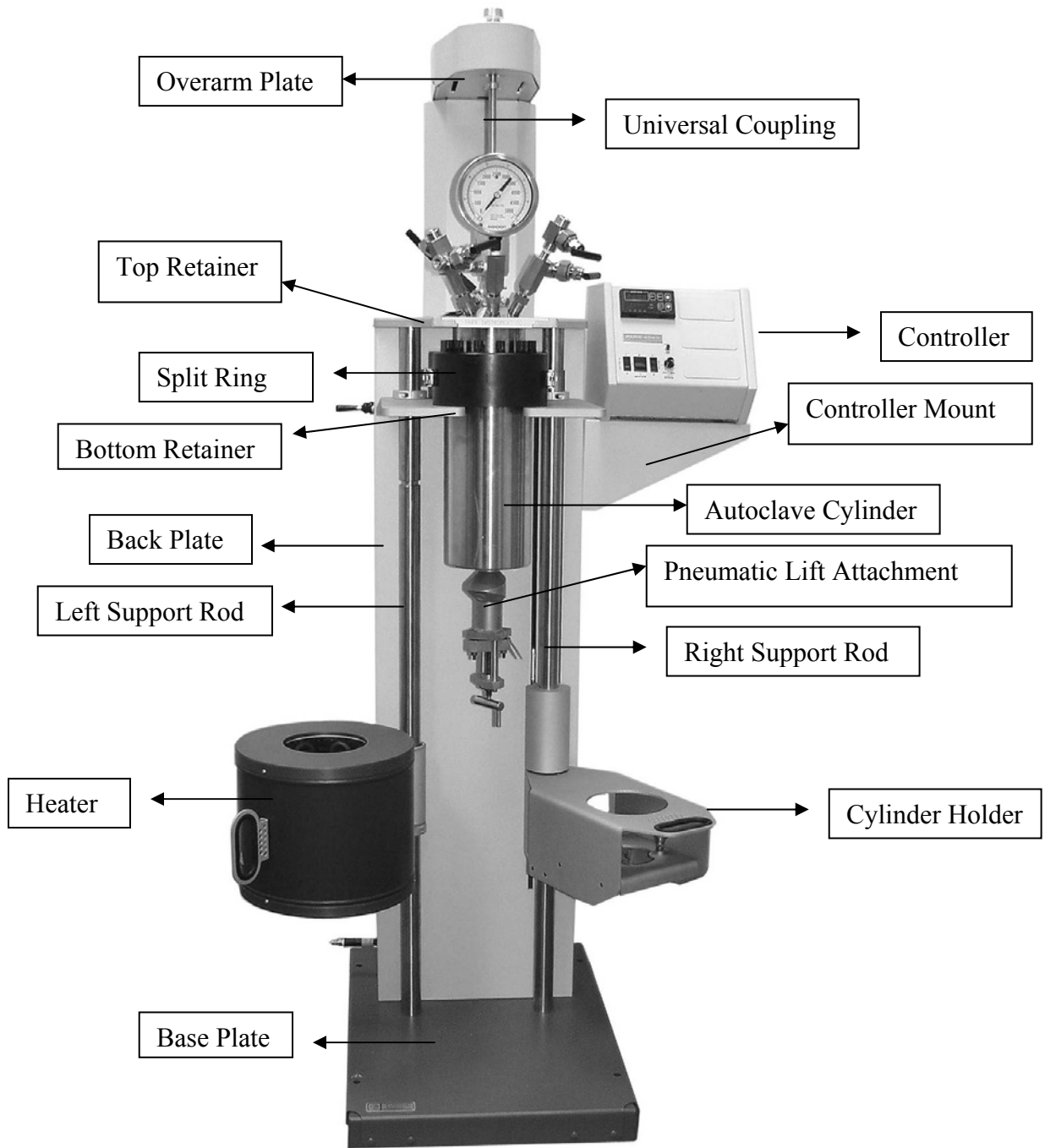
Figure 2-1. Autoclave support stand with cylinder, heater and controller.
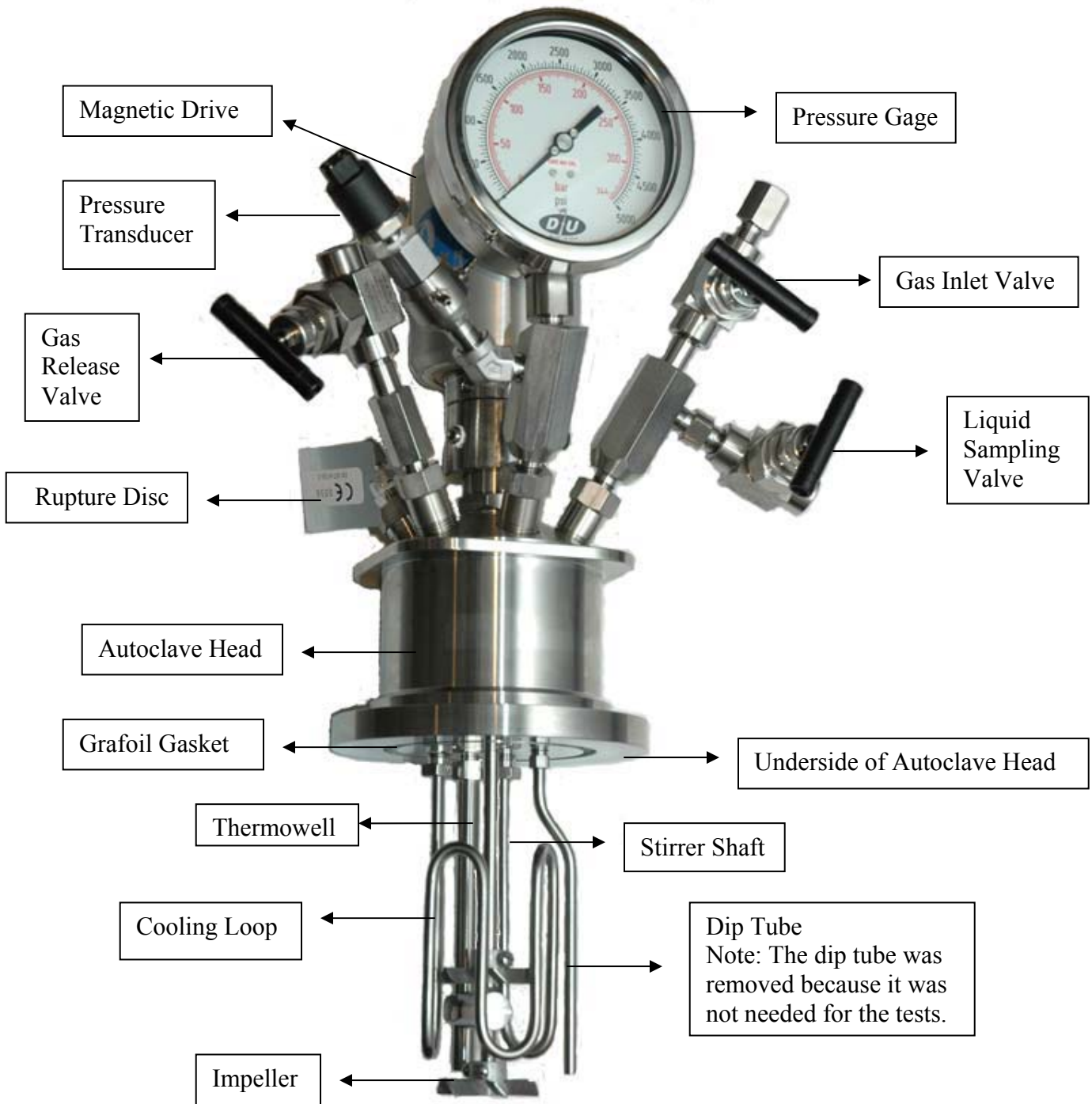
Figure 2-2.   Autoclave head and its attachments.

Figure 2-3.   Rear panel of the autoclave controller.

A 1-gallon per minute pump (Model AC-2CP-MD, March Manufacturing Inc., Glenview, Illinois) supplies cooling water from the bath via a braided Tygon® hose (1/4-inch ID & 3/8-inch OD) that connects between a spout at the bottom of the bath and the inlet of the pump and then via a similar braided Tygon® hose connected to the outlet of the pump. At the other end of the braided Tygon® hose, the stream splits into two. The first split stream connects to a Norprene® tubing (1/8-inch ID & 1/4-inch OD) which further branches into two to the sleeves of the pressure transducer and the stirrer motor. The cooling water exits the pressure transducer and the magnetic drive motor via two Norprene® tubings (1/8-inch ID & 1/4-inch OD) that later combine downstream to one tubing back to the cooling water bath.

The pump also supplies cooling water to the cooling loop in the autoclave via the second split stream. The second split stream is a 7-inch 316/316L stainless steel tubing (1/4-inch OD & 0.035-inch wall thickness) that has a 2-way valve near where the stream splits. The 7-inch stainless steel tubing connects directly to the cooling loop inlet on the autoclave head. The

cooling water exits the cooling loop via the cooling loop outlet on the autoclave head which connects directly to another 7-inch stainless steel tubing and serially to another braided Tygon® hose (1/4-inch ID & 3/8-inch OD) back to the cooling water bath. Note that this cooling is needed only during the latter stage of the cooling period which starts immediately at the end of the oxidation reaction. Hence, the 2-way valve mentioned above is closed during the preheating and reaction periods as well as the initial portion of the cooling period.

Figure 2-4.   Front panel of the autoclave controller.

The same pump is further used to supply house air used to purge the autoclave cooling loop of residual water at the start of each test to prevent steam formation in the cooling loop. This is facilitated by use of a Tygon® tubing (1/4-inch ID & 3/8-inch OD) connected to the 3-way valve at the pump inlet and through the other pump outlet hose to the 2-way valve on the cooling loop outlet line mentioned earlier. Note that the other end of the Tygon® hose tubing connects to a pressure regulator (Model R74G-4AT-NMG, Norgren Inc., Littleton, Colorado) that is preset to 15-20 psig and also in turn connects to house air valve.

Figure 2-5 shows a portion of the first cooling water system – bath with coils, pump with attached 3-way valve, the returning cooling lines (black Norprene® tubing and grey Tygon® hose) on top of the bath, and the recirculating chiller return line (front of bath).

Figure 2-5.   Portion of the first cooling water system.

The second cooling system involved a 5.8-liter 304 stainless steel cylinder (referred to as cooling water bucket) filled with flowing water. When in operation, the cooling water bucket sits on a support stand (25-kg [55-lb] heavy duty lab lift, Model EW-08057-18, Cole-Palmer, Vernon Hills, Illinois) and encloses the entire autoclave cylinder and about two-thirds of the height of the split rings with flowing water to aid in cooling the autoclave at the end of the oxidation reaction. In other words, the cylinder is submerged in the water in the cooling bucket. The two inlets (located at the top and bottom) of the cooling water bucket connect to two tap water valves via braided Tygon® tubing (1/4-inch ID & 3/8-inch OD) and the outlet

(located at the top) discharges to the drain or sink via braided Tygon® tubing (0.875-inch ID & 1.25-inch OD). Only the bottom inlet was used for the radioactive tests due to the smaller size of the receiving sink or container. Figure 2-6 shows a portion of the second cooling water system.

Figure 2-6.   Portion of the second cooling water system.

The compressed air cylinder/pressure regulator (Model NA385VB, 3000 psig rated, 0-1500 psig delivery pressure, Parr Instrument Company) assembly connects to a 7500 psig rated 1/8 inch OD stainless steel tubing that is used to charge the autoclave with air through connection to the gas inlet valve on the autoclave head. All the readouts or displays of the measuring devices (thermocouples, pressure transducer/gage, were checked against National Institute of Standards and Technology traceable standards within the planned range of operation (0-300 ^{o}C for temperature and 0-2,400 psig for pressure) and found to be satisfactory. For the temperature devices, all were within 1%. For the pressure devices, all were within 2% except the gage on top of the autoclave that was within 3%. The off-gas sampling cylinder and accessories will be described in the next section.

2.3 TEST PROCEDURE

A test run began by adding the materials/chemicals below to the autoclave cylinder in sequential order to give a total volume of 100 mL.

(i)   The mass equivalent of a known volume of the Tank 48H material (simulant or radioactive waste) containing a measured volume of IIT B52 antifoam agent (not added for radioactive waste tests because it does not foam).

(ii)   The mass equivalent of a known volume of 0.785M $CuSO_4 \cdot 5H_2O$ solution (catalyst).

(iii)   The mass equivalent of a known volume of 2M NaOH solution (diluent).

(iv)   A known volume of benzene (not added for radioactive waste tests) equivalent to benzene concentration of 55 mg/L in the Tank 48H simulant. Benzene is highly volatile. To minimize loss by evaporation, it is not added to the simulant during its preparation. It is rather added just before a test begins.

Note that some of the 2M NaOH solution is used to rinse the bottles after steps (i) and (ii) above. It is followed by closing the cylinder with the autoclave head, slipping the two split ring sections on the head, and tightening the sealing bolts to the specified torque.

The cooling loop in the autoclave is then purged with air. Air is charged into the autoclave from the compressed gas cylinder to a predetermined pressure. The pump is turned on to activate the first cooling system for the cooling of the pressure transducer and the magnetic drive motor of the stirrer. Note that the recirculating chiller should be on and running at least 20 minutes prior to the start of the test. The heater is then slipped over the cylinder and the stirrer is turned on and set to a predetermined speed. The heater is turned on to heat the autoclave to the desired temperature (setpoint temperature).

The reaction time begins when the reaction temperature or setpoint temperature is reached. The reaction proceeds for a specified time. The temperature and pressure in the autoclave are monitored by both the main controller and the two additional controllers connected to the data acquisition computer (via the main controller). The pressure is also monitored using the gage on the top of the autoclave.

Note also that the temperature of the cooling water bath and the temperature in the tubing connected to the cooling loop outlet (just outside the autoclave) were monitored directly by the data acquisition computer in the initial test runs. The monitoring was discontinued because the temperatures were found to be fairly constant and/or within ranges considered to be good from operational and safety standpoints.

The pressure, temperature, and stirrer displays on the main controller as well as the pressure gage reading on the top of the autoclave were manually recorded periodically. The temperature of the recirculating chiller was also monitored and manually recorded periodically.

At the end of the specified reaction period, the heater is switched off and the cooling water bucket is used (second cooling system) to cool the autoclave to stop the oxidation reaction. Again, the temperature of the cooling water bucket was also monitored directly by the data acquisition computer in the initial test runs and discontinued for same reasons as mentioned earlier.

Cooling water through the cooling loop in the autoclave is initiated about five minutes after cooling starts using the 2-way valve near the cooling loop inlet. When the temperature in the autoclave reaches 28 $^{\circ}$C, flow of cooling water to the bucket is stopped and the bucket is lowered from the autoclave to ensure the autoclave temperature does not go below room temperature.

Cooling via the cooling loop is stopped about 1-2 $^{\circ}$C above room temperature and house air is immediately used to purge or remove the water in the cooling loop by switching the 3-way valve next to the cooling water pump to the air-flow position. After cooling to room temperature, the temperature and pressure are recorded from the pressure gage and controller displays. The duration of the cooling was about 13 minutes for the simulant runs and about 28 minutes for the radioactive runs. The flow rate of cooling water to the cooling water bucket was reduced for the radioactive runs to prevent overflow of the receiving sink/container in the shielded cells. Hence, the longer duration for the radioactive runs.

After the cooling loop is purged, the 3-way valve next to the cooling water pump and the cooling loop valve are closed followed by turning off the cooling water pump, the recirculating chiller, and the stirrer. The autoclave is then allowed to idle for about 10 minutes to relieve any residual heat that may be in the autoclave before sampling of the off-gas begins. The off-gas is sampled by connecting a pre-vacuumed sampling cylinder to the quick connect device attached to the gas release valve on the head of the autoclave.

The 150-mL 304L stainless steel double-ended sampling cylinder (Model 304L-HDF4-150, 1800 psig rating, The Swagelok Company, Solon, Ohio) was plugged (Swagelok SS-400-P stainless steel Plug) at one end and opened at the other. A Swagelok 3-way stainless steel ball valve (Model SS-42GXS4, 2500 psig rating) was connected to the opened end. The 3-way valve allowed purging of the line between the autoclave gas release valve and the sampling cylinder valve. Note that the purging of the above line was not done for the radioactive tests because of the risk of losing all the off-gas if the valve was not switched back fast enough

with the manipulators. However, the line is relatively short and therefore is not expected to affect the off-gas composition. The sampling cylinders were pre-vacuumed to approximately zero mm Hg (torrs) using a vacuum pump (Model Pascal 2015 SD, Alcatel Vacuum Products, Hingham, Massachusetts) and leak-checked using a Baratron pressure gage (Model 390HA, MKS Instruments, Andover, Massachusetts).

Sampling begins by opening the gas release valve slowly to admit off-gas into the sampling cylinder until the pressure in the autoclave becomes constant (at about 400 psig). The gas release valve is then closed and the sampling cylinder is disconnected from the quick connect device connected to the gas release valve. The off-gas remaining in the autoclave at this time is discharged in the hood or cell until the pressure in the autoclave becomes constant at or near zero psig.

The sampling cylinder (designated as first sampling cylinder) is then connected to the high pressure side of a pressure regulator assembly (Model 5114C540, 2-50 psig delivery pressure, Scott Specialty Gases, Inc., Plumsteadville, PA). A pre-vacuumed second sampling cylinder is connected to the low pressure side of the pressure regulator assembly and some of the off-gas from the first sampling cylinder is transferred to the second sampling cylinder at 20 psig.

The above is repeated for a pre-vacuumed third sampling cylinder. Three sampling cylinders were used to speed up analysis by the various analytical outfits. Note that the pressure regulator assembly had a Swagelok stainless steel in-line particulate filter (Model SS-4F-7, 7-μm pore size) installed between the first sampling cylinder and the pressure regulator.

The second and third sampling cylinders were similar to the first except the opened end was connected to a Swagelok 2-way stainless steel ball valve (Model SS-42GS4, 2500 psig rating). Note that the prior to connecting the second or third sampling cylinder, the line between the first cylinder valve and the outlet of the pressure regulator assembly was purged to minimize off-gas sample contamination

Finally, the autoclave is opened and the treated material is transferred from the cylinder into a beaker (for subsequent sub-sampling for analysis) by swirling gently and pouring (for the simulant tests) or using an in-house designed pourer (for the radioactive tests). Figure 2-7 is a picture of the pourer.

2.4 TEST CONDITIONS

All the tests were conducted in the batch mode. The tests aimed at matching to the extent practical the autoclave used for the prior batch bench-scale autoclave testing conducted by Siemens Water Technologies Corporation (SWT) in Rothschild, Wisconsin in 2006[19] in terms of autoclave volume (500 mL) and baffle configuration as well as total volume (100 mL) of feed to the autoclave.

The work was approached in three ways.

(i)   Replication of the 2006 batch bench-scale shaking autoclave simulant tests (at the same conditions as those identified in 2006) that was performed by SWT;

(ii) Batch bench-scale stirred autoclave simulant tests at nearly the same (i.e., conservative) conditions identified in the January 2009 Phase 1 continuous-flow pilot-scale testing conducted by SWT in Rothschild, Wisconsin; and

(iii) Replication of item # (ii) above using actual or radioactive Tank 48H waste.

The rationale for the above was as follows. Approach 1 tests were required to ensure confidence in the performance or results obtained with the stirred autoclave because results of the 2006 SWT tests were known. The continuous-flow pilot-scale testing conditions are the ultimate for the Tank 48H WAO treatment process. It was therefore important that batch bench-scale stirred autoclave simulant tests (approach 2) were conducted at these conditions. The approach 3 tests allowed direct comparison of the treatment performance of the simulant (approach 2) and actual waste (approach 3). This, in turn, will permit correlation of the performance of the batch bench-scale radioactive waste tests (approach 3) with that of the continuous-flow pilot-scale simulant testing via the performance of the batch bench-scale simulant tests (approach 2).

Figure 2-7.   In-house designed pourer for transferring treated radioactive waste to a beaker.

Table 2-1 gives the test conditions for each of the test runs. The first two (simulant tests 1 and 4 were identical to the optimum conditions identified by SWT (shaking autoclave test) in 2006.[19] Simulant tests 2/3 were abandoned because of leaks around the thermowell and the gas inlet valve. The pressures at the run temperature of 300 °C were lower than expected (about 1,700 versus 2,000 psig). Tightening of the thermowell and the gas inlet valve prevented further leaks.

Simulant tests 5/6/7 and radioactive tests 1/2 were chosen to match the conditions from the SWT Phase I pilot-scale testing using Tank 48H simulant. Simulant test 7 was a demonstration for SWT personnel. The pilot-scale testing exact optimum conditions were not available at the start of this stirred autoclave testing. However, the major conditions (temperature, reaction time, diluent concentration) were known. Hence, conservative conditions were selected based on information available from the Phase 1 pilot-scale testing. The conditions identified at the pilot-scale testing were as follows.

> A temperature of 280 °C, a reaction time of 1 hour, a diluent/Tank 48H material volume ratio of 2:1, $CuSO_4 \cdot 5H_2O$ solution (100 mg/L Cu) as catalyst, and 0.21 mL/L of antifoam agent. The diluent comprises a mixture of 2M NaOH solution and $CuSO_4 \cdot 5H_2O$ solution.

The diluent/Tank 48H material volume ratio of 1:1 used for simulant tests 5/6/7 and radioactive tests 1/2 is conservative. Even though 250 mg Cu/L $CuSO_4 \cdot 5H_2O$ solution was used for simulant tests 5/6/7 and radioactive tests 1/2 versus 100 mg Cu/L for the Phase 1 pilot-scale testing, it is not expected to impact treatment performance. This is because it is only the soluble portion of the $CuSO_4 \cdot 5H_2O$ that functions as a catalyst. The amount that remains in solution is less than 100 mg Cu/L.[20-23]

The TPB solids in the slurry simulant float and foam even when antifoam (IIT B52) is added. Preliminary stirrer speed tests in an open glass beaker with the feed mixture (simulant, 2M NaOH, catalyst, antifoam) indicated high speeds suppress or eliminate the foam. The optimum was about 800 rpm.

As stated earlier, radioactive tests 1 and 2 are the radioactive counterparts of simulant tests 5 and 6. Hence, they were conducted at the same conditions as simulant tests 5 and 6. However, no antifoam agent was added for the radioactive tests. The radioactive Tank 48H waste does not foam and also does not have floating TPB solids. Figures 2-8 and 2-9 are pictures of the Tank 48H simulant and radioactive waste respectively. They depict the foaming/floating and no-foaming/settling characteristics of the simulant and radioactive waste.

Table 2-1. Conditions for the various tests conducted.

Test	Diluent & Catalyst/Tank 48H Material Volume Ratio	Catalyst Conc., mg Cu/L	Antifoam Conc., mL/L	Air Charge Pressure, psig	Reaction Temp., °C	Reaction Time, hours
Simulant Test 1	1:1	500	1	597	300	3
Simulant Test 4	1:1	500	1	607	300	3
Simulant Test 5	1:1	250	0.21	612	280	1
Simulant Test 6	1:1	250	0.21	617	280	1
Simulant Test 7	1:1	250	0.21	614	280	1
Radioactive Test 1	1:1	250	0	600	280	1
Radioactive Test 2	1:1	250	0	599	280	1
Pilot-Scale Testing	2:1	100	0.21	n/a	280	1

Nominal stirrer speed for all tests was 800 rpm.

Reaction pressure was about 2,000 psig for the 300-°C tests and 1,800 psig for 280-°C tests.

Simulant tests 2 and 3 were abandoned because of leaks.

Simulant test 7 was a demonstration for SWT.

Pilot-scale testing was not part of this study. It is furnished for comparison.

n/a – Not applicable
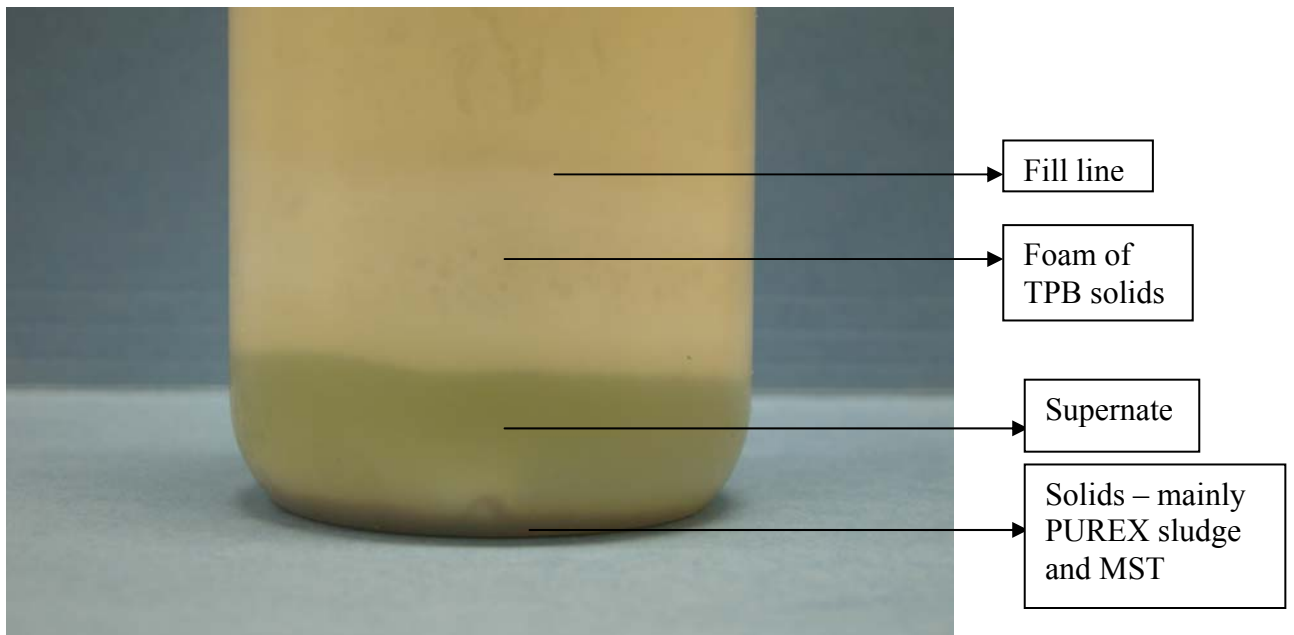
Figure 2-8. Tank 48H simulant depicting three distinct layers. Top of fill line are stains of residual TPB solids from pouring.
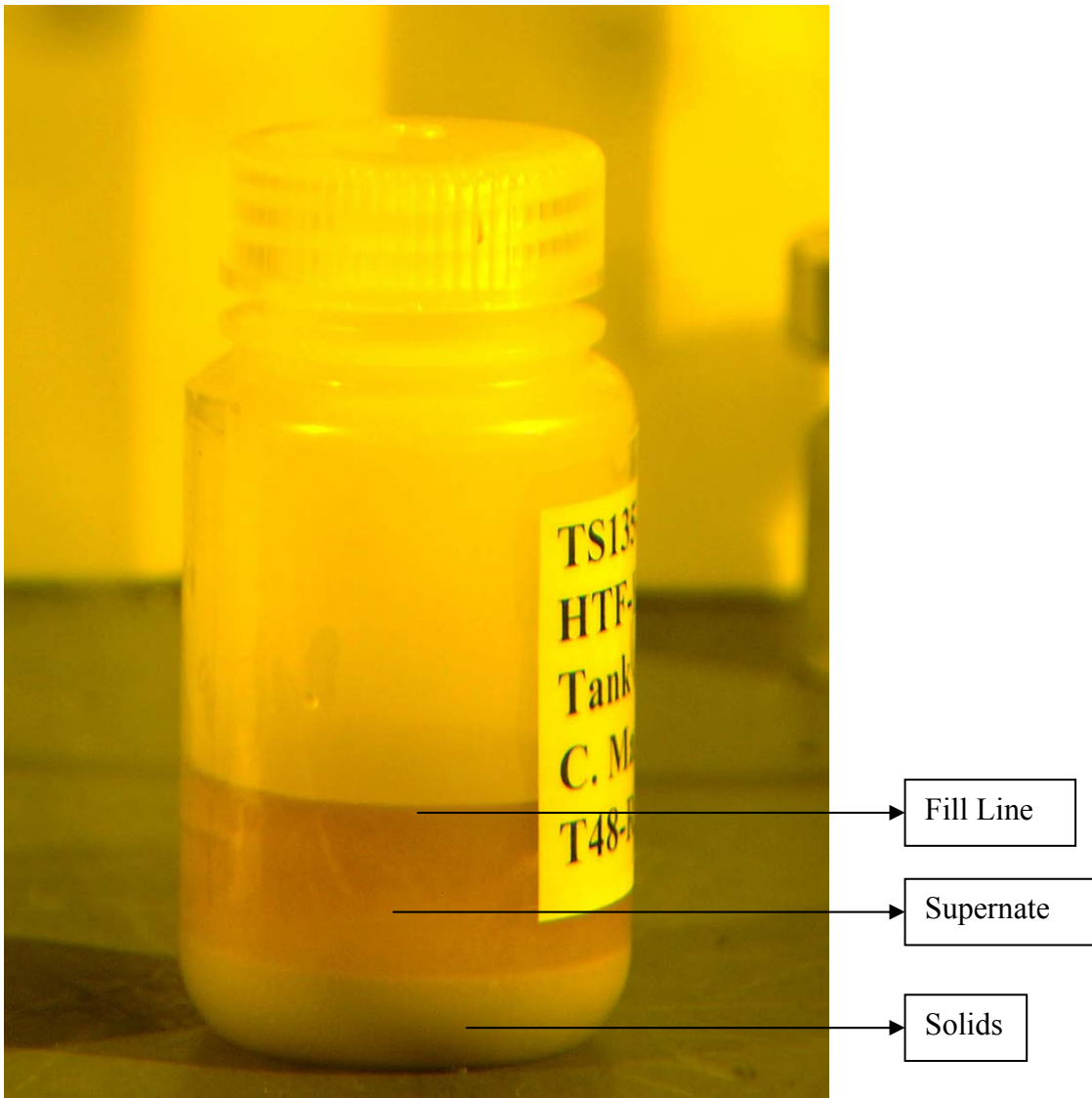
Figure 2-9. **Tank 48H radioactive waste depicting two distinct layers with no foam layer.**

3.0 RESULTS AND DISCUSSION

3.1 COMPOSITION OF TANK 48H SIMULANT

As mentioned in Section 2.1.1, two 250-mL batches of simulant were prepared for the simulant portion of the testing. The first batch was characterized. The fourth column of Table 3-1 gives the measured constituent concentrations of the first batch of simulant. The corresponding nominal or target values are given in the third column. The method of analysis is also given in column 2. Note that because of the 1:1 dilution of the simulant with NaOH/catalyst solutions, all the concentrations (except those with "<" values or detection limits) have been halved.

Overall agreement between the nominal and measured values especially the major constituents (e.g., TPB, phenol, free hydroxide, nitrite, nitrate, boron, potassium, etc.) are good with few exceptions. Notable among them are Total Organic Carbon (TOC), Total Carbon (TC), Al, Cs, Fe, Hg, K by Atomic Absorption Spectroscopy (AAS), Mn, Ni, Ti, and Zr.

The low value for Al may stem from the highly hygroscopic nature of the sodium aluminate (NaAlO2·xH2O) used to prepare the simulant. The amount of Cs in the first batch of simulant was inadvertently low because of fixed decimalization in the simulant recipe spreadsheet. The spreadsheet essentially makes the Cs amount zero for volumes of less than about 240 mL. Recall, 100 mL of simulant was prepared as makeup for the first 250-mL batch. The first batch was from a combination of two sub-batches of 180 and 100 mL. Fe, Ni, K by AAS, TOC, and TC are anomalies. Hg, Mn, Ti, Zr may be due to poor or incomplete dissolution in the Parr Bomb digestion with nitric acid that precedes the analysis. As pointed out in Section 2.1.2, the radioactive waste was not re-characterized prior to the tests.

3.2 SIMULANT TESTS 1 & 4

Columns 1 to 3 of Table 3-1 were explained in the previous section. Columns 5 and 6 of Table 3-1 give the treated slurry simulant analytical data for simulant tests 1 and 4 respectively. Columns 7 and 8 give the analytical data of the filtrate of the treated simulant for simulant tests 1 and 4 respectively.

The top portion of columns 5 and 6 indicates virtually all the organics in the simulant (i.e., TPB, its daughter compounds (triphenylborane [3PB], diphenylborinic acid [2PB], phenylboronic acid [1PB]), phenol, biphenyl and other semi-volatile organic compounds [SVOCs], volatile organic compounds [VOCs]) excluding benzene were destroyed to below their respective detection limits for simulant tests 1 and 4. Table 3-2 provides the destruction efficiencies for the various compounds in the waste.

Table 3-1.   Analytical data of Tank 48H treated simulant for simulant tests 1 & 4.

Column 1 Analyte	Column 2 Analytical Method	Column 3 Feed Slurry Nominal Conc.[a], mg/L	Column 4 Feed Slurry Measured Conc.[a], mg/L	Column 5 Test 1 Treated Slurry Conc., mg/L	Column 6 Test 4 Treated Slurry Conc., mg/L	Column 7 Test 1 Treated Slurry Filtrate Conc., mg/L	Column 8 Test 4 Treated Slurry Filtrate Conc., mg/L
TPB	HPLC	9,186	8,515	< 0.25	< 0.25	nm	nm
3PB	HPLC	None	<100	< 10	< 10	nm	nm
2PB	HPLC	None	<100	< 10	< 10	nm	nm
1PB	HPLC	None	<100	< 10	< 10	nm	nm
Phenol	HPLC	476	486	< 10	< 10	nm	nm
Biphenyl (soluble)	HPLC	Unknown	nm	nm	nm	nm	nm
Biphenyl (total)	HPLC	309	224	< 10	< 10[b]	nm	nm
Biphenyl (Floating)	HPLC	n/a	n/a	negligible	< 0.0402	nm	nm
Other SVOCs	GC-MS	Unknown	< 1	< 1	< 1	nm	nm
Benzene (includes added benzene)	P&T/GC-MS	27.5	27.5	< 0.05	< 0.05	nm	nm
Other VOCs	P&T/GC-MS	Unknown	< 0.25	< 0.05	< 0.05	nm	nm
TOC	TIC/TOC	8,951 (excludes antifoam)	4,760 (excludes antifoam)	negligible	negligible	negligible	negligible
TIC	TIC/TOC	2,739	2,540	11,900	14,200	12,100	14,300
TC	TIC/TOC	11,690 (excludes antifoam)	7,300 (excludes antifoam)	10,800	12,800	11,300	13,000
OH⁻ (includes 2M NaOH as diluent)	Titration	1.80M	1.78M[c]	nm	nm	0.597M	0.143M
CO_3^{2-}	TIC/TOC	13,681	12,700	54,000	64,000	56,500	65,000
NO_2^-	IC	10,469	9,950[c]	nm	nm	2,850	5,760
NO_3^-	IC	6,541	6,600[c]	nm	nm	15,700	12,300
PO_4^{3-}	IC	252	< 250[c]	nm	nm	< 500	< 500
SO_4^{2-} (includes calalyst)	IC	889	882[c]	nm	nm	921	901
Cl⁻	IC	61	< 250[c]	nm	nm	< 125	< 125
F⁻	IC	8.7	< 25[c]	nm	nm	< 125	< 125
Formate	IC	None	< 25[c]	nm	nm	< 125	< 125
Oxalate	IC	None	< 25[c]	nm	nm	< 125	< 125

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8
Analyte	Analytical Method	Feed Slurry Nominal Conc.[a], mg/L	Feed Slurry Measured Conc.[a], mg/L	Test 1 Treated Slurry Conc., mg/L	Test 4 Treated Slurry Conc., mg/L	Test 1 Treated Slurry Filtrate Conc., mg/L	Test 4 Treated Slurry Filtrate Conc., mg/L
Density	Gravimetric	1.1665 g/mL (undiluted)	1.09 g/mL (undiluted)	1.12 g/mL	1.12 g/mL	1.12 g/mL	1.12 g/mL
Total solids	Gravimetric	18.42 wt% (undiluted)	16.92 wt% (undiluted)	12.6 wt%	12.37 wt%	nm	nm
Dissolved solids	Gravimetric	16.60 wt% (undiluted)	15.52 wt% (undiluted)[c]	nm	nm	12.62 wt%	12.23 wt%
Insoluble Solids	Calculation	2.02 wt% (undiluted)	1.66 wt% (undiluted)	~ 0 wt%	0.16 wt%	n/a	n/a
Ag	ICP-ES	Unknown	< 0.217	< 1.60	< 1.49	< 0.383	< 2.49
Al	ICP-ES	992	643	629	616	636	620
B	ICP-ES	311	293	284	298	270	282
Ba	ICP-ES	0.64	1.12	0.669	0.62	< 0.140	< 0.28
Ca	ICP-ES	15.7	19.0	15.9	9.96	< 0.778	< 1.56
Cd	ICP-ES	0.65	0.72	< 0.644	< 0.60	< 0.182	< 1.00
Ce	ICP-ES	2.75	2.28	< 3.34	< 3.1	< 3.57	< 5.19
Co	ICP-ES	Unknown	< 0.239	< 0.541	< 0.502	< 0.420	< 0.84
Cr	ICP-ES	23.4	22.2	89.0	27.7	89.8	27.3
Cs	ICP-MS	7.4	3.93	4.37	11.42	3.84	12.1
Cu (includes calalyst)	ICP-ES	501	502	400	259	37.5	8.03
Fe	ICP-ES	59	60.0	58.9	31.5	< 1	< 0.971
Hg	AAS	5	2.29	< 1.41	2.22	1.04	1.34
K	AAS	1,260	638	1,014	1,082	1,080	868
K	ICP-ES	1,260	1,139	1,131	1,154	1,140	1,160
La	ICP-ES	0.49	0.53	< 2.58	< 2.39	< 1.00	< 4.00
Li	ICP-ES	Unknown	< 0.126	< 0.290	< 0.27	< 0.750	< 0.45
Mg	ICP-ES	0.70	1.75	< 1.62	< 1.51	< 1.26	< 2.53
Mn	ICP-ES	12	12.1	8.02	5.24	< 1.00	< 0.03
Mo	ICP-ES	4.5	4.49	4.67	4.35	4.3	4.11
Na (includes 2M NaOH as diluent)	ICP-ES	60,600	59,100	59,100	55,800	57,100	53,800
Na (includes 2M NaOH as diluent)	AAS	60,600	55,600	56,100	53,100	65,500	50,600
Ni	ICP-ES	6.4	7.1	68.1	9.60	< 0.5	< 2.00

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8
Analyte	Analytical Method	Feed Slurry Nominal Conc.[a], mg/L	Feed Slurry Measured Conc.[a], mg/L	Test 1 Treated Slurry Conc., mg/L	Test 4 Treated Slurry Conc., mg/L	Test 1 Treated Slurry Filtrate Conc., mg/L	Test 4 Treated Slurry Filtrate Conc., mg/L
P	ICP-ES	82.0	89.0	90.3	86.6	81.2	78.8
Pb	ICP-ES	17.0	15.9	< 12.9	< 12.0	< 3.00	< 20.0
Pd	ICP-MS	0.04	0.031	< 0.258	< 0.239	<0.04	<0.04
Rh	ICP-MS	0.12	0.103	< 0.129	< 0.120	<0.01	<0.01
Ru	ICP-MS	0.13	0.106	0.419	0.1904	<0.0749	0.0499
S (includes calalyst)	ICP-ES	296	302	347	344	340	335
Si	ICP-ES	44	39.9	43.8	39.0	43.7	32.4
Sn	ICP-ES	6.2	5.55	< 6.44	< 5.97	< 19	< 10
Sr	ICP-ES	2.89	2.91	2.26	1.25	< 0.25	< 2.00
Ti	ICP-ES	380	368	273	149	< 0.237	< 0.6
U	ICP-ES	Unknown	nm	nm	nm	nm	nm
V	ICP-ES	Unknown	< 0.279	< 0.496	< 0.46	< 0.495	< 0.77
Zn	ICP-ES	4.52	4.55	4.75	3.37	3.69	2.11
Zr	ICP-ES	6.2	0.219	< 0.644	< 0.600	< 0.248	< 1.00

[a] Values have been divided by 2 (except detection limits or indicated otherwise) because of the 1:1 dilution with NaOH and Cu catalyst.

[b] This strictly excludes the sheet-like graphite laden biphenyl that was attached to the wall of the cylinder (designated as "floating"). However, even if the "floating" biphenyl is included, it will still be less than 10 ppm as evidenced by the floating biphenyl value in the cell directly below this cell.

[c] Value is for the filtrate of the slurry.

Note:

Slurry analysis of all the elements was preceded by Parr Bomb digestion with nitric acid.

Values with < symbols are detection limits

nm – Not measured

n/a – Not applicable

AAS: Atomic Absorption Spectroscopy

GC-MS: Gas Chromatography-Mass Spectrometry

HPLC: High Performance Liquid Chromatography

IC: Ion Chromatography

ICP-ES: Inductively Coupled Plasma-Emissions Spectroscopy

ICP-MS: Inductively Coupled Plasma-Mass Spectroscopy

P&T: Purge and Trap

TC: Total Carbon

TIC/TOC: Total Inorganic Carbon/Total Organic Carbon

Table 3-2. **Destruction efficiencies for the various organics in the simulant - tests 1 & 4.**

	Percent Destruction Efficiency	
Compound	Simulant Test 1	Simulant Test 4
TPB	> 99.997	> 99.997
Phenol	> 98	> 98
Biphenyl	> 96	> 96

Recall that both tests were run at identical conditions (see Table 2-1) except the stirrer speed for simulant test 4. The graphite bushing holding the stirrer shaft disintegrated into the slurry about 82 minutes from the start of the reaction period. Hence, to lessen the noise that ensued, the stirrer speed was reduced from 800 to 500 rpm for the remainder of the test.

There was a sheet-like graphite laden biphenyl that was attached to the wall of the cylinder during simulant test 4 (designated as "floating" in Table 3-1) as shown in Figure 3-1. However, the biphenyl in it was below detection limits (< 0.0402 mg/L). It seems it disproportionally contained more graphite. The graphite was from two sources – the bushing mentioned earlier and the graphite (grafoil) gasket. Pieces of the graphite gasket tend to break into the cylinder anytime the cylinder is closed. Note that the sheet-like material was also analyzed for TPB, 3PB, 2PB, 1PB, and phenol. The concentration of each was also < 0.0402 mg/L. The sheet-like graphite laden biphenyl may be attributed to the reduction in stirrer speed (from 800 to 500 rpm) during the latter part of simulant test 4 when the bushing disintegrated into the slurry.

The TOC data for both simulant tests 1 and 4 (at least indirectly) attest to the complete destruction of the organics in the Tank 48H simulant. Note that the reason for the TIC values being greater than TC values is believed to be due to the graphite. Graphite is not expected to convert to CO_2 at the combustion temperature (680 ^{o}C) used to determine TC. On the other hand, the ash that is typically in graphite will increase the TIC value. The true TIC values are therefore probably close to the TC values. Hence, the TC values were used to calculate the carbonate concentrations instead of the TIC values. The high TIC value for simulant test run 4 is due to the bushing disintegrating into the slurry.

Figure 3-2 and 3-3 show pictures of the treated simulants. There is practically no biphenyl (floating) on the surface of the treated simulants. Note that this was not the case for almost all of the SWT tests conducted in 2006 at the same conditions as depicted from both their biphenyl values and picture (see Figure 3-4 and Table 3-3).[19] Floating biphenyl, by all accounts, is biphenyl vapor that solidifies when the autoclave is cooled at the end of the oxidation reaction. Biphenyl is a solid below 68 – 70 ^{o}C.

The reason for the better destruction performance is due to the fact that mixing is better in the stirred autoclave than the SWT's shaking autoclave especially when one considers the

foaming and floating characteristics of the simulant. It is even more important since WAO occurs in the aqueous phase.

Figure 3-1. **Sheet-like graphite laden biphenyl that was attached to the wall of the cylinder during simulant test 4.**

As expected, the carbonate concentration levels in the treated simulants were significantly higher than the carbonate concentration in the untreated simulant or feed. The CO_2 that forms from the oxidation reaction dissolves and reacts in the alkaline aqueous phase to form carbonate/bicarbonate compounds.

About 71 and 42% of the nitrite in the feed were converted or oxidized to nitrate for simulant tests 1 and 4 respectively. Again, the lower nitrite conversion for simulant test 4 may be due to the lower stirring speed that ensued during latter portion of the test as alluded to earlier. It is worthwhile to mention that the nitrite percent conversion for simulant test 4 compares favorably with the 2006 SWT shaking autoclave tests (40%).

The free hydroxide values translate to a pH of 13.8 and 13.2 for simulant tests 1 and 4 respectively. The reason for the disparity in the free hydroxide values for the two tests is unclear. The role of the graphite and its ash content is uncertain but simulant test 4 is expected to have more graphite based on earlier deductions. Along the same vein, it is difficult to make any meaningful comparisons with the free hydroxide data of the 2006 SWT shaking autoclave tests.
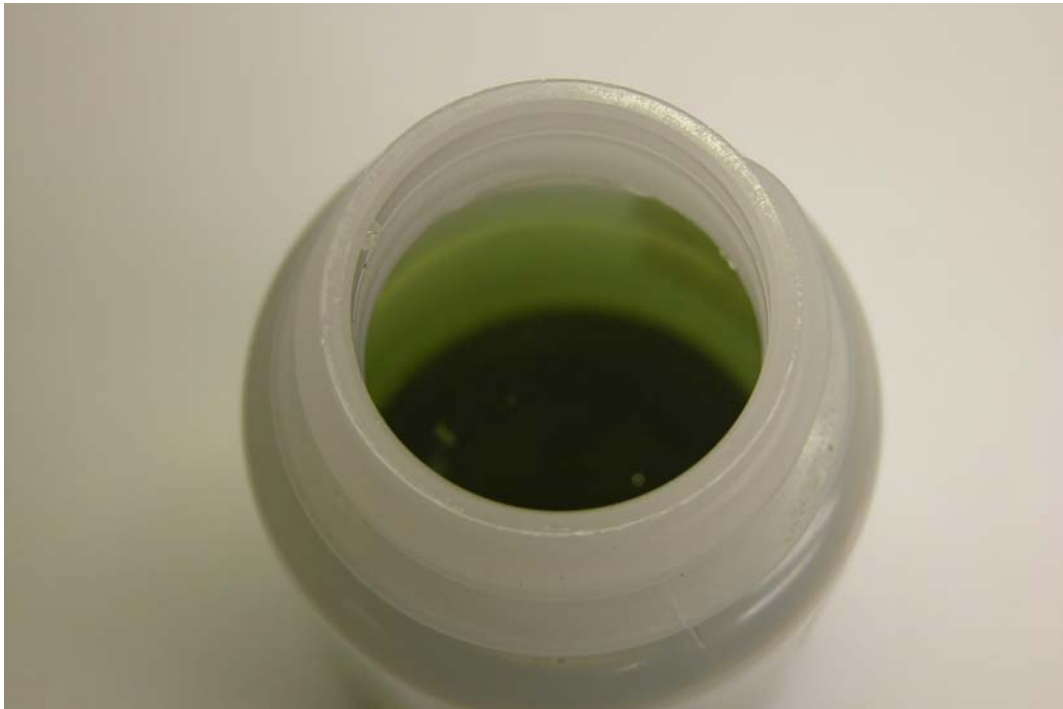
Figure 3-2.   Top view of treated simulant (test 1) with a few specs of floating biphenyl.
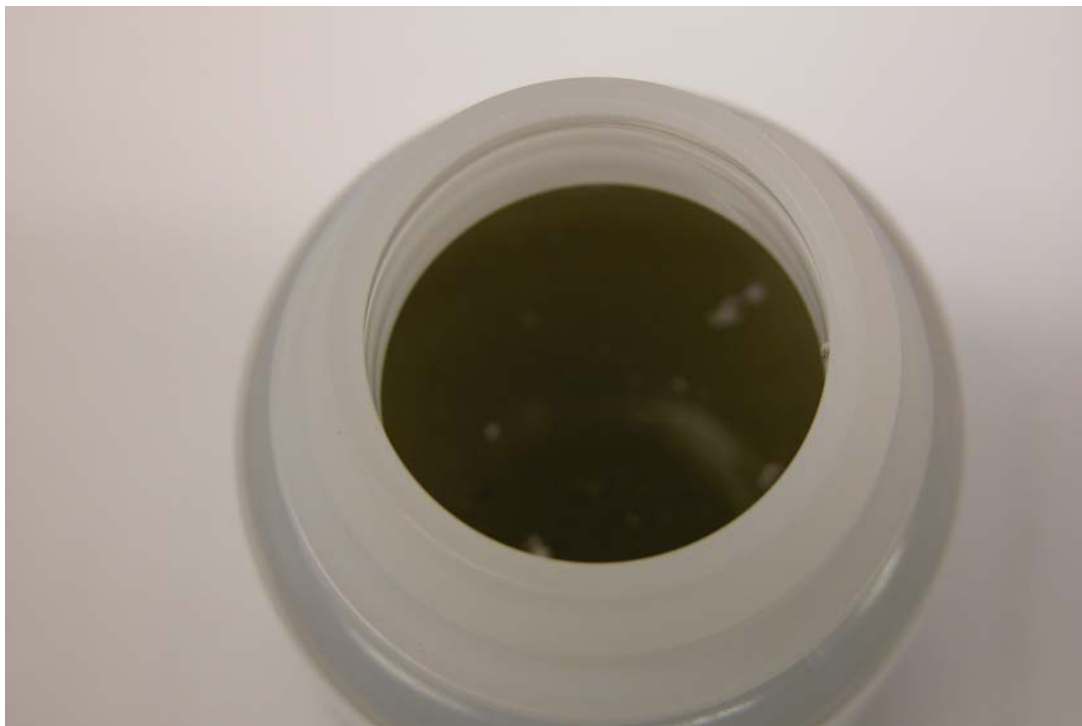
Figure 3-3.   Top view of treated simulant (test 4) with a few specs of floating biphenyl.
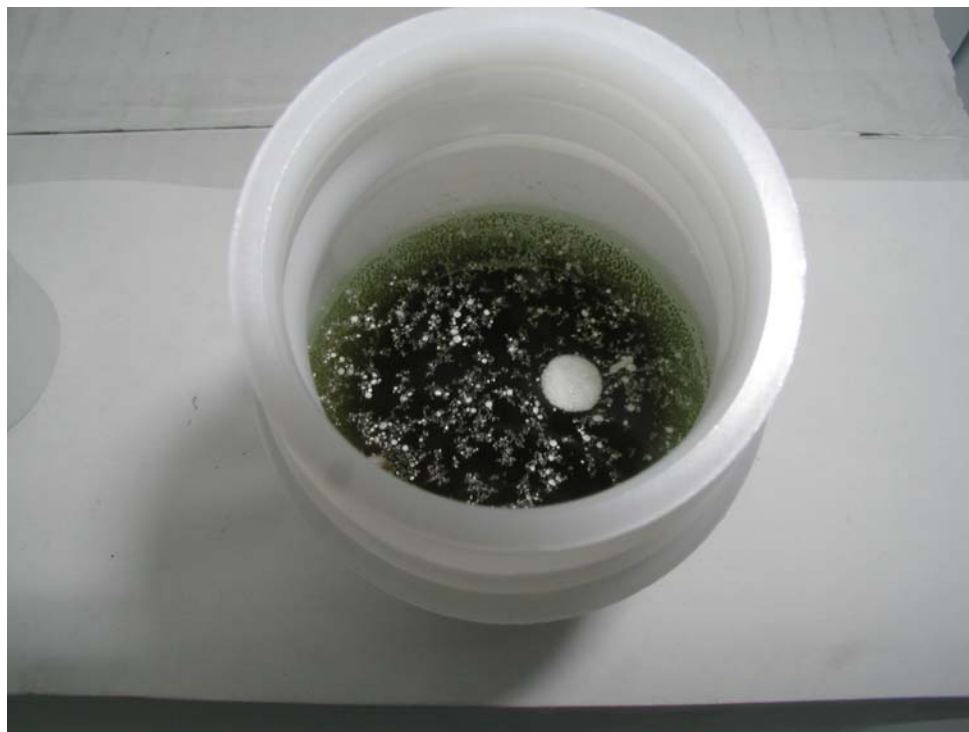
Figure 3-4. **Top view of treated simulant with floating biphenyl – test 16A of 2006 SWT study.**

Table 3-3. **Comparison of treated simulant data of the current study with the 2006 SWT testing.**

Analyte	Current Stirred Autoclave Testing		2006 SWT Shaking Autoclave Testing			
	Simulant Test 1	Simulant Test 4	Test 16A[a]	Test 16B[a]	Test 16C[a]	Test 16D[a]
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
TPB	< 0.25	< 0.25	< 0.8	< 1.0	< 0.8	< 1.0
3PB	< 10	< 10	< 10	< 10	< 10	< 10
2PB	< 10	< 10	< 10	< 10	< 10	< 10
1PB	< 10	< 10	< 10	< 10	< 10	< 10
Phenol	< 10	< 10	< 10	< 10	< 10	< 10
Biphenyl (total)	< 10	< 10	127	144[b]	51	21[b]
OH⁻	0.597M	0.143M	0.229M	nm	0.271M	nm
CO_3^{2-}	54,000	64,000	33,874	nm	36,332	nm
NO_2^-	2,850	5,760	6,310	nm	6,300	nm
NO_3^-	15,700	12,300	10,600	nm	10,800	nm

[a] Catalyst concentration was 500 mg Cu/L.
[b] Floating biphenyl was picked from the surface and analyzed.
nm – Not measured

As observed in the 2006 SWT shaking autoclave tests, formate and oxalate in the treated simulant are below detection limits. This may indicate the other low molecular weight carboxylic acid compounds may have been destroyed as well. Like the 2006 SWT tests, it is believed the Cu catalyst may have aided in their destruction because WAO typically does not destroy these compounds.

The elemental analysis data give an indication as to whether their compounds are present as insoluble or soluble species when one compares the corresponding slurry and filtrate concentration values of the treated simulant. For example, the boron and aluminum compounds are soluble while the copper and titanium compounds are largely insoluble. Note that Parr Bomb digestion with nitric acid preceded the slurry analysis of all the elements.

Overall, with the exception of few anomalies, the elemental analysis data of the treated slurry agree with the corresponding feed slurry data. The elemental analysis data with unexpected values included Ca, Cr, Cu, Fe, Hg, Mn, Ni, Ru, Ti, and Zr. The lower values obtained for Cu, Fe, Hg, Mn, Ti, and Zr for the treated slurry are most likely attributed to poor digestion that precedes the ICPES analysis. These elements may have formed compounds during the WAO treatment process that remain largely insoluble during the digestion step. The others seem to be anomalies. Note that generally the unexpected values do not affect the deduction as to whether the element is present in the treated simulant as soluble or insoluble compounds.

The B, Cs and K values for the filtrates of the treated simulants for both tests 1 and 4 corroborate the complete destruction of the TPB in the Tank 48H simulant. B, Cs and K filtrate values indicate all the B, Cs and K in the treated simulants are in the soluble form. Most of the B, Cs and K in the untreated simulant are present as insoluble CsTPB [$CsB(C_6H_5)_4$] and KTPB [$KB(C_6H_5)_4$] solids. The Cs treated slurry and filtrate data for the two tests confirm the deductions made in Section 3.1 regarding the amount of cesium originally put in the two batches of simulant. Recall, simulant batch 1 was used for test 1 and simulant batch 2 was used for test 4.

Some solids are lost at the end of each test run because it is generally difficult to recover all the solids in the treated slurry during transfer from the autoclave cylinder to the beaker. As a result, the total solids and the insoluble solids values shown are expected to be lower than the true values. Hence, no inference/meaningful comparisons can be made from the data. Also, the data should serve as a guide rather than be used on an absolute basis. The zero insoluble solids value for simulant test 1 is definitely an anomaly because there were solids in the treated slurry, as shown in Figure 3-5.

Figures 3-6 and 3-7 show X-ray diffractograms of the washed and air-dried solids in the treated slurry for simulant tests 1 and 4 respectively. The compounds identified by X-ray diffraction (XRD) in each test are (see top right corner) CuO (tenorite), carbon (graphite), $Na_2CO_3 \cdot H_2O$ (thermonatrite), and $Na_2Ti_3O_7$ (sodium titanium oxide). Note that the scale for Figure 3-6 is such that the peak intensities of most of the identified compounds are relatively small.

With the exception of graphite, all the above compounds were also identified in the SWT 2006 shaking autoclave tests run at similar conditions.[19]   Note that the SWT 2006 tests identified one more compound i.e., $Na_3H(CO_3)_2 \cdot 2H_2O$ (trona). However, a true comparison cannot be made because the 2006 material underwent freezing/thawing en route to SRNL for analysis. The $Na_2CO_3 \cdot H_2O$ (thermonatrite) results from the dissolution of the CO_2 that is generated from the reaction in the slurry as mentioned before. The reason for having graphite solids in the treated slurry has been discussed earlier. The titanium in the feed is present as amorphous $NaTi_2O_5H$ (MST - monosodium titanate). This indicates it transforms during the WAO reaction to crystalline $Na_2Ti_3O_7$ (sodium titanium oxide)

All in all, the treated simulant data for simulant tests 1 and 4 exhibit good reproducibility especially when one factors the change or reduction in stirrer speed for test 4 for the latter portion of the reaction period. Temperature-time and pressure-time plots of simulant tests 1 and 4 are in Appendix B.

Figure 3-5.   Side view of treated simulant (test 1) with settled solids at the bottom.
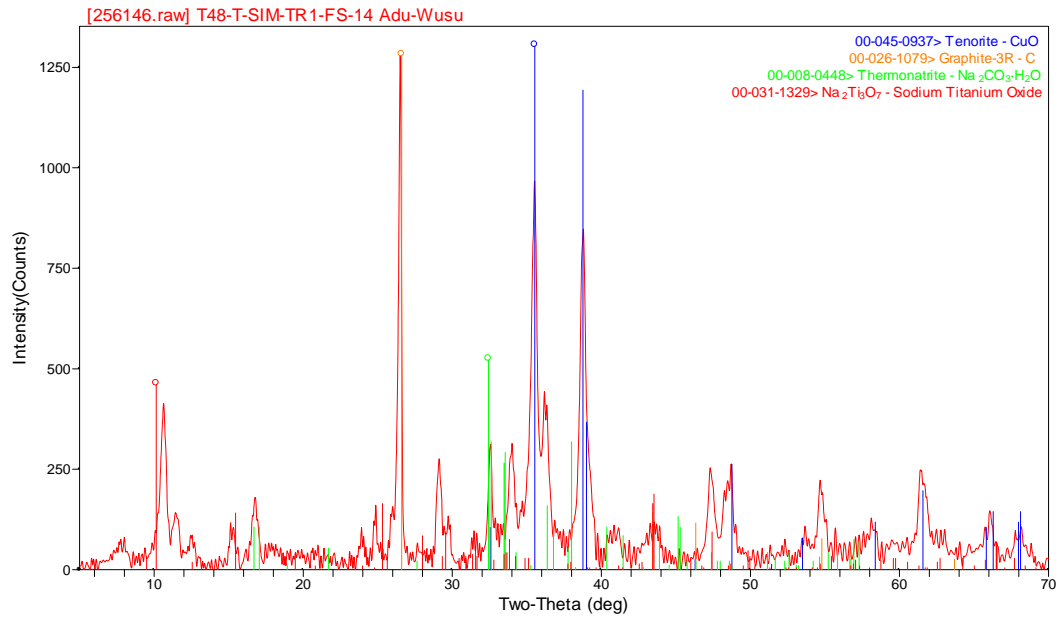
Figure 3-6.   X-ray diffractogram of solids in the treated simulant (test 1).
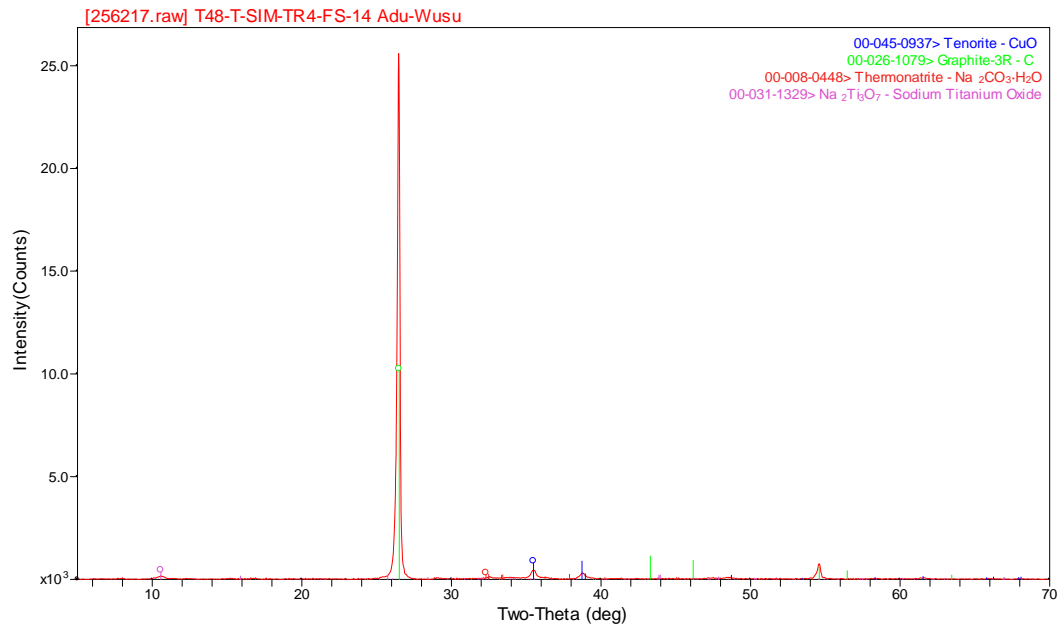
Figure 3-7.   X-ray diffractogram of solids in the treated simulant (test 4).

3.3 SIMULANT TESTS 5, 6, & 7

The discussion of the results for simulant tests 5 and 6 are similar to simulant tests 1 and 4. Hence, only the major similarities and differences will be highlighted.

Note that both tests were run at identical conditions (see Table 3-1). For these tests, the graphite bushing holding the stirrer shaft was moved up above the slurry feed. Therefore, loss of graphite from the bushing into the slurry is expected to be less than those of test 1 and 4. Note further that the loss of graphite into the slurry from the graphite (grafoil) gasket seal is expected to be roughly the same for all tests. In other words, graphite in the treated slurry is still expected or unavoidable for this test apparatus. However, overall the graphite in the treated slurry is expected to be less in simulant tests 5 and 6 compared to those of tests 1 and 4 because of moving the stirrer graphite bushing above the slurry. The generally lower TIC values for tests 5 and 6 compared to those of tests 1 and 4 lend support to this claim. It is also quite possible that lower TIC values may be due to less complete oxidation to CO_2 (which eventually converts to carbonate) as evidenced by the higher biphenyl concentration and the higher off-gas benzene concentration (see Table 3-9).

Again, Columns 5 and 6 of Table 3-4 give the treated slurry simulant analysis data for simulant tests 5 and 6 respectively. Columns 7 and 8 are analysis data of the filtrate of the treated simulant. The data in the fourth column are analysis data for the first batch of simulant which was used for test 1. Tests 4, 5, 6, and 7 used the second batch of simulant, which was not analyzed.

The top portion of columns 5 and 6 indicates, with the exception of biphenyl for test run 6, almost all the organics in the simulant (i.e., TPB, its daughter compounds [3PB, 2PB, 1PB], phenol and SVOCs, and VOCs excluding benzene) were destroyed to below their respective detection limits for simulant tests 5 and 6. The destruction efficiencies for the various compounds in the waste are given in Table 3-5. Test 6 had little floating biphenyl but not negligible in the treated simulant compared to test 5. Figures 3-8 and 3-9 show pictures of the treated simulant for tests 5 and 6 respectively.

Simulant test 7 was run at the same conditions as tests 5 and 6 as a demonstration for SWT visiting personnel. As a result, only HPLC analysis was done. The HPLC data for test 7 treated simulant were the same as test 6 except the total biphenyl was 35 mg/L (converts to 84% destruction efficiency). Again, an indication of an almost total destruction of all the organics in the simulant similar to tests 5 and 6.

The higher reaction temperature and longer residence time led directly to decreased floating biphenyl on the surface of the treated simulant for tests 1 and 4 compared to simulant tests 5, 6, and 7. High temperatures and long residence lead to more complete organic destructions. However, complete destruction of TPB was achieved in the three tests. The actual WAO process is a continuous-flow system. The undestroyed biphenyl will be in the off-gas in a continuous-flow system.

A comparison of the pictures/data of simulant tests 5, 6, and 7 to those of the 2006 SWT tests (see Figure 3-10 and Table 3-6) conducted at similar conditions (280 $^{\circ}$C for 1 hour) indicates better performance of the current stirred autoclave tests than the SWT shaking autoclave tests. This is due to the better mixing characteristics of stirred autoclaves as mentioned earlier.

About 17 and 20% of the nitrite in the feed were oxidized to nitrate for simulant tests 5 and 6 respectively. Again, the lower nitrite conversion for tests 5 and 6 compared to for simulant tests 1 and 4 is due to more stringent conditions of the latter.

Like simulant tests 1 and 4, the formate and oxalate values indicate they were destroyed to below detection levels. This is quite remarkable despite the less stringent conditions of simulant tests 5 and 6 and the fact that WAO does not generally do well with these compounds.

Figures 3-11 and 3-12 shows X-ray diffractograms of the washed and air-dried solids in the treated slurry for simulant tests 5 and 6 respectively. The compounds identified by XRD (see top right corner) in each test are as follows: CuO (tenorite), carbon (graphite), and $Na_2Ti_3O_7$ (sodium titanium oxide).

The same compounds were identified in simulant tests 1 and 4. However, unlike tests 1 and 4, $Na_2CO_3 \cdot H_2O$ (thermonatrite) is absent from simulant tests 5 and 6. This implies the $Na_2CO_3 \cdot H_2O$ that formed is soluble at the reaction temperature of 280 $^{\circ}$C. This is roughly in agreement with the scale formation observed in the WAO Phase 1 pilot-scale testing performed by SWT.[20-23]

On the whole, the reproducibility of the data for simulant tests 5 and 6 is fairly good. Plots of temperature versus time and pressure versus time for simulant tests 5 and 6 are in Appendix B.

Table 3-4.   Analytical data of Tank 48H treated simulant for simulant tests 5 & 6.

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8
Analyte	Analytical Method	Feed Slurry Nominal Conc.[a], mg/L	Feed Slurry Measured Conc.[a], mg/L	Test 5 Treated Slurry Conc., mg/L	Test 6 Treated Slurry Conc., mg/L	Test 5 Treated Slurry Filtrate Conc., mg/L	Test 6 Treated Slurry Filtrate Conc., mg/L
TPB	HPLC	9,186	8,515	< 0.25	< 0.25	nm	nm
3PB	HPLC	None	<100	< 10	< 10	nm	nm
2PB	HPLC	None	<100	< 10	< 10	nm	nm
1PB	HPLC	None	<100	< 10	< 10	nm	nm
Phenol	HPLC	476	486	< 10	< 10	nm	nm
Biphenyl (soluble)	HPLC	Unknown	nm	nm	< 10	nm	nm
Biphenyl (total)	HPLC	309	224	< 10	87	nm	nm
Biphenyl (Floating)	HPLC	n/a	n/a	negligible	Little but not measured[b]	nm	nm
Other SVOCs	GC-MS	Unknown	< 1	< 1	< 1	nm	nm
Benzene (includes added benzene)	P&T/GC-MS	27.5	27.5	< 0.25	< 0.25	nm	nm
Other VOCs	P&T/GC-MS	Unknown	< 0.25	< 0.25	< 0.25	nm	nm
TOC	TIC/TOC	8,951 (excludes antifoam)	4,760 (excludes antifoam)	negligible	negligible	negligible	negligible
TIC	TIC/TOC	2,739	2,540	11,100	12,200	10,800	10,900
TC	TIC/TOC	11,690 (excludes antifoam)	7,300 (excludes antifoam)	9,870	9,830	9,590	10,000
OH$^-$ (includes 2M NaOH as diluent)	Titration	1.80M	1.78M[c]	nm	nm	0.732M	0.721M
CO$_3^{2-}$	TIC/TOC	13,681	12,700	49,350	49,150	47,950	50,000
NO$_2^-$	IC	10,469	9,950[c]	nm	nm	8,250	7,980
NO$_3^-$	IC	6,541	6,600[c]	nm	nm	8,180	7,730
PO$_4^{3-}$	IC	252	< 250[c]	nm	nm	456	446
SO$_4^{2-}$ (includes calalyst)	IC	511	504[c]	nm	nm	576	558
Cl$^-$	IC	61	< 250[c]	nm	nm	88	88
F$^-$	IC	8.7	< 25[c]	nm	nm	< 125	< 125
Formate	IC	None	< 25[c]	nm	nm	< 125	< 125
Oxalate	IC	None	< 25[c]	nm	nm	< 125	< 125

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8
Analyte	Analytical Method	Feed Slurry Nominal Conc.[a], mg/L	Feed Slurry Measured Conc.[a], mg/L	Test 5 Treated Slurry Conc., mg/L	Test 6 Treated Slurry Conc., mg/L	Test 5 Treated Slurry Filtrate Conc., mg/L	Test 6 Treated Slurry Filtrate Conc., mg/L
Density	Gravimetric	1.1665 g/mL (undiluted)	1.09 g/mL (undiluted)	1.13 g/mL	1.13 g/mL	1.12 g/mL	1.12 g/mL
Total solids	Gravimetric	18.42 wt% (undiluted)	16.92 wt% (undiluted)	12.65 wt%	12.81 wt%	nm	nm
Dissolved solids	Gravimetric	16.60 wt% (undiluted)	15.52 wt% (undiluted)[c]	nm	nm	11.49 wt%	12.32 wt%
Insoluble Solids	Calculation	2.02 wt% (undiluted)	1.66 wt% (undiluted)	1.31 wt%	0.56 wt%	n/a	n/a
Ag	ICP-ES	Unknown	< 0.217	< 5.58	< 5.57	< 2.49	< 2.49
Al	ICP-ES	992	643	669	669	638	634
B	ICP-ES	311	293	290	304	288	286
Ba	ICP-ES	0.64	1.12	0.704	0.808	< 0.28	< 0.28
Ca	ICP-ES	15.7	19.0	14.2	12.7	< 1.56	< 1.56
Cd	ICP-ES	0.65	0.72	< 2.24	< 2.24	< 1.00	< 1.00
Ce	ICP-ES	2.75	2.28	< 11.6	< 11.6	< 5.19	< 5.19
Co	ICP-ES	Unknown	< 0.239	< 1.88	< 1.88	< 0.84	< 0.84
Cr	ICP-ES	23.4	22.2	26.0	27.8	24.6	23.5
Cs	ICP-MS	7.4	3.93	12.4	12.1	12.3	11.9
Cu (includes calalyst)[c]	ICP-ES	251.3	251.3	211	157	44.8	52.9
Fe	ICP-ES	59	60	47.3	52.4	< 0.971	< 0.971
Hg	AAS	5	2.29	< 2.46	2.58	1.36	1.30
K	AAS	1,260	638	1,187	1,164	1,170	1,200
K	ICP-ES	1,260	1,139	1,209	1,209	1,170	1,180
La	ICP-ES	0.49	0.53	< 8.95	< 8.94	< 4.00	< 4.00
Li	ICP-ES	Unknown	< 0.126	< 1.01	< 1.01	< 0.45	< 0.45
Mg	ICP-ES	0.70	1.75	< 5.65	< 5.64	< 2.53	< 2.53
Mn	ICP-ES	12	12.1	6.85	6.54	< 0.03	< 0.03
Mo	ICP-ES	4.5	4.49	5.25	5.38	3.91	4.20
Na (includes 2M NaOH as diluent)	ICP-ES	60,600	59,100	61,700	61,700	58,000	57,400
Na (includes 2M NaOH as diluent	AAS	60,600	55,600	62,600	58,500	56,100	61,800

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8
Analyte	Analytical Method	Feed Slurry Nominal Conc.[a], mg/L	Feed Slurry Measured Conc.[a], mg/L	Test 5 Treated Slurry Conc., mg/L	Test 6 Treated Slurry Conc., mg/L	Test 5 Treated Slurry Filtrate Conc., mg/L	Test 6 Treated Slurry Filtrate Conc., mg/L
Ni	ICP-ES	6.4	7.1	9.53	18.2	< 2.00	< 2.00
P	ICP-ES	82	89	84.6	87.1	83.2	80.5
Pb	ICP-ES	17	15.9	< 44.7	< 44.6	< 20	< 20
Pd	ICP-MS	0.04	0.031	< 0.0559	< 0.0558	0.0534	0.0297
Rh	ICP-MS	0.12	0.103	0.0622	0.0746	0.018	< 0.01
Ru	ICP-MS	0.13	0.106	0.1051	0.1074	0.0886	< 0.085
S (includes calalyst)	ICP-ES	171	176	183	199	185	179
Si	ICP-ES	44	39.9	42.0	45.0	32.3	27.6
Sn	ICP-ES	6.2	5.55	< 22.4	< 22.4	< 10.0	< 10.0
Sr	ICP-ES	2.89	2.91	< 4.47	< 4.46	< 2.00	< 2.00
Ti	ICP-ES	380	368	188	151	< 0.600	< 0.600
U	ICP-ES	Unknown	nm	nm	nm	nm	nm
V	ICP-ES	Unknown	< 0.279	< 1.72	< 1.72	< 0.77	< 0.77
Zn	ICP-ES	4.52	4.55	5.60	6.27	4.88	4.63
Zr	ICP-ES	6.2	0.219	< 2.24	< 2.24	< 1.00	< 1.00

[a] Values have been divided by 2 (except detection limits or indicated otherwise) because of the 1:1 dilution with NaOH and Cu catalyst.
[b] Amount is essentially equal to the total biphenyl value in the cell directly above this cell.
[c] Value is for the filtrate of the slurry.
Note:
Slurry analysis of all the elements was preceded by Parr Bomb digestion with nitric acid.
Values with < symbols are detection limits
nm – Not measured
n/a – Not applicable
AAS: Atomic Absorption Spectroscopy
GC-MS: Gas Chromatography-Mass Spectrometry
HPLC: High Performance Liquid Chromatography
IC: Ion Chromatography
ICP-ES: Inductively Coupled Plasma-Emissions Spectroscopy
ICP-MS: Inductively Coupled Plasma-Mass Spectroscopy
P&T: Purge and Trap
TC: Total Carbon
TIC/TOC: Total Inorganic Carbon/Total Organic Carbon

Table 3-5.   **Destruction efficiencies for the various organics in the simulant - tests 5 & 6.**

Compound	Percent Destruction Efficiency	
	Simulant Test 5	**Simulant Test 6**
TPB	> 99.997	> 99.997
Phenol	> 98	> 98
Biphenyl	> 96	61
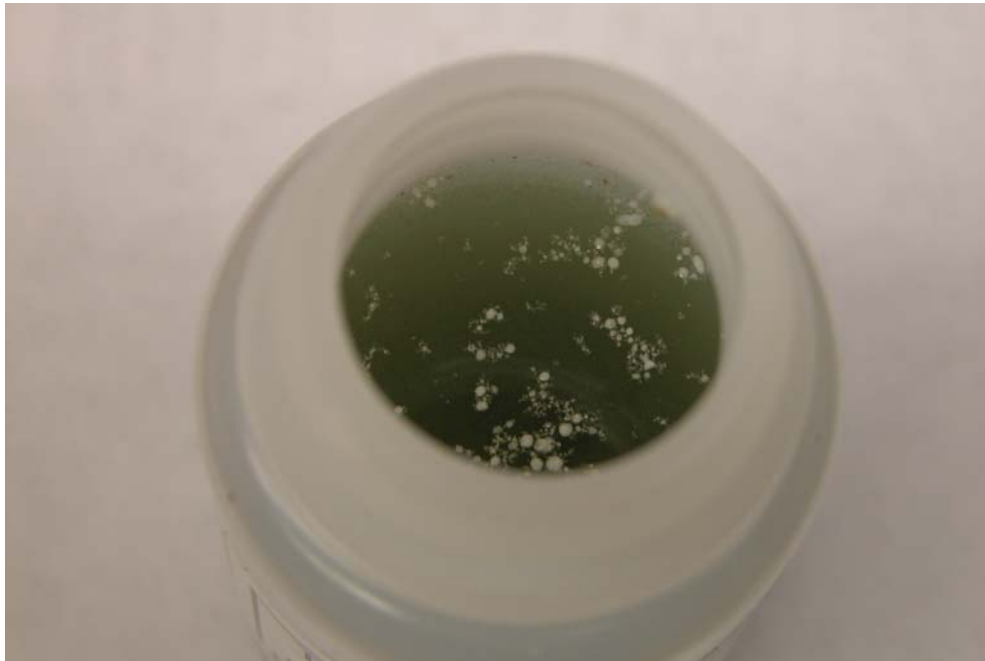
Figure 3-8.   **Top view of treated simulant (test 5) with floating biphenyl.**

Figure 3-9.   Top/side view of treated simulant (test 6) with floating biphenyl.

Savannah River
280 °C, 60 minutes
500 ppm Cu
pH 14.1
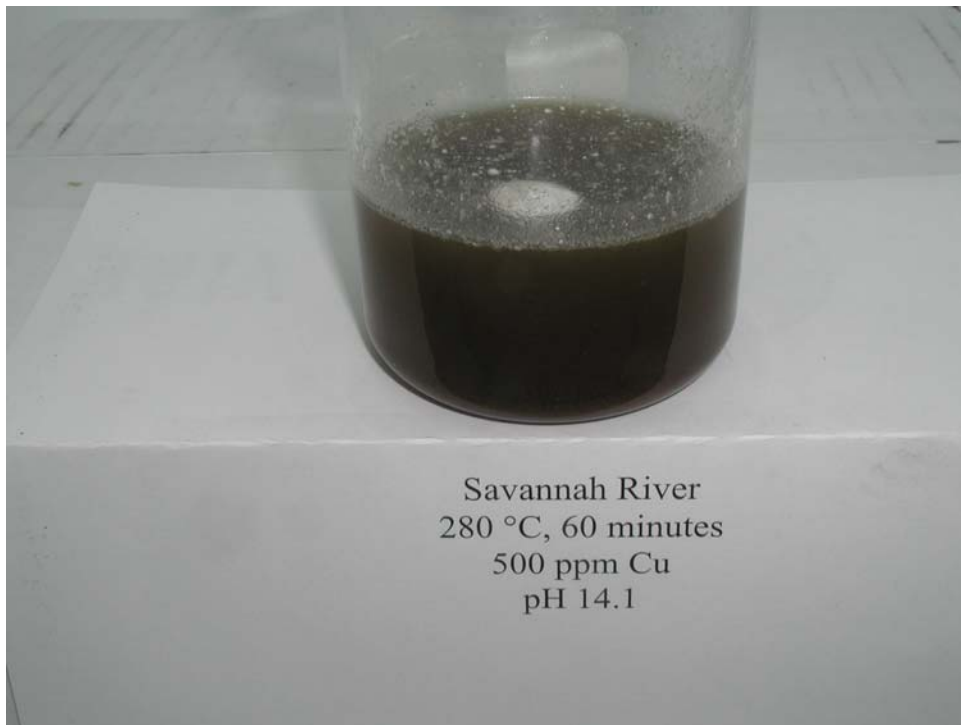
Figure 3-10.   Top/side view of treated simulant with floating biphenyl – test 7 of 2006 SWT study.

Table 3-6.   **Comparison of treated simulant data of the current study with the 2006 SWT testing.**

| Analyte | Current Stirred Autoclave Testing | | | 2006 SWT Shaking Autoclave Testing |
| | Simulant Test 5 | Simulant Test 6 | Simulant Test 7 | Test 7[a] |
	mg/L	mg/L	mg/L	mg/L
TPB	< 0.25	< 0.25	< 0.25	< 1.0
3PB	< 10	< 10	< 10	< 10
2PB	< 10	< 10	< 10	< 10
1PB	< 10	< 10	< 10	< 10
Phenol	< 10	< 10	< 10	< 10
Biphenyl (total)	< 10	87	35	1,190 [b]
OH^-	0.732M	0.721M	nm	nm
CO_3^{2-}	49,350	49,150	33,874	nm
NO_2^-	2,850	8,250	7,980	nm
NO_3^-	15,700	8,180	7,730	nm

[a] 4M NaOH was used as diluent and catalyst concentration was 500 mg Cu/L.
[b] Floating biphenyl was picked from the surface and analyzed.
nm – Not measured
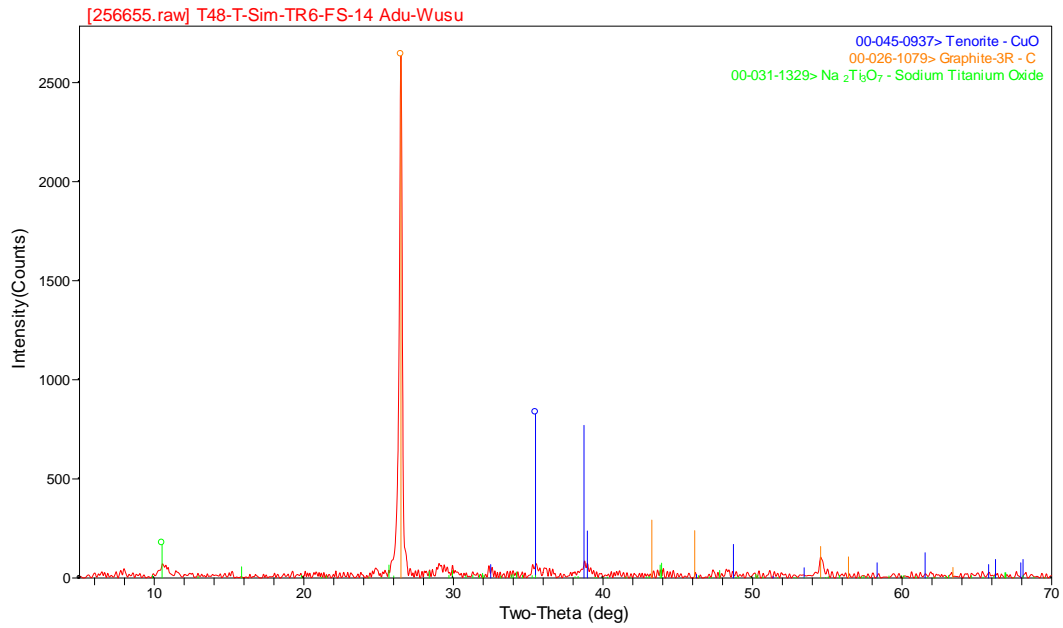
Figure 3-11. X-ray diffractogram of solids in the treated simulant (test 5).
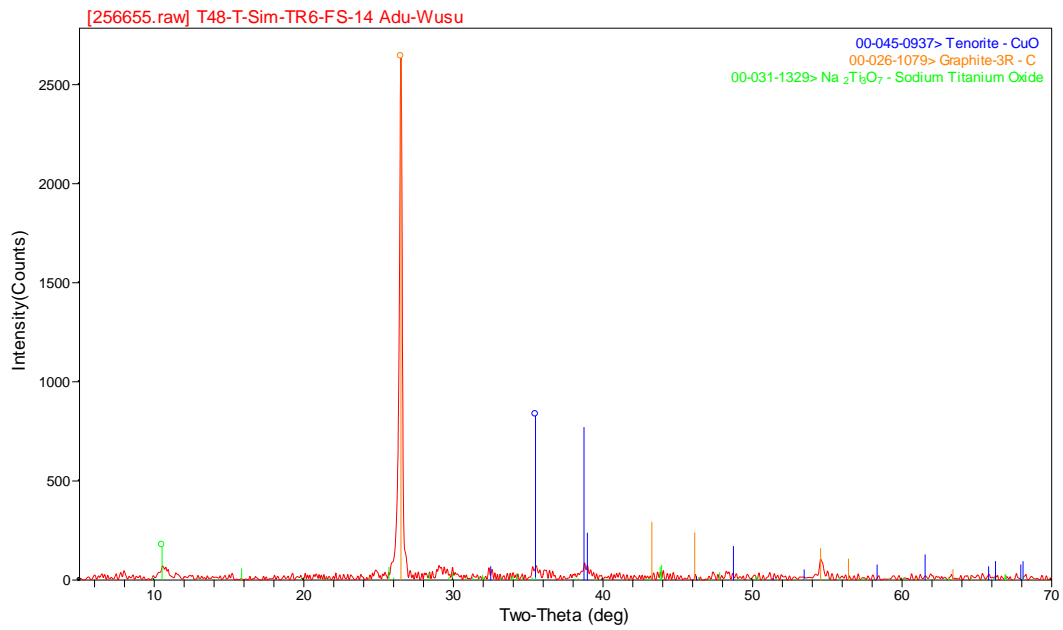
Figure 3-12. X-ray diffractogram of solids in the treated simulant (test 6).

3.4 RADIOACTIVE WASTE TESTS 1 & 2

The discussion of the results for the radioactive tests 1 and 2 is roughly similar to that of the simulant tests, especially simulant tests 5 and 6. Hence, only the salient features will be elucidated. Radioactive tests 1 and 2 and simulant tests 5 and 6 were run at identical conditions except no antifoam agent was added to the radioactive feed (see Table 2-1).

Table 3-7 is similar to Table 3-4 except the nominal concentration of the feed slurry simulant is included (column 3) to make comparisons more convenient. Columns 4 and 5 are the measured slurry and filtrate data of radioactive Tank 48H waste. The waste used for this test was not analyzed. The data in columns 4 and 5 are the latest analysis data available for the same batch of Tank 48H waste (batch ID #: HTF-E-05-021).[13] The 2003 analysis data (batch ID #: HTF-E-03-127)[12] were used in situations where data are not available from the 2005 analysis. Columns 6 and 7 of Table 3-7 give the treated radioactive waste slurry characterization data for radioactive tests 1 and 2 respectively. Columns 8 and 9 are the characterization data of the filtrate of the treated radioactive waste slurry.

The top portion of columns 6 and 7 indicates with the exception of biphenyl most of the organics in the radioactive waste (i.e., TPB; its daughter compounds [3PB, 2PB, 1PB]; phenol, nitrobenzene, nitrosobenzene, p-terphenyl, and SVOCs; and VOCs excluding benzene) were destroyed to below their respective detection limits for radioactive test runs 1 and 2. The TPB detection limits were slightly higher than the detection limits for the simulant tests because smaller volumes (4 - 5 mL instead of 10 mL) were sampled for analysis due to radiation dose concern. The difference in the TPB detection limit for radioactive tests 1 and 2 is due to the difference in the volumes submitted for analysis. In other words, the detection limit is indirectly proportional (for volumes less than 10 mL) to the sample volume used for the analysis.

Table 3-8 provides the destruction efficiencies for the various compounds in the waste. It is worthy to note that most of the compounds with relatively low destruction efficiencies (compared to that of TPB) have fairly high detection limits and/or low initial concentrations in the waste.

The biphenyl in the treated waste in both tests was mostly present as floating biphenyl. Even though the soluble biphenyl was not measured it is expected to be the same as in the simulant tests (i.e., < 10 mg/L). Again, the undestroyed biphenyl will be in the off-gas in an actual WAO process because it is a continuous-flow system.

Figures 3-13 and 3-14 show pictures of the treated waste for both radioactive tests. A comparison with those for simulant tests 5 and 6 (Figures 3-8 and 3-9) indicates the radioactive tests seem to have more biphenyl than the simulant tests. On the other hand, the biphenyl concentrations for the radioactive tests seem higher than what is perceived visually. This implies the high biphenyl concentration in the treated waste may be due to less than adequate mixing during sampling. The treated simulant sampling occurred simultaneously with magnetic stirrer mixing. Sampling of the treated radioactive waste was done by manual

shaking followed by sample withdrawal. It is quite possible a disproportionate amount of biphenyl may have been withdrawn or sampled.

The other reason is that the radioactive waste contains relatively more organics (formate, oxalate, nitrobenzene, nitrosobenzene, 3PB, 2PB, 1PB, etc.) than the simulant. In addition, the initial amount of oxygen was lower in the radioactive tests than simulant tests 5 and 6 (see Table 2-1 initial air charge pressure). Note that even though the biphenyl concentration in the treated waste is high, overall biphenyl was not created or generated.

Unlike the simulant, the radioactive waste contains formate and oxalate. The percent destruction achieved for formate and oxalate (see Table 3-8) attests to the statement made earlier for the simulant tests that the Cu catalyst helps to destroy, at least partially, these and possibly other low molecular weight carboxylic acid compounds which WAO typically does not destroy.[5,24] Even though all the oxalate in the radioactive waste was not destroyed, oxalate (unlike biphenyl) is used in SRS processes (e.g., waste tank sludge/heel dissolution) and therefore does not pose any risk to Tank Operations. In addition, use of a diluent/Tank 48H material volume ratio of 2:1 (instead of the 1:1 used for the current tests) as identified in the pilot-scale testing would increase the oxalate destruction efficiency. Along the same lines, formic acid is also used in SRS processes (glass processing in Defense Waste Processing Facility).

Because of limitations in the shielded cells, swirling or shaking of the autoclave cylinder that preceded transfer or pouring of the treated material into a beaker as was done for the simulant tests could not be done. As a result, some of the settled solids in the treated radioactive waste at the bottom of the cylinder could not be retrieved from the pouring operation in both tests. The solids were retrieved to the best extent possible by wiping them on a rag. The solids-laden rag for the radioactive test 2 was analyzed for TPB, 3PB, 2PB, 1PB, and phenol by HPLC. Since the mass of the solids was unknown, the concentrations were given on per gram of rag. The total mass of which was 11 grams.

Each of the above compounds had a value of < 50 mg/kg of rag. This value converts to < 5.5 mg/L of treated waste slurry. Even though the mass of the solids is unknown, by all accounts it is expected to be less than 2 grams based on the treated simulant wt% solids (see Table 3-4). Using 2 grams as the mass of the solids gives a concentration of < 0.4 mg/L of treated waste slurry. This implies the solids did not have any appreciable amounts of the above compounds and that the deduction made earlier that virtually all the organics were destroyed to below detection limits still holds.

Note that some biphenyl and terphenyl were observed in the HPLC analysis of the solids-laden rag but their concentrations could not be determined. Presumably, they were very small. Biphenyl in the treated Tank 48H material typically floats. Therefore, little if any is expected to be in the settled solids at the bottom of the autoclave cylinder. Terphenyl has not been identified in the past and was also not identified in the simulant tests in this study and, hence, is expected to be negligible. Although the settled solids at the bottom of the autoclave cylinder in the radioactive test 1 were not analyzed, the expectation is that the results will be similar to that of the radioactive test 2.

Table 3-7. Analytical data of actual Tank 48H treated waste for radioactive tests 1 & 2.

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8	Column 9
Analyte	Analytical Method	Simulant Feed Slurry Nominal Conc. [a], mg/L	Radioactive Feed Slurry Measured Conc. [a], mg/L	Radioactive Feed Slurry Filtrate Measured Conc. [a], mg/L	Test 1 Treated Radioactive Slurry Conc., mg/L	Test 2 Treated Radioactive Slurry Conc., mg/L	Test 1 Treated Radioactive Slurry Filtrate Conc., mg/L	Test 2 Treated Radioactive Slurry Filtrate Conc., mg/L
TPB	HPLC	9,186	10,500	< 10	< 0.4	< 0.3	nm	nm
3PB	HPLC	None	37	< 10	< 10	< 10	nm	nm
2PB	HPLC	None	71	< 10	< 10	< 10	nm	nm
1PB	HPLC	None	76	< 10	< 10	< 10	nm	nm
Phenol	HPLC	476	386	268	< 10	< 10	nm	nm
Biphenyl (soluble)	HPLC	Unknown	nm	nm	nm	nm	nm	nm
Biphenyl (total)	HPLC	309	210	< 10	195	136	nm	nm
Biphenyl (Floating)	HPLC	n/a	n/a	n/a	nm[b]	nm[b]	nm	nm
Nitrobenzene	GC-MS	n/a	90	< 10	< 1	< 1	nm	nm
Nitrosobenzene	GC-MS	n/a	91	< 10	< 1	< 1	nm	nm
p-terphenyl	GC-MS	n/a	12.7	< 10	< 1	< 1	nm	nm
Other SVOCs	GC-MS	Unknown	< 10	< 10	< 1	< 1	nm	nm
Benzene	P&T/GC-MS	27.5	9.0	< 10	0.2	< 0.05	nm	nm
Acetone	P&T/GC-MS	Unknown	nd	nd	0.06	< 0.05	nm	nm
Toluene	P&T/GC-MS	Unknown	nd	nd	< 0.05	0.16	nm	nm
Other VOCs	P&T/GC-MS	Unknown	nd	nd	< 0.05	< 0.05	nm	nm
TOC	TIC/TOC	8,951 (excludes antifoam)	10,700[c] (excludes antifoam)	1,505[c]	Negligible	Negligible	Negligible	Negligible
TIC	TIC/TOC	2,739	3,650[c]	3,920[c]	11,700	11,700	11,600	12,100
TC	TIC/TOC	11,690 (excludes antifoam)	14,350[c] (excludes antifoam)	5,425[c]	10,600	10,900	10,300	10,200
OH⁻ (includes 2M NaOH as diluent)	Titration	1.80M	nm	1.67M	nm	nm	0.272M	0.262M
CO_3^{2-}	TIC/TOC	13,681	nm	14,760[d]	53,000	54,500	51,500	51,000

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8	Column 9
Analyte	Analytical Method	Simulant Feed Slurry Nominal Conc. [a], mg/L	Radioactive Feed Slurry Measured Conc. [a], mg/L	Radioactive Feed Slurry Filtrate Measured Conc. [a], mg/L	Test 1 Treated Radioactive Slurry Conc., mg/L	Test 2 Treated Radioactive Slurry Conc., mg/L	Test 1 Treated Radioactive Slurry Filtrate Conc., mg/L	Test 2 Treated Radioactive Slurry Filtrate Conc., mg/L
NO_2^-	IC	10,469	nm	11,875	nm	nm	11,300	11,300
NO_3^-	IC	6,541	nm	7,125	nm	nm	8,110	8,180
PO_4^{3-}	IC	252	nm	214	nm	nm	613	617
SO_4^{2-} (includes calalyst)	IC	511.4	nm	539.4	nm	nm	768	770
Cl^-	IC	61	nm	86	nm	nm	472	473
F^-	IC	8.7	nm	7	nm	nm	< 125	< 125
Formate	IC	None	nm	251	nm	nm	< 125	< 125
Oxalate	IC	None	nm	720	nm	nm	273	289
Density	Gravimetric	1.1665 g/mL (undiluted)	1.165 g/mL (undiluted)	1.14 g/mL (undiluted)	1.11 g/mL	1.12 g/mL	1.12 g/mL	1.16 g/mL
Total solids	Gravimetric	18.42 wt% (undiluted)	20.19 wt% (undiluted)	n/a	14.42 wt%	14.34 wt%	nm	nm
Dissolved solids	Gravimetric	16.60 wt% (undiluted)	n/a	17.68 wt%	nm	nm	14.04 wt%	13.84 wt%
Insoluble Solids	Calculation	2.02 wt% (undiluted)	3.05 wt%	n/a	0.44 wt%	0.58 wt%	n/a	n/a
Ag	ICP-ES	Unknown	< 0.01	< 3	< 2.05	< 2.06	< 1.13	< 1.13
Al	ICP-ES	992	1,007	1,105	1,240	1,249	1230	1230
As	AA	Unknown	< 4.6	nm	< 0.463	< 0.464	< 0.0525	< 0.253
B	ICP-ES	311	434	230	548	554	540	539
Ba	ICP-ES	0.64	1.12	< 6	< 0.471	< 0.472	< 0.524	< 0.524
Be	ICP-ES	Unknown	nm	nm	< 0.054	< 0.054	< 0.0767	< 0.0767
Ca	ICP-ES	15.7	22	nm	3.04	2.75	< 0.892	< 0.892
Cd	ICP-ES	0.65	< 0.017	< 1	< 0.565	< 0.565	< 0.370	< 0.370
Cd	ICP-MS	0.65	0.007	nm	[f]	[f]	< 0.0438	< 0.0438
Ce	ICP-ES	2.75	2.5	< 35	< 12.49	< 12.51	< 4.10	< 4.10
Cr	ICP-ES	23.4	35	nm	29.0	28.9	28.5	28.4
Cs-133	ICP-MS	7.4	6.0	nm	7.69	6.97	6.95	6.56

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8	Column 9
Analyte	Analytical Method	Simulant Feed Slurry Nominal Conc. [a], mg/L	Radioactive Feed Slurry Measured Conc. [a], mg/L	Radioactive Feed Slurry Filtrate Measured Conc. [a], mg/L	Test 1 Treated Radioactive Slurry Conc., mg/L	Test 2 Treated Radioactive Slurry Conc., mg/L	Test 1 Treated Radioactive Slurry Filtrate Conc., mg/L	Test 2 Treated Radioactive Slurry Filtrate Conc., mg/L
Cu (includes calalyst)	ICP-ES	251	252	n/a	115	124	28.0	95.6
Fe	ICP-ES	59	85	< 3	15.6	11.4	< 0.582	1.14
Hg	AAS	5	< 10.23	nm	3.91	3.97	3.00	2.22
K	AAS	1,260	1,155	134	1,278	1,259	1,290	1,340
K	ICP-ES	1,260	1,285[c]	133	1,218	1,216	1,220	1,210
La	ICP-ES	0.49	< 0.032	< 13	< 1.01	< 1.02	< 0.784	< 0.784
Li	ICP-ES	Unknown	< 00263	< 12	< 1.72	< 1.73	< 1.07	< 1.07
Mg	ICP-ES	0.70	9.5	< 1	2.10	2.00	< 0.090	< 0.090
Mn	ICP-ES	12	3.0	< 1	< 2.15	< 2.17	< 0.267	< 0.267
Mo	ICP-ES	4.5	< 0.053	nm	< 3.60	< 3.61	3.10	3.59
Na (includes 2M NaOH as diluent)	ICP-ES	60,572	60,490	66,950	65,914	66,677	65,900	65,100
Na (includes 2M NaOH as diluent	AAS	60,572	55,200[c]	nm	56,112	53,112	62,800	61,700
Ni	ICP-ES	6.4	< 0.015	< 10	< 2.70	< 2.70	< 1.71	< 1.71
P	ICP-ES	82	65	nm	120	123	129	126
Pb	ICP-ES	17	< 0.283	< 196	< 11.6	< 11.6	< 5.22	< 5.22
Pd	ICP-MS	0.04	0.041[c]	0.037[c]	[f]	[f]	0.0360	0.0243
Rh	ICP-MS	0.12	0.103	< 0.7	< 1.39	< 1.38	0.0274	< 0.025
Ru	ICP-MS	0.13	0.106	< 1.16	< 3.82	< 3.80	< 0.131	< 0.131
S (includes calalyst)	ICP-ES	171	315	286	239	262	248	< 225
Se	AA	Unknown	< 4.8	nm	< 0.926	< 0.928	0.0968	< 0.505
Si	ICP-ES	44	63	< 125	74.2	75.5	72.8	73.8
Sn	ICP-ES	6.2	< 0.11	< 77	< 5.48	< 5.50	< 6.19	< 6.19
Sr	ICP-ES	2.89	4.5	nm	< 0.58	< 0.58	< 0.422	< 0.422
Ti	ICP-ES	380	413	< 1.00	58.0	34.0	< 0.342	< 0.342
U	ICP-ES	Unknown	3.5	< 50	< 48.2	< 48.2	< 26.4	< 26.4

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8	Column 9
Analyte	Analytical Method	Simulant Feed Slurry Nominal Conc. [a], mg/L	Radioactive Feed Slurry Measured Conc. [a], mg/L	Radioactive Feed Slurry Filtrate Measured Conc. [a], mg/L	Test 1 Treated Radioactive Slurry Conc., mg/L	Test 2 Treated Radioactive Slurry Conc., mg/L	Test 1 Treated Radioactive Slurry Filtrate Conc., mg/L	Test 2 Treated Radioactive Slurry Filtrate Conc., mg/L
V	ICP-ES	Unknown	< 0.007	0.44[c]	< 1.02	< 1.02	< 0.443	< 0.443
Zn	ICP-ES	4.52	2.5	2.71[c]	4.80	4.83	4.38	4.44
Zr	ICP-ES	6.2	0.74	< 2	< 0.47	< 0.47	< 0.257	< 0.257
Radionuclides								
Tc-99	ICP-MS	n/a	0.62	nm	< 1.47[h]	< 1.38[h]	0.57	0.58
Th-232	ICP-MS	n/a	nm	0.0098	< 3.48[h]	< 3.45[h]	0.0221	< 0.0125
Np-237	ICP-MS	n/a	0.087	0.0093	< 0.695[h]	< 0.691[h]	0.0621	0.0613
Pu-239	ICP-MS	n/a	< 0.045	< 0.0005[c]	< 1.39[h]	< 1.38[h]	< 0.0125	< 0.0125
Am-241	ICP-MS	n/a	< 0.09	nm	< 0.695[h]	< 0.691[h]	< 0.0188	< 0.0188
Am-243	ICP-MS	n/a	< 0.09	nm	< 0.695[h]	< 0.691[h]	< 0.0375	< 0.0375
Cm-244	ICP-MS	n/a	< 0.09	nm	< 0.695	< 0.691[h]	< 0.0125	< 0.0125
U-233	ICP-MS	n/a	< 0.09	0.0051	< 0.695[h]	< 0.691[h]	0.0279	0.0313
U-234	ICP-MS	n/a	0.134	0.036	< 0.695[h]	< 0.691[h]	0.142	0.113
U-235	ICP-MS	n/a	0.282	0.072	< 1.39[h]	< 1.38[h]	0.278	0.263
U-236	ICP-MS	n/a	0.063	0.016	< 0.695[h]	< 0.691[h]	0.0595	0.0521
U-238	ICP-MS	n/a	1.66	0.413	3.09[g,h]	2.94[g,h]	1.56	1.60
			dpm/mL	dpm/mL	dpm/mL	dpm/mL	dpm/mL	dpm/mL
Sr-90	LSC	n/a	8.15E+04[c]	1.08E+03[c]	< 2.81E+05	< 6.10E+05	< 9.73E+03	< 4.53E+03
Cs-137, dpm/mL	GAMMA SPEC	n/a	3.77E+08, current= 4.04E+08[e]	1.5E+07	4.22E+08[e]	4.26+08[e]	4.15E+08	3.86E+08
Pu-238	PUTTA	n/a	nm	8.45E+02[c]	2.10E+04[h]	2.50E+04[h]	2.84E+04	1.74E+04
Pu-239/240	PUTTA	n/a	nm	1.25E+02[c]	< 3.210E+03[h]	< 2.58E+04[h]	< 6.84E+02	< 5.51E+02
Gross Alpha,	LSC	n/a	1.40E+05[c]	< 1.33E+04[c]	< 1.32E+06[h]	< 1.48E+06[h]	< 9.09E+05	< 8.56E+05
Gross Beta	LSC	n/a	nm	nm	4.77E+08[h]	4.73E+08[h]	5.43E+08	4.82E+08

[a] Values have been divided by 2 (except detection limits or indicated otherwise) because of the 1:1 dilution with NaOH and Cu catalyst.
[b] Amount is essentially equal to the total biphenyl value in the cell directly above this cell.

^c Not measured in 2005. Used 2003 value.[12] 2003 analysis was used to develop the simulant recipe.

^d Analytical method = titration

^e Direct anaslysis without aqua regia digestion or sodium peroxide fusion digestion.

^f Zr contamination interfered with analysis

^g Value is comparable to blank

^h Sodium peroxide fusion followed by hydrochloric acid dissolution preceded the analysis.

<u>Note:</u>

Slurry analysis of all the elements was preceded by aqua regia digestion unless stated otherwise.

Values with < symbols are detection limits

nd – Not detected

nm – Not measured

n/a – Not applicable

AAS: Atomic Absorption Spectroscopy

GAMMA SPEC: Gamma Spectroscopy

GC-MS: Gas Chromatography-Mass Spectrometry

HPLC: High Performance Liquid Chromatography

IC: Ion Chromatography

ICP-ES: Inductively Coupled Plasma-Emissions Spectroscopy

ICP-MS: Inductively Coupled Plasma-Mass Spectroscopy

LSC: Liquid Scintillation Counting

P&T: Purge and Trap

PUTTA: Plutonium by Thenoyltrifluoroacetone

TC: Total Carbon

TIC/TOC: Total Inorganic Carbon/Total Organic Carbon

Table 3-8. **Destruction efficiencies for the various organics in the actual waste - Tests 1 & 2.**

	Percent Destruction Efficiency	
Compound	Radioactive Test 1	Radioactive Test 2
TPB	> 99.997	> 99.997
3PB	> 73	> 73
2PB	> 86	> 86
1PB	> 87	> 87
Phenol	> 98	> 98
Biphenyl	7	35
Nitrobenzene	> 99	> 99
Nitrosobenzene	> 99	> 99
p-terphenyl	> 92	> 92
Formate	> 62	> 59
Oxalate	50	50
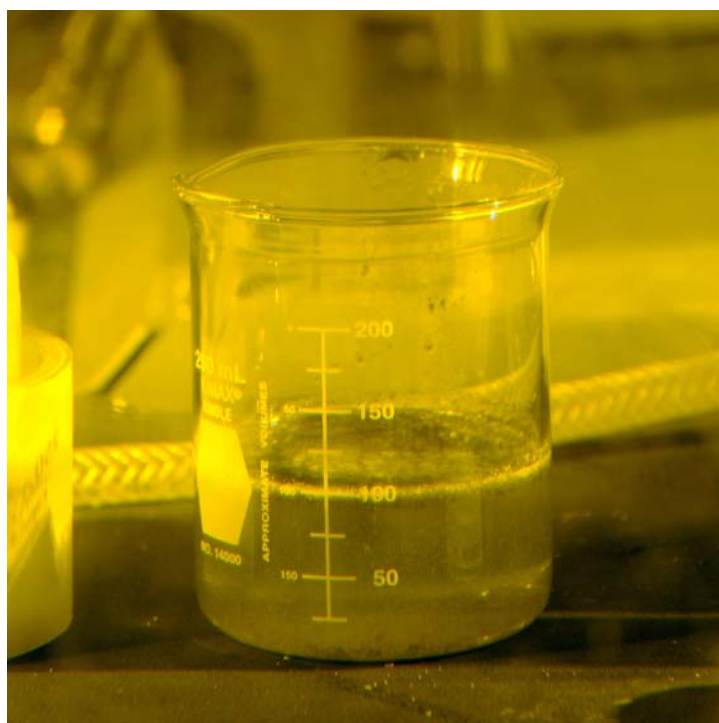
Figure 3-13.   Top/side view of treated radioactive waste (test 1) with floating biphenyl.
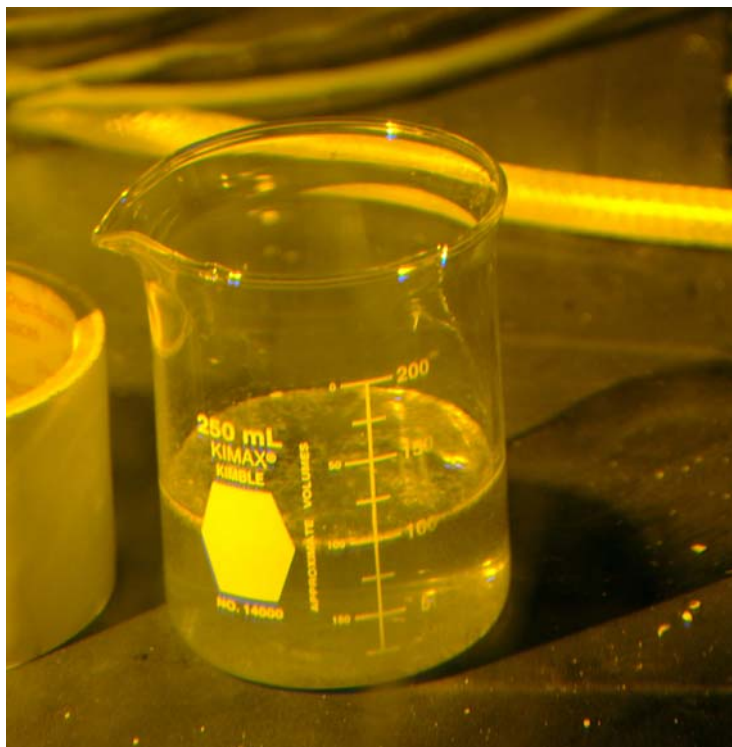
Figure 3-14.   Top/side view of treated radioactive waste (test 2) with floating biphenyl.

About 5% of the nitrite in the feed was converted to nitrate for both radioactive tests 1 and 2. It is unclear why this nitrite conversion value is lower than the nitrite conversion obtained for simulant tests 5 and 6. Interestingly, the off-gas oxygen concentration (Table 3-9 in next section) for simulant tests 5 and 6 and radioactive tests 1 and 2 are all roughly the same despite the fact that higher initial amount of oxygen was used for simulant tests 5 and 6 (see Table 2-1). What should have been excess oxygen from the simulant tests was used to react with the nitrite. Recall, the radioactive waste contains more organics (oxalate, formate, nitrobenzene, etc.) than the simulant. It seems the organics-oxygen reaction supersedes the nitrite-oxygen reaction.

The free hydroxide values may imply more residual low molecular weight carboxylic acid compounds when compared to simulant tests 5 and 6. This is not surprising since unlike the simulant, the radioactive waste contains formate and oxalate. It is quite possible the waste contains other low molecular weight carboxylic acid compounds that have not been analyzed for. The free hydroxide values also translate to a pH of 13.4 for both radioactive tests 1 and 2.

The discussion of the elemental analysis data for the non radionuclides is same as the previous two sections. The emphasis will now be on the radionuclides. The major radionuclide in the waste, Cs-137, is present in the treated waste as soluble species even though it is in the untreated waste as CsTPB [^{137}CsB(C$_6$H$_5$)$_4$] solids. The treated slurry and

filtrate data of the following radionuclides indicate they are present in treated waste as soluble species: Np-237, U-233, U-233, U-234, U-235, U-236, U-238, and Pu-238 by PUTTA. The Pu-238 by PUTTA data for test 2 indicate about 70% is in the soluble form. Sr-90 is in the treated waste in insoluble form.

The data for the rest of the radionuclides do not permit determination of their distribution (soluble/insoluble) in the treated waste. Both aqua regia digestion and sodium peroxide fusion/hydrochloric acid dissolution were utilized prior to the elemental analysis. The analytical data of the latter were not included because the detection limits were too high. Note that Parr Bomb digestion with nitric acid was used for the simulant tests. The simulant data show that generally Parr Bomb digestion faired better in dissolving Ca, Fe, Mn, Ni, and Ti than aqua regia digestion. It is quite possible a large portion of the above elements were in the settled solids left in the autoclave cylinder.

Figure 3-15 is X-ray diffractogram of the washed and air-dried solids in the treated slurry for radioactive test 1. The compounds identified by XRD (see top right corner) are CuO (tenorite), carbon (graphite), $Na_2Ti_3O_7$ (sodium titanium oxide), and $H_2(Ti_2SiO_7)(H_2O)_{1.5}$ (hydrogen titanium silicate hydrate). Figure 3-16 shows X-ray diffractogram of the washed and air-dried solids in the treated slurry for radioactive test 2. The compounds identified by XRD (see top right corner) are FeO(OH) (goethite), CuO (tenorite), carbon (graphite), and $Na_2Ti_3O_7$ (sodium titanium oxide).

It is hard to compare solids identified in both tests and also with simulant tests 5 and 6 because of the settled solids left in the autoclave cylinder. Strikingly, $Na_2CO_3 \cdot H_2O$ (thermonatrite) is absent from radioactive tests 1 and 2 just like simulant tests 5 and 6. Again, it may be affirming that $Na_2CO_3 \cdot H_2O$ that formed is soluble at the reaction temperature of 280 ^{o}C versus 300 ^{o}C.

The $H_2(Ti_2SiO_7)(H_2O)_{1.5}$ and FeO(OH) compounds identified in the radioactive tests 1 and 2 respectively may also be present in the simulant tests. However, the relative amounts in them may be too small for XRD to detect since the settled solids lost (from pouring of the treated material from the cylinder) in the simulant tests were minimal compared to the radioactive tests. Along the same vein, the above compounds not identified in either of the radioactive test may also be present.

The reproducibility of the radioactive tests 1 and 2 data is quite good overall. Temperature-time and pressure-time plots of radioactive tests 1 and 2 are in Appendix B.
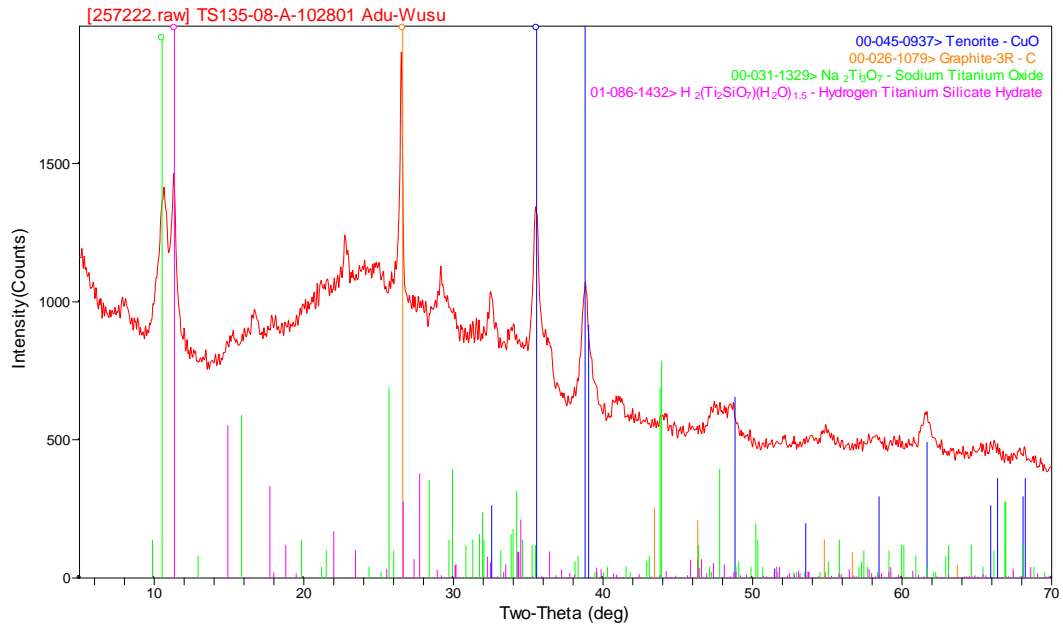
Figure 3-15.   X-ray diffractogram of solids in the treated radioactive waste (test 1).
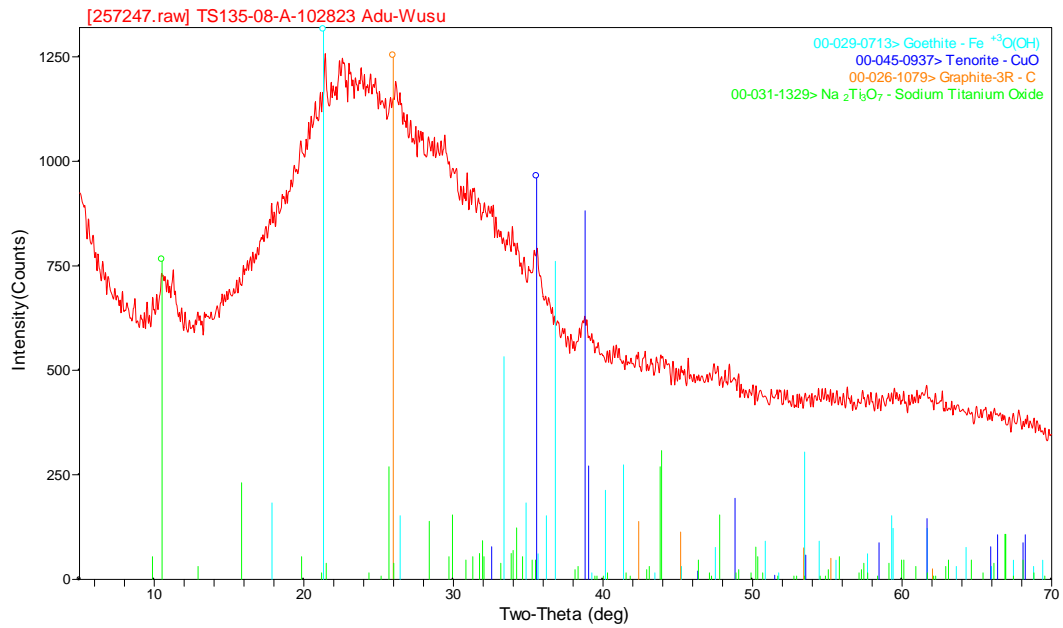

Figure 3-16.   X-ray diffractogram of solids in the treated radioactive waste (test 2).

3.5 SIMULANT AND RADIOACTIVE TESTS OFF-GAS DATA

Table 3-9 are untreated off-gas data for the simulant and radioactive tests given in both vol% and ppm$_v$. Benzene, methane, other gases/VOCs were analyzed by Purge and Trap/Gas Chromatography-Mass Spectroscopy (GC-MS). With the exception of a few of the nitrogen off-gas samples that were analyzed directly by Mass Spectroscopy (see footnote below the table), the rest of the off-gas data in Table 3-9 were obtained by GC using a thermal conductivity detector.

As expected, the major component in the untreated off-gas for all the tests is nitrogen followed by oxygen. Benzene in the off-gas for all the tests is relatively low. The highest value obtained (simulant test 6) is 6.9% of benzene lower flammability limit (LFL) of 1.4 vol% at 25 ^{o}C. Methane and other VOC gases were all below detection limits. Hydrogen in the off-gas for all the tests is also relatively low. The highest value obtained (radioactive test 1) is 0.16% of the hydrogen LFL of 4 vol% at 25 ^{o}C

Carbon dioxide, nitric oxide, and nitrous oxide were not detected in the off-gas. Even though carbon dioxide is the major product from the oxidation reaction, it dissolves in the alkaline Tank 48H material to form sodium carbonate compounds as alluded to earlier.

The bbenzene value for simulant test 4 is expected to be lower than that for simulant test 1 because the stirrer speed was reduced at the latter portion of simulant test 4 (see Section 3.5). Increased stirring speeds will drive relatively more volatile compounds out of the slurry to the headspace of the autoclave. However, it seems much lower than expected. It is probably an anomaly in the analysis. Note that the stirrer speed explanation is consistent with the hydrogen values for simulant tests 1 and 2.

For simulant tests 1 and 4, the off-gas data generally compares favorably with those obtained for the 2006 SWT shaking autoclave tests conducted at similar conditions (see Table 3-10). A notable exception is the benzene. The two 2006 tests with benzene data had disparities similar to simulant tests 1 and 4. As a result, it is hard to make any reasonable deductions. The oxygen values for simulant tests 1 and 4 are higher because their initial amounts of oxygen are higher than those of 2006 SWT shaking autoclave tests even though the initial charge pressure are the same. This is because the stirred autoclave has a bigger volume (525 mL versus ≈500 mL for the shaking autoclave).

The off-gas data for simulant tests 5 and 6 also compares favorably with those obtained for the 2006 SWT shaking autoclave tests (see Table 3-11) except benzene was not measured in the 2006 test. The higher benzene values for simulant tests 5 and 6 versus simulant tests 1 and 4 are the result of harsher test conditions (300 ^{o}C/3-hour reaction time versus 280 ^{o}C/1-hour reaction time) of simulant tests 1 and 4.

It is not clear why the benzene values for radioactive tests 1 and 2 are lower than those for simulant tests 5 and 6. The only speculative reason that comes to mind is the fact that the KTPB/CsTPB solids in the radioactive waste has a settling or sinking characteristic while the KTPB/CsTPB solids in the simulant float. This implies the reaction for the former occurs

deeper in the liquid than the latter. Benzene that is generated from the reaction deeper in the liquid has a higher probability of getting destroyed than benzene generated near the top of the liquid.

The higher hydrogen values for radioactive tests 1 and 2 versus simulant tests 5 and 6 are most likely due to radiolysis reaction that typical occurs in radioactive wastes. It is not clear why the hydrogen values for simulant tests 1 and 4 are higher than those of simulant tests 5 and 6. It may be due to the harsher test conditions (300 $^{\circ}$C/3-hour reaction time versus 280 $^{\circ}$C/1-hour reaction time) of simulant tests 1 and 4.

The oxygen values for radioactive tests 1 and 2 and simulant tests 5 and 6 are roughly the same even though the initial amount of oxygen in simulant tests 5 and 6 was higher. This was explained in the previous section.

The caution from the foregoing is that batch autoclave off-gas data may not match those of continuous-flow systems. Hence, the data should be viewed as giving an idea of the constituents that may be present in the off-gas of Tank 48H radioactive waste that has undergone WAO treatment. Also, the actual continuous-flow WAO system will have an off-gas treatment unit to destroy the constituents in the off-gas.

Table 3-9.   Off-Gas Data for the Simulant and Radioactive Tests.

	Units	Simulant Test 1	Simulant Test 4	Simulant Test 5	Simulant Test 6	Radioactive Test 1	Radioactive Test 2
Off-Gas Temperature	°C	20	25	18	22	23	23
Benzene	vol%	0.068	0.0001	0.082	0.096	0.017	0.016
Benzene	ppm$_v$	680	< 1	820	960	170	160
Methane	vol%	< 0.001	< 0.0001	< 0.001	< 0.001	< 0.001	< 0.001
Methane	ppm$_v$	< 10	< 1	< 10	< 10	< 10	< 10
Other Gases/VOCs	vol%	< 0.001	< 0.0001	< 0.001	< 0.001	< 0.001	< 0.001
Other Gases/VOCs	ppm$_v$	< 10	< 1	< 10	< 10	< 10	< 10
Nitrogen	vol %	92[a]	89	95[a]	94[a]	87[b]	88[b]
Nitrogen	ppm$_v$	920,000	890,000	950,000	940,000	870,000	880,000
Oxygen	vol %	12.6	10.3	14.4	14.6	14.8	15.3
Oxygen	ppm$_v$	126,000	103,000	144,000	146,000	148,000	153,000
Hydrogen	vol%	0.0030	0.0025	0.0016	0.0016	0.0063	0.0059
Hydrogen	ppm$_v$	30	25	16	16	63	59
Carbon Dioxide	vol %	nd	nd	nd	nd	nd	nd
Carbon Dioxide	ppm$_v$	nd	nd	nd	nd	nd	nd
Carbon Monoxide	vol %	nd	nd	nd	nd	nd	nd
Carbon Monoxide	ppm$_v$	nd	nd	nd	nd	nd	nd
Nitric Oxide	vol%	nd	nd	nd	nd	nd	nd
Nitric Oxide	ppm$_v$	nd	nd	nd	nd	nd	nd
Nitrous Oxide	vol%	nd	nd	nd	nd	nd	nd
Nitrous Oxide	ppm$_v$	nd	nd	nd	nd	nd	nd

[a] Value is beyond the calibration range of the mass spectroscopy instrument.
[b] Value is beyond the calibration range of the GC-thermal conductivity detector instrument.
nd – Not detected i.e., no distinct or visible chromatogram peaks at the typical expected times.

Table 3-10.   Comparison of off-gas data of the current study with the 2006 SWT testing.

		Current Stirred Autoclave Testing		2006 SWT Shaking Autoclave Testing			
	Units	Simulant Test 1	Simulant Test 4	Test 16A	Test 16B	Test 16C	Test 16D
Off-Gas Temperature	°C	20	25	18	17	21	25
Benzene	vol%	0.068	0.0001	0.0347	nm	0.1243	nm
Benzene	ppm_v	680	< 1	347	nm	1,243	nm
Methane	vol%	< 0.001	< 0.0001	< 0.005	< 0.005	< 0.005	< 0.005
Methane	ppm_v	< 10	< 1	< 50	< 50	< 50	< 50
Other Gases/VOCs	vol%	< 0.001	< 0.0001	nm	nm	nm	nm
Other Gases/VOCs	ppm_v	< 10	< 1	nm	nm	nm	nm
Nitrogen	vol %	92[a]	89	91	92	90	92
Nitrogen	ppm_v	920,000	890,000	910,000	920,000	900,000	920,000
Oxygen	vol %	12.6	10.3	7.9	6.5	9.0	7.8
Oxygen	ppm_v	126,000	103,000	79,000	65,000	90,000	78,000
Hydrogen	vol%	0.0030	0.0025	< 0.05	< 0.05	< 0.05	< 0.05
Hydrogen	ppm_v	30	25	< 500	< 500	< 500	< 500
Carbon Dioxide	vol %	nd	nd	< 0.5	< 0.5	< 0.5	< 0.5
Carbon Dioxide	ppm_v	nd	nd	< 5,000	< 5,000	< 5,000	< 5,000
Carbon Monoxide	vol %	nd	nd	< 0.1	< 0.1	< 0.1	< 0.1
Carbon Monoxide	ppm_v	nd	nd	< 1,000	< 1,000	< 1,000	< 1,000
Nitric Oxide	vol%	nd	nd	nm	nm	nm	nm
Nitric Oxide	ppm_v	nd	nd	nm	nm	nm	nm
Nitrous Oxide	vol%	nd	nd	nm	nm	nm	nm
Nitrous Oxide	ppm_v	nd	nd	nm	nm	nm	nm
Total Hydrocarbons	vol% as ethane	nm	nm	1,460	1,612	1,140	1,180
Total Hydrocarbons	ppm_v as ethane	nm	nm	6.8	6.2	8.9	8.5

[a] Value is beyond the calibration range of the mass spectroscopy instrument.
nd – Not detected i.e., no distinct or visible chromatogram peaks at the typical expected times.
nm – Not measured

Table 3-11.   Comparison of off-gas data of the current study with the 2006 SWT testing.

	Units	Current Stirred Autoclave Testing		2006 SWT Shaking Autoclave Testing[a]
		Simulant Test 5	Simulant Test 6	Test 7
Off-Gas Temperature	°C	18	22	20
Benzene	vol%	0.082	0.096	nm
Benzene	ppm$_v$	820	960	nm
Methane	vol%	< 0.001	< 0.001	< 0.005
Methane	ppm$_v$	< 10	< 10	< 50
Other Gases/VOCs	vol%	< 0.001	< 0.001	nm
Other Gases/VOCs	ppm$_v$	< 10	< 10	nm
Nitrogen	vol %	95[b]	94[b]	90
Nitrogen	ppm$_v$	950,000	940,000	900,000
Oxygen	vol %	14.4	14.6	10.8
Oxygen	ppm$_v$	144,000	146,000	108,000
Hydrogen	vol%	0.0016	0.0016	< 0.05
Hydrogen	ppm$_v$	16	16	< 500
Carbon Dioxide	vol %	nd	nd	< 0.5
Carbon Dioxide	ppm$_v$	nd	nd	< 5,000
Carbon Monoxide	vol %	nd	nd	< 0.1
Carbon Monoxide	ppm$_v$	nd	nd	< 1,000
Nitric Oxide	vol%	nd	nd	nm
Nitric Oxide	ppm$_v$	nd	nd	nm
Nitrous Oxide	vol%	nd	nd	nm
Nitrous Oxide	ppm$_v$	nd	nd	nm
Total Hydrocarbons	vol% as ethane	nm	nm	1,170
Total Hydrocarbons	ppm$_v$ as ethane	nm	nm	8.5

[a] 4M NaOH was used as diluent.
[b] Value is beyond the calibration range of the mass spectroscopy instrument.
nd – Not detected i.e., no distinct or visible chromatogram peaks at the typical expected times.
nm – Not measured

4.0 CONCLUSIONS

The conclusions of the study are as follows.

The Tank 48H waste simulant is valid for the following nominal WAO test conditions:

> A temperature of 280 °C, a reaction time of 1 hour, $CuSO_4 \cdot 5H_2O$ solution (250 mg/L Cu) as catalyst, and 1:1 Tank 48H radioactive waste dilution with 2M $NaOH/CuSO_4 \cdot 5H_2O$ solutions.

The above conditions are the same as the conditions identified in the Phase 1 continuous-flow pilot-scale testing conducted by SWT except the diluent/Tank 48H waste volume ratio and the catalyst concentration were 2:1 and 100 mg/L Cu respectively. The diluent/Tank 48H waste volume ratio of 1:1 used in the current study is conservative to the 2:1 ratio for the pilot-scale testing. Further, the 250 mg/L Cu catalyst concentration used in the in the current tests (versus the 100 mg/L Cu used in the Phase 1 continuous-flow pilot-scale testing) is not expected to impact the destruction performance. Only the soluble form of the Cu performs the catalytic action. The amount of Cu that remains soluble is less than 100 mg/L.

TPB, its daughter compounds (3PB, 2PB, 1PB), phenol, nitrobenzene, nitrosobenzene, etc. in the radioactive waste were all destroyed to below their respective detection limits. In fact, biphenyl is the only organic compound of interest in the treated waste that was not completely destroyed. The partial destruction of biphenyl stems from its propensity to go to the vapor phase during the oxidation reaction.

The undestroyed biphenyl is essentially biphenyl vapor that solidifies (because of its low melting point – about 68 ^{o}C) when the autoclave is cooled at the end of the WAO reaction. The undestroyed biphenyl is expected to be in the off-gas in the continuous flow WAO system for Tank48H material.

Destruction efficiency of TPB was > 99.997% while that of the other organic compounds (except biphenyl) were for the most part > 85%. The fairly low destruction efficiencies (compared to that of TPB) for most of the other compounds are due to their relatively high detection limits and/or low initial concentrations in the waste.

The autoclave radioactive waste tests were a confirmation to earlier simulant tests performed at identical conditions. The radioactive waste tests and the simulant tests were fairly comparable particularly the destruction efficiencies of the major organic compounds (TPB and phenol).

The above results should be viewed under the perspective that the test conditions are conservative relative to the conditions identified in the Phase 1 continuous-flow pilot-scale testing conducted by Siemens Water Technologies Corporation (SWT) in Rothschild, Wisconsin. By all accounts, had the tests been conducted at a 2:1 diluent/Tank 48H waste volume ratio as identified in the continuous-flow pilot-scale testing (versus the 1:1

diluent/Tank 48H waste volume ratio used for the current tests), the destruction efficiency of all the organic constituents in the Tank 48H waste, especially biphenyl, would most likely have been greater.

The reaction byproducts were identified and quantified to the extent possible. The major ones are mentioned below.

The common compounds identified by x-ray diffraction (XRD) in all four tests (i.e., two radioactive waste tests and two simulant tests) were CuO (tenorite), carbon (graphite), and $Na_2Ti_3O_7$ (sodium titanium oxide). Graphite is an artifact of the tests. It is the result of autoclave graphite gasket breakage and possibly erosion from graphite stirrer bushing.

Additional compounds identified by XRD in radioactive tests 1 and 2 were $H_2(Ti_2SiO_7)(H_2O)_{1.5}$ (hydrogen titanium silicate hydrate) and FeO(OH) (goethite) respectively. Even though these compounds were not identified in the simulant tests, they are most likely present in all the treated material. Smaller loss of solids during pouring of treated material in the simulant tests compared to the radioactive tests precluded their identification by XRD.

The percent conversion of nitrite to nitrate was higher in the simulant tests (17%) than radioactive tests (5%). The organics-oxygen reaction from the increased number of organic constituents or compounds (oxalate, formate, nitrobenzene, etc.) in the radioactive waste seems to supersede the nitrite-oxygen reaction.

The major radionuclide in the waste, Cs-137, is present in the treated waste as soluble species even though it is in the untreated waste as $^{137}CsB(C_6H_5)_4$ solids. The same is true for B and K which are also present in the untreated waste as insoluble $^{137}CsB(C_6H_5)_4$ and $KB(C_6H_5)_4$ solids. Cs-133, the non radionuclide cesium in the waste behaves in a similar manner. Np-237, U-233, U-233, U-234, U-235, U-236, U-238, and Pu-238 are largely present in the treated waste as soluble species while Sr-90 is present in insoluble form.

The untreated off-gas from both the radioactive waste and the simulant tests indicated the major components are nitrogen, oxygen, benzene, and hydrogen in that order. All other gases (methane/other volatile organic compounds, carbon dioxide, carbon monoxide, nitric oxide, and nitrous oxide) were either below detection limits or were not detected at all. Benzene and hydrogen in the off-gas for all the tests were fairly low. The highest concentrations of benzene and hydrogen in the off-gas obtained for all six tests were 0.096 and 0.0063 vol% respectively. These convert to 6.9% of benzene lower flammability limit (LFL) of 1.4 vol% at 25 °C and 0.16% of hydrogen LFL of 4 vol% at 25 °C.

Prior to the above tests at the pilot-scale testing conditions, the 2006 batch bench-scale shaking autoclave simulant tests conducted by SWT was replicated with the stirred autoclave at the same conditions as those identified in 2006. The test conditions were a temperature of 300 °C, a reaction time of 3 hours, $CuSO_4 \cdot 5H_2O$ solution (500 mg/L Cu) as catalyst, and 1:1 Tank 48H simulant dilution with 2M $NaOH/CuSO_4 \cdot 5H_2O$ solutions, and 1 mL/L of antifoam agent.

The tests demonstrated a good replication of the results of the 2006 SWT testing. TPB, 3PB, 2PB, 1PB, phenol, and biphenyl in the simulant were all destroyed to below their respective detection limits. It must be noted that biphenyl was only partially destroyed in the 2006 SWT shaking autoclave testing. The nearly total destruction of biphenyl is attributed to the better mixing characteristic of stirred autoclaves. Other results in terms of conversion of nitrite to nitrate, solid compounds in the treated simulant identified by x-ray diffraction, and constituents in the off-gas, etc. were by and large comparable.

5.0 RECOMMENDATIONS

The batch bench-scale autoclave testing demonstrated WAO is feasible technology for the destruction of TPB and other organics in Tank 48H radioactive waste. Therefore, the activities or programs outlined in the technology maturation plan should continue.

6.0 ACKNOWLEDGEMENTS

Many people in the organizations below at SRNL contributed to the successful completion of this work. Sincere thanks to all the people who provided assistance.

Environmental & Chemical Process Technology
Analytical Development
SRNL Engineering
SRNL Facility Training
Shielded Cells Operations
Remote & Specialty Equipment

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8.0 APPENDIX A

Table A-1.   Concentration of major constituents in Tank 48H.

Constituent	Concentration, M
KTPB	0.0574
CsTPB	0.0001
NaOH	1.5973
$NaNO_2$	0.4551
Na_2CO_3	0.4560
$NaNO_3$	0.2042
$NaAlO_2$	0.0735
$Na_3PO_4 \cdot 12H_2O$	0.0053
Na_2SO_4	0.0028
NaCl	0.0034
NaF	0.0009
KNO_3	0.0068

Table A-2.   Concentration of minor constituents (metals/other compounds) in Tank 48H.

Constituent	Metal Concentration, mg/L	Compound Added	Constituent	Concentration, mg/L	Compound Added
Pd	0.0801	$Pd(NO_3)_2$	Phenol	952	Phenol
Cu	1.9276	$Cu(SO_4) \cdot 5H_2O$	Biphenyl	618	Biphenyl
Mo	8.9957	$Na_2MoO_4 \cdot 2H_2O$	Benzene	55.0	Benzene
Cr	45.5981	Na_2CrO_4	Purex sludge[b]	435	Purex sludge[b]
Zn	7.7367	$Zn(NO_3)_2 \cdot 6H_2O$			
Pb	30.8228	$Pb(NO_3)_2$			
Sn	12.2313	$SnCl_2 \cdot 2H_2O$			
Ca	19.2765	$Ca(NO_3)_2 \cdot 4H_2O$			
Sr	5.5155	$Sr(NO_3)_2$			
La	0.9687	$La(NO_3)_3 \cdot 6H_2O$			
Cd	1.2916	$Cd(NO_3)_2 \cdot 4H_2O$			
Ce	5.4894	$Ce(NO_3)_3 \cdot 6H_2O$			
Rh	0.2251	$Rh(NO_3)_3$			
Ru	0.2476	$RuCl_3 \cdot xH_2O$			
Si	88.00	$Na_2SiO_3 \cdot 9H_2O$			
Hg	10.0	Diphenyl Hg			
Ti	759	MST[a]			

[a] Monosodium titanate (MST) is added as slurry.
[b] Plutonium-uranium extraction (PUREX) sludge is added as slurry.

Table A-3.   PUREX sludge simulant composition (balance of mass is oxide/hydroxide).

Constituent Element	Wt% as dry solid[a]	mg/L contribution in slurry[b]
Al	4.53	19.68
B	0.08	0.34
Ba	0.29	1.27
Ca	2.77	12.03
Cr	0.29	1.24
Cu	0.15	0.67
Fe	26.85	116.8
K	1.90	8.27
Mg	0.32	1.40
Mn	5.54	24.10
Na	2.45	10.66
Ni	2.94	12.77
Pb	0.44	1.90
Si	1.51	6.57
Sr	0.06	0.25
Zn	0.30	1.32
Zr	2.83	12.31

[a] PUREX sludge simulant: ~17 wt% metal hydroxide/oxide slurry, quantity shown is dry solid weight.
[b] mg/L contribution for 435 mg/L dry solids added.

9.0 APPENDIX B
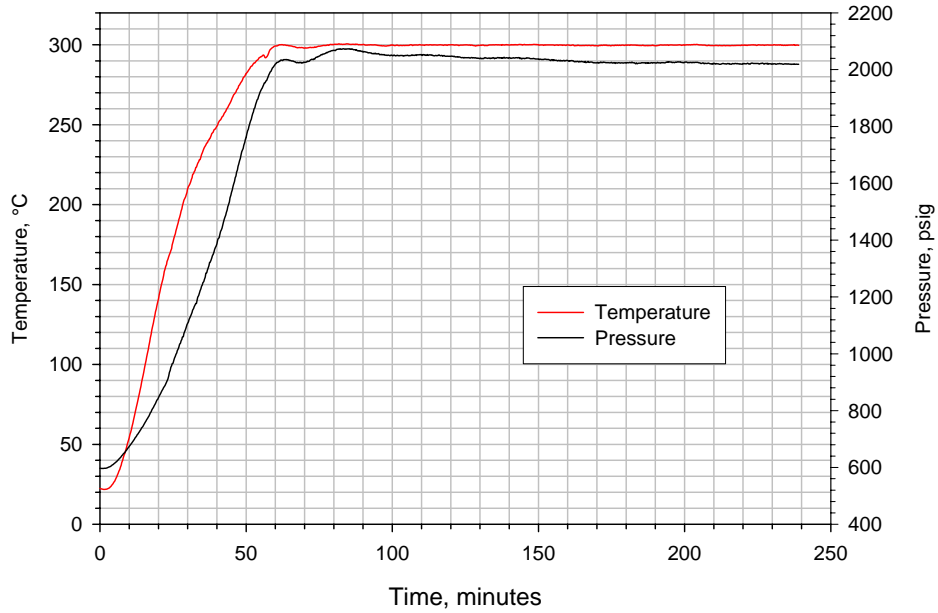
Figure B-1.   Temperature and pressure profiles for simulant test 1.
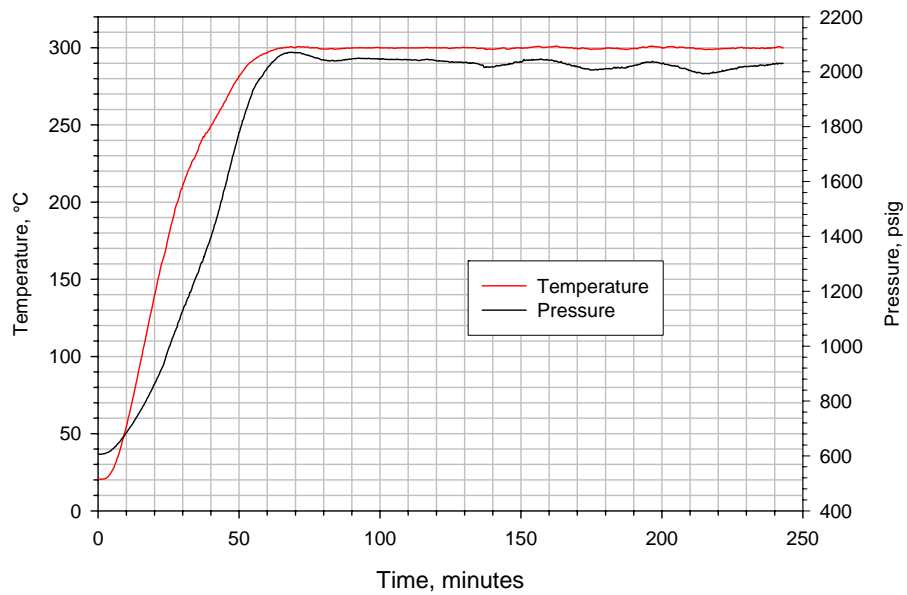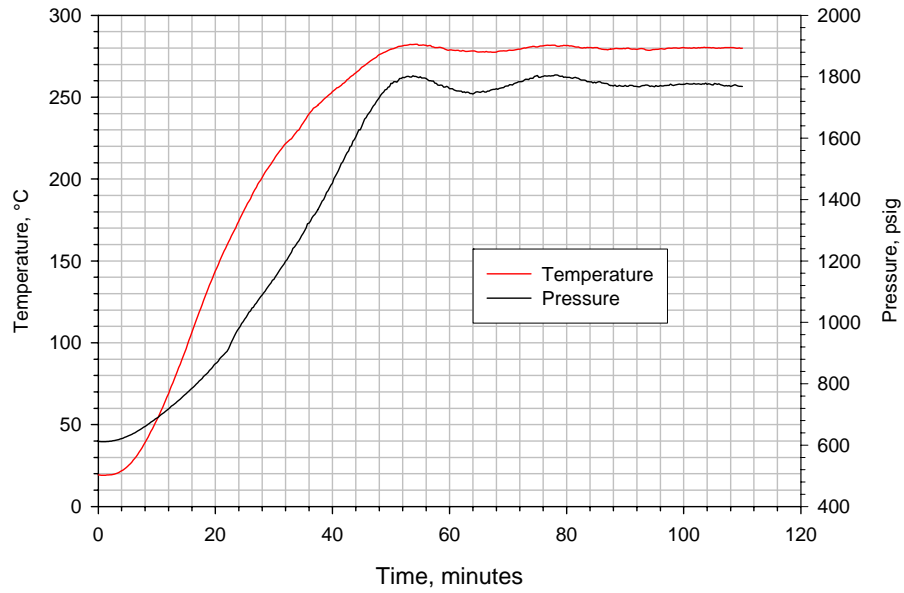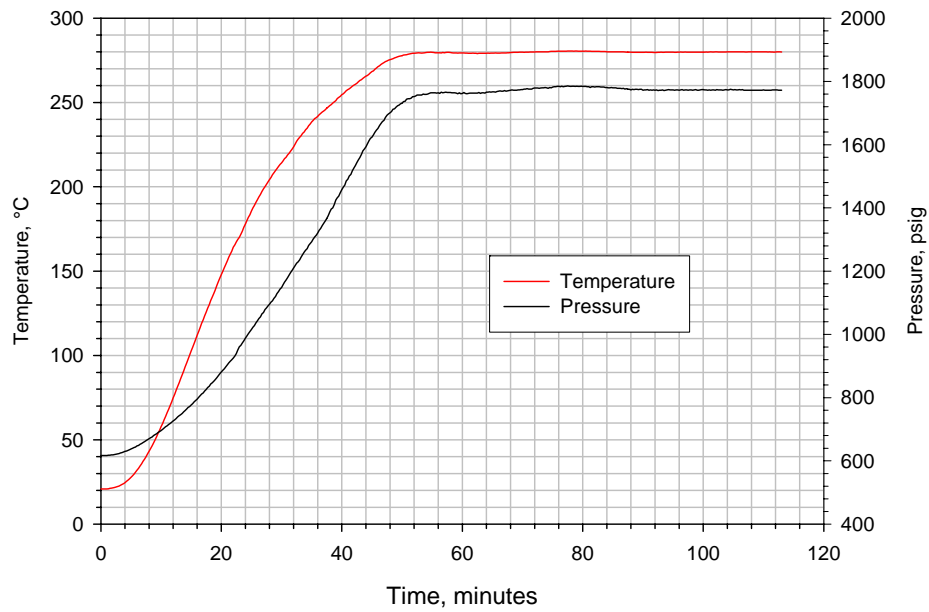

Figure B-2.   Temperature and pressure profiles for simulant test 4.

Figure B-3.   Temperature and pressure profiles for simulant test 5.

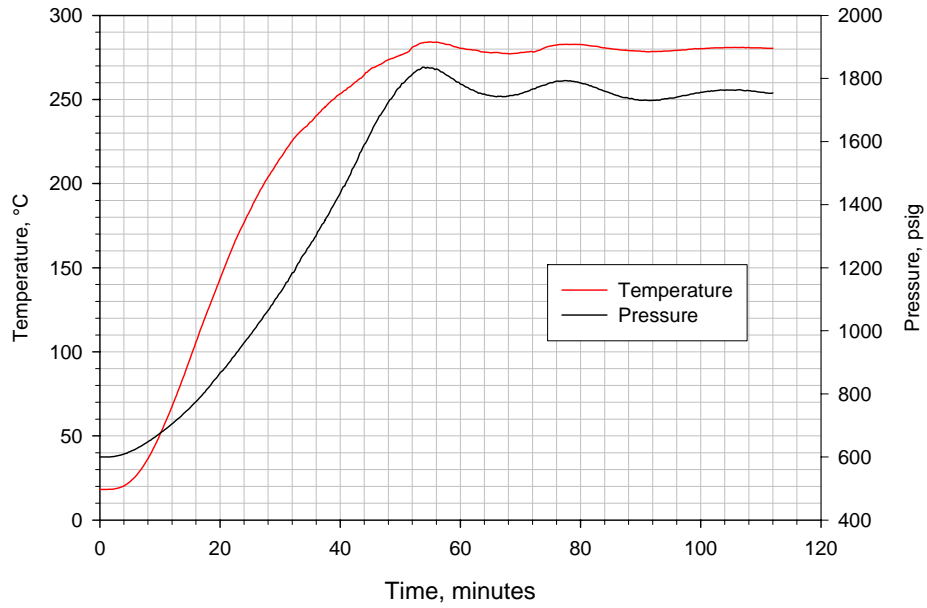**Figure B-4.   Temperature and pressure profiles for simulant test 6.**

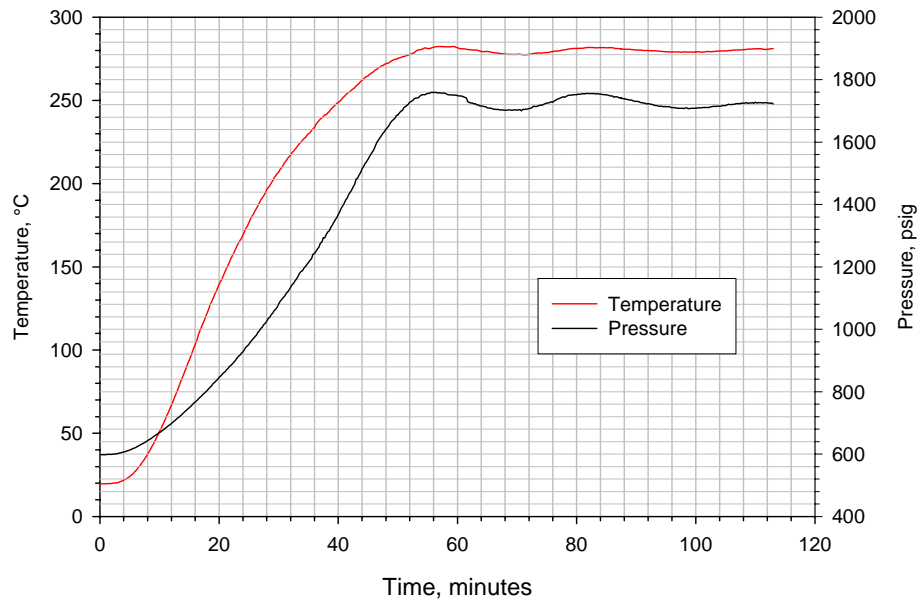**Figure B-5.   Temperature and pressure profiles for radioactive test 1.**

Figure B-6.   Temperature and pressure profiles for radioactive test 2.