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Using Wet Air Oxidation Technology to Destroy Tetraphenylborate

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ABSTRACT

A bench-scale feasibility study on the use of a Wet Air Oxidation (WAO) process to destroy a slurry laden with tetraphenylborate (TPB) compounds has been undertaken. WAO is an aqueous phase process in which soluble and/or insoluble waste constituents are oxidized using oxygen or oxygen in air at elevated temperatures and pressures ranging from 150 °C and 1 MPa to 320 °C and 22 MPa. The products of the reaction are CO₂, H₂O, and low molecular weight oxygenated organics (e.g. acetate, oxalate).

Test results indicate WAO is a feasible process for destroying TPB, its primary daughter products [triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB)], phenol, and most of the biphenyl byproduct. The required conditions are a temperature of 300 °C, a reaction time of 3 hours, 1:1 feed slurry dilution with 2M NaOH solution, the addition of CuSO₄·5H₂O solution (500 mg/L Cu) as catalyst, and the addition of 2000 mL/L of antifoam. However, for the destruction of TPB, its daughter compounds (3PB, 2PB, and 1PB), and phenol without consideration for biphenyl destruction, less severe conditions (280 °C and 1-hour reaction time with similar remaining above conditions) are adequate.

INTRODUCTION

Tank 48H at the Department of Energy's (DOE) Savannah River Site (SRS) in Aiken, South Carolina currently holds about 240,000 gallons of alkaline slurry containing tetraphenylborate (TPB) compounds. The TPB material is not compatible with the current waste treatment facilities at SRS. Hence, it must be removed or undergo treatment to destroy the organic compounds before the tank can be returned to routine Tank Farm service.

Wet Air Oxidation (WAO) is an aqueous phase process in which soluble and/or suspended waste components are oxidized using oxygen or oxygen in air. The process operates at elevated temperatures and pressures ranging from 150 °C and 1 MPa to 320 °C and 22 MPa. The products of the reaction are CO₂, H₂O, and low molecular weight oxygenated compounds (e.g. acetate, oxalate).(1-5)

The basic flow scheme for a typical WAO system is as follows. The feed solution or slurry is pumped through a high-pressure pump. Compressed air or oxygen at a concentration commensurate with the oxygen requirements of the feed stream is injected into the pressurized feed stream, and the air/liquid or air/slurry mixture is preheated to the required reactor inlet temperature. The reactor provides adequate retention time to allow the oxidation to reach the desired level of organic destruction. Typical reaction time is about 15 - 120 minutes.(6)

The energy or heat of the reactor effluent is typically recovered by using it to preheat the incoming air/feed mixture in a heat exchanger system. The oxidation reactions are exothermic, so the heat of the reactor effluent may be enough to make the process autothermal. Thus, in most cases, energy is needed for startup and also as auxiliary heat if needed during normal operation.

After cooling, the oxidized reactor effluent passes through a pressure control valve for depressurization to facilitate separation of the depressurized and cooled vapor from the liquid or slurry. Homogeneous and heterogeneous catalysts can be used to enhance the effectiveness (i.e., to lower temperature, pressure, and residence time as well as increase oxidation efficiencies) of the WAO reaction if deemed necessary. (5-9)

WAO is routinely used to destroy organics in spent caustic (high pH similar to SRS waste) waste streams generated by ethylene plants and oil refineries (petrochemical industry). It is also used to treat organic wastes in pharmaceutical and chemical industries as well as municipal/sewage sludges. (1-5). In the radioactive arena, bench-scale WAO was successfully tested in the 1990s for the destruction of organics (ethylenediaminetetraacetic acid, formate, citrate, acetate, and N-(2-hydroxyethyl) ethylenediaminetetraacetic acid) in DOE's Hanford Site (Richland, Washington) simulated and radioactive wastes. Organics destruction based on total organic carbon was > 98% in most cases. (10,11)

The objective of this study was therefore to assess the ability of the WAO process to destroy TPB and associated compounds [triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB)] using Tank 48H simulated slurry via bench-scale testing. Specifically, the study measured TPB decomposition and the off-gas generated.

EXPERIMENTAL

Slurry Simulant Preparation

The bench-scale testing used SRS Tank 48H simulated (nonradioactive) slurry. The simulated slurry was prepared per the recipe developed at SRNL. (12) Reagent grade chemicals and deionized water were used to prepare the slurry simulant. The slurry simulant contains about 2 wt% insoluble solids. The insoluble solids comprise potassium tetraphenylborate (KTPB), cesium tetraphenylborate (CsTPB), PUREX (Plutonium Uranium Extraction) sludge simulant, and monosodium titanate (MST).

Table I gives the composition of the major constituents in the simulated slurry. Table II gives the concentration of the trace metals and other compounds in the slurry simulant. Benzene has the tendency to volatilize or evaporate. Hence, the benzene (0.0628 mL/L of feed slurry) was added to the simulant just prior to the beginning of each test. Table III gives the composition of the solid simulated sludge.

Table I. Concentration of the Major Constituents in the Simulated Slurry

Component	Concentration (M)
KTPB	0.0574
CsTPB	0.0001
NaOH	1.5973
NaNO ₂	0.4551
Na ₂ CO ₃	0.4560
NaNO ₃	0.2042
NaAlO ₂	0.0735
Na ₃ PO ₄ ·12H ₂ O	0.0053
Na ₂ SO ₄	0.0028
NaCl	0.0034
NaF	0.0009
KNO ₃	0.0068

Table II. Concentration of Minor Constituents (Metals and Compounds) in Simulated Slurry

Component	Metal Concentration ^a (mg/L)	Compound Added	Component	Concentration (mg/L)	Compound Added
Pd	0.080	Pd(NO ₃) ₂	Ce	5.49	Ce(NO ₃) ₃ ·6H ₂ O
Cu	1.97	Cu(SO ₄)·5H ₂ O	Rh	0.225	Rh(NO ₃) ₃
Mo	9.00	Na ₂ MoO ₄ ·2H ₂ O	Ru	0.248	RuCl ₃ ·xH ₂ O
Cr	45.6	Na ₂ CrO ₄	Si	88.0	Na ₂ SiO ₃ ·9H ₂ O
Zn	7.74	Zn(NO ₃) ₂ ·6H ₂ O	Hg	10.0	Diphenyl Hg
Pb	30.8	Pb(NO ₃) ₂	Ti	759	MST ^b
Sn	12.2	SnCl ₂ ·2H ₂ O	Phenol	952	Phenol
Ca	19.3	Ca(NO ₃) ₂ ·4H ₂ O	Biphenyl	618	Biphenyl
Sr	5.52	Sr(NO ₃) ₂	Benzene	55.0	Benzene
La	0.969	La(NO ₃) ₃ ·6H ₂ O	Simulated Sludge ^c	435	Simulated Sludge ^c
Cd	1.29	Cd(NO ₃) ₂ ·4H ₂ O			

^a The total concentration of some of the trace metals is higher than indicated because of the contribution from the constituents of the simulated sludge. See Table 3 for sludge composition.

^b MST (monosodium titanate - NaTi₂O₅H) is added as slurry.

^c Simulated sludge is added as slurry. Value shown is as dry solids. See Table 3 for composition.

Table III. Simulated Sludge Composition (balance of mass is oxide/hydroxide)

Constituent Element	Dry Solid ^a (wt%)	Contribution in Slurry ^b (mg/L)
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 Simulated Sludge: ~17 wt% metal hydroxide/oxide slurry.

Quantity shown is dry solid weight.

^b mg/L contribution for 435 mg/L dry solids added.

Bench-Scale Shaking Autoclave Apparatus

A bench scale shaking autoclave was used for the testing.(12) The autoclave consists of a head and a body. The body holds the feed to be tested and the head serves as cover to the body opening. The head seals the opening using bolts. A pressure gauge, gas charge port, and valve are connected to the head. The autoclave is constructed of Nickel 200 alloy and has a volume of 500 mL.

Bench-Scale Shaking Autoclave Experiments

A test begins by adding a known volume of feed slurry to the autoclave (13) followed by screwing on the autoclave head or cover to the body and tightening the sealing bolts. High pressure air is then charged into the autoclave to a predetermined pressure (about 3.9 - 4.1 MPa or 560 - 600 psig) and the autoclave is inserted into a heater/rocker unit. The autoclave is rocked back-and-forth and electrically heated simultaneously for a predetermined time. The temperature and pressure are monitored by a computer controlled data acquisition system. The test ends by removing the autoclave from the heater/rocker unit and cooling with tap water to stop the oxidation reaction.

During venting, the off-gas pressure and volume are measured using a pressure gauge and mass flow meter, respectively. The off-gas is sampled during the venting of the autoclave. The off-gas is analyzed for oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen, methane and total hydrocarbons (THC) using a gas chromatograph. For a few of the tests, the off-gas was also analyzed

for semi-volatile/ volatile organic compounds (SVOC/VOC) such as benzene and biphenyl by Gas Chromatography-Mass Spectrometry (GC-MS).

The treated slurry is transferred from the autoclave into a sample bottle and analyzed for TPB, 3PB, 2PB, 1PB, phenol, biphenyl by High Performance Liquid Chromatography (HPLC). Again, for a few of the tests, the treated slurry was also analyzed for SVOC/VOC by GC-MS, organic acids by HPLC, anions by Ion Chromatography, free hydroxide by titration, metals by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Atomic Absorption Spectroscopy (AAS), carbonate by a Total Inorganic Carbon/Total Organic Carbon (TIC/TOC) method, and insoluble solids by a gravimetric method.

Tables IV and V give the conditions of all tests performed in this study. The variables studied were temperature, time, feed slurry dilution with water, feed slurry dilution with caustic (NaOH) solution and its concentration, catalyst and its concentration, and antifoam. The tests were grouped into three series and performed in sequential order: screening (series 1: tests 1-7, 9-11); optimization (series 2: tests 12-15); and confirmation (series 3: tests 16 A-D). The range of conditions for the screening tests was broad while that for the optimization tests was narrow. The confirmation tests were quadruplicate runs of the optimum conditions selected at the end of the series 2 tests. In other words, all the confirmation tests were conducted at the same conditions.

The slurry simulant has a tendency to foam. In addition, the solids in the slurry simulant float. Hence, the slurry simulant was diluted initially to help reduce the floating tendency. Note that the oxidation reactions occur in the aqueous phase and it is imperative for the compounds to be destroyed to be in the aqueous phase.

Table IV. Screening (Series 1) Test Conditions

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 9	Test 10	Test 11
Temp. (°C)	300	300	240	300	200	280	280	300	300	300
Time (hr.)	1	3	3	3	3	3	1	3	4	3
Baffles	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Antifoam (IIT B52) (ppmv)	No	2000	2000	2000	2000	No	No	No	2000	2000
Cu Catalyst (mg/L)	No	No	No	500	500	500	500	1000	500	750
Feed Slurry Dilution	1:1 (water)	1:1 (water)	1:1 (water)	1:1 (2M NaOH)	1:1 (2M NaOH)	1:1 (4M NaOH)	1:1 (4M NaOH)	1:1 (4M NaOH)	1:1 (2M NaOH)	1:1 (2M NaOH)

Feed volume: 100 mL

Cu catalyst: CuSO₄·5H₂O solution

Antifoam IIT B52: Illinois Institute of Technology KTPB Slurry Antifoam B52

Operating pressure: 7.6 - 16.5 MPa (1100 - 2400 psig). Note: Operating pressure for a continuous flow system is typically about 5 to 50 % lower.

Test 8 was discarded because of leakage during testing.

RESULTS AND DISCUSSION

Destruction of TPB, its Daughter Compounds, and Phenol

Tables VI and VII show the treated slurry simulant data for all the tests except test 16. Tables VI and VII indicate that for all test conditions where treated slurry simulant analytical data are available TPB, 3PB, 2PB, 1PB and phenol are destroyed to below their respective detection limits (except for a few tests) - an indication of the conduciveness of the WAO system for the above compounds. In fact, TPB destruction was either >99.97% or >99.99% depending on the effluent TPB concentration. Based on all the conditions tested, the minimum conditions required to destroy the above compounds (TPB, 3PB, 2PB, 1PB and phenol) are:

- (a) 1. temperature of 280 °C
 2. reaction time of 1 hour
 3. 1:1 feed slurry dilution with 2M NaOH solution
 4. addition of 500 mg/L copper catalyst
 5. addition of 2000 mL/L of antifoam
 (These conditions essentially match those of test 7. Note that 4M NaOH was used for the testing but it will be shown later that 2M NaOH is enough.)

and

- (b) 1. temperature of 300 °C
 2. a reaction time of 3 hours
 3. 1:1 feed slurry dilution with water
 4. addition of 2000 mL/L of antifoam without the addition of copper catalyst
 (These conditions essentially match those of test 2.)

Table V. Optimization and Confirmation Test Conditions

	Optimization (Series 2)				Confirmation (Series 3)
	Test 12	Test 13	Test 14	Test 15	Test 16
Temp. (°C)	280	300	280	300	300
Time (hr.)	3	3	3	3	3
Baffles	Yes	Yes	Yes	Yes	Yes
Antifoam (IIT B52) (ppmv)	2000	2000	2000	2000	2000
Cu Catalyst (mg/L)	500	500	500	500	500
Feed Slurry Dilution	1:1 (2M NaOH)	1:1 (2M NaOH)	1:2 (2M NaOH)	1:2 (2M NaOH)	1:1 (2M NaOH)

However, varying amounts (depending on the test conditions) of residual biphenyl were found floating on the treated slurry of all the tests. As a result, efforts of the testing were directed towards seeking more aggressive conditions that will destroy the above compounds (TPB, 3PB, 2PB, 1PB and phenol) and the residual biphenyl. Note that it is quite possible that less stringent conditions (in terms of temperature, time, dilution, concentration of catalyst) than those specified in (a) and (b) above may destroy these compounds but they have yet to be investigated.

Table VI. Treated Slurry Simulant Data for the Screening Tests (Series 1)

	Units	Undiluted Feed	Test 1 ^a	Test 2	Test 3 ^a	Test 4	Test 5 ^a	Test 6	Test 7	Test 9	Test 10	Test 11
TPB	mg/L	17,980	---	<0.8	---	<0.8	---	<1.0	<0.8	<1.0	2	3
3PB	mg/L	<10	---	<10	---	<10	---	<10	<10	<10	<10	<10
2PB	mg/L	<10	---	<10	---	<10	---	<10	<10	<10	<10	<10
1PB	mg/L	<10	---	<10	---	<10	---	<10	<10	<10	<10	<10
Phenol	mg/L	958	---	<10	---	<10	---	<10	<10	<10	<10	<10
Soluble Biphenyl ^b	mg/L	---	---	<10	---	<10	---	<10	<10	<10	<10	<10
Floating Biphenyl	mg/L	560	---	85	---	<10	---	503	1,190	61	43	176
pH	---	---	12.0	9.4	12.6	12.8	12.9	14.5	14.1	14.4	14.3	14.4

^a Treated slurry simulants from tests 1, 3, and 5 were not analyzed.

^b Soluble biphenyl is biphenyl dissolved in the aqueous phase.

Table VII. Treated Slurry Simulant Data for the Optimization Tests (Series 2)

	Units	Undiluted Feed	Test 12	Test 13	Test 14	Test 15
TPB	mg/L	17,980	<0.8	<0.8	0.8	1
3PB	mg/L	<10	<10	<10	<10	<10
2PB	mg/L	<10	<10	<10	<10	<10
1PB	mg/L	<10	<10	<10	<10	<10
Phenol	mg/L	958	<10	<10	<10	<10
Soluble Biphenyl ^a	mg/L	---	<10	<10	<10	<10
Floating Biphenyl	mg/L	560	91	8	14	<10
pH	---	---	14.3	13.3	14.4	14.2

^a Soluble biphenyl is biphenyl dissolved in the aqueous phase.

Tables VIII and IX show the off-gas data for all the tests except Test 16. These tables will be discussed in detail later. It is worthy to mention here that the THC in the off-gas from the above tests (2 and 7) were 3,160 and 1,170 ppmv (or 0.32 and 0.12 vol%). Assuming all the off-gas THC is benzene, these amounts are about 23 and 8% respectively of the lower flammability limit of benzene (1.4 vol% at 25 °C). These values indicate flammability may not be an issue. However, caution is warranted because off-gas data from batch autoclave tests may not match those of continuous flow systems. Continuous flow tests will give more realistic off-gas data. In short, the treated slurry simulant data indicate TPB, 3PB, 2PB, 1PB and phenol are fairly easy to destroy by WAO. The next section discusses the results in more detail and includes biphenyl destruction.

Destruction of TPB, its Daughter Compounds, Phenol, and Biphenyl

As stated earlier, the tests were conducted in sequence even though some were done in parallel. As shown in Table IV, the first test used no baffles, catalyst, or antifoam. There was a large amount of

floating white solids in the treated slurry to the extent that the treated slurry was not analyzed for TPB, 3PB, 2PB, 1PB and phenol. The floating white solids were identified by HPLC and GC-MS as biphenyl. Biphenyl has limited solubility in the aqueous phase because it is hydrophobic, and also has a density less than that of water. The deduction at this stage of the study was that better mixing, more time, and probably a catalyst were needed to destroy the residual biphenyl. As a result, baffles and antifoam were used in tests 2 and 3. The antifoam (IIT B52) used was specifically developed for this slurry simulant. The concentration (2000 ppmv) of antifoam used is the optimum based on previous study.(14)

For test 2, the floating residual biphenyl in the treated slurry was relatively small compared to test 1 by visual inspection and the pH was low. It was therefore deduced that catalyst and/or caustic are needed to destroy the residual biphenyl. Note that the floating residual biphenyl was analyzed separately by physically picking the solid pieces from the top of the treated slurry. Test 3 had large amounts of floating residual biphenyl in the treated slurry such that the treated slurry was not analyzed for organics. Test 3 indicated 240 °C was not adequate to destroy the residual biphenyl.

Test 4 onwards used $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution as catalyst and 2M or 4M NaOH solution as diluent. The reason for using NaOH as a diluent instead of water is as follows. Copper tends to form insoluble copper oxides which, in turn, render the catalyst ineffective. The oxidation reactions occur in the aqueous phase, and high pH allows the copper to remain soluble. Test 4 had just two small specks of floating residual biphenyl. In fact, of all the tests, it had the smallest amount of biphenyl. However, because it had specks of biphenyl, the addition of more catalyst or time may be needed to destroy the residual biphenyl. Note that a deliberate decision was made not to exceed 300 °C because WAO typically does not go beyond 320 °C due to material of construction concerns among others. Also, process economics generally favor using increased time instead of increased temperature to improve destruction efficiency.

Test 5 was attempted to see if a lower temperature (200 °C) will lead to similar or better biphenyl destruction as test 4. It was postulated that it may lead to less intermediate biphenyl formation or to a different reaction path. Test 5 showed lower temperature was inadequate and also does not avoid biphenyl formation. It had large amounts of floating residual biphenyl in the treated slurry such that the treated slurry was not analyzed for organics.

Tests 6 and 7 indicated increased caustic concentration was not helpful and that antifoam may be needed. Test 9 indicated increased catalyst concentration (1000 versus 500 mg/L Cu) was not effective and that antifoam may be needed. It is possible insoluble copper oxides may have formed.

Test 10 is essentially test 4 with more time (4 versus 300 hours) but the amount of floating residual biphenyl was considerably higher than the two small specks obtained in test 4. This observation seems to indicate increased time is ineffective, which cannot be true. The speculation is that all the antifoam gets consumed at the end of 3 hours and that increased concentration of antifoam may be required for longer reaction times but this was not tested.

Test 11 is basically test 4 with increased catalyst concentration (750 versus 500 mg/L Cu) but again the amount of floating residual biphenyl was considerably higher than that of test 4, implying increased catalyst concentration was not helpful - an indication that insoluble copper oxides may have formed.

Test 13 is a repeat of test 4 but the amount of floating residual biphenyl was considerably higher than the specks obtained in test 4. This observation seems to indicate there are inherent reproducibility issues with the batch method testing.

Test 12 is similar to test 6 except test 6 used 4M instead of 2M NaOH and no antifoam. Since the role of the NaOH is to ensure that the pH of the slurry is high enough to make the copper catalyst soluble, it appears the difference in the biphenyl concentrations in the treated slurry from the two tests is due to the use of antifoam in test 12, which is an indication that antifoam seems to improve performance.

Tests 14 and 15 were done to investigate whether increased dilution will be more effective in destroying the biphenyl. Comparison of tests 14 and 12, and tests 15 and 13 indicates on the whole that 1:2 dilution instead of 1:1 seems to decrease residual biphenyl concentration. However, it cannot be ruled out that it is solely due to the low initial TBP or organic concentrations due to the increased initial dilution.

All the treated slurry data, especially the biphenyl concentration values, should be regarded as rough at best because of the following:

- a. Inherent reproducibility issues with the batch method testing mentioned earlier.
- b. Inconsistent batch-to-batch feed slurry composition. However, analysis of soluble boron and potassium (data not shown) in the treated slurry for tests 10-15 seems to imply batch-to-batch feed slurry composition was fairly representative of the original feed slurry.
- c. Inconsistent feed and treated slurry sampling for analysis.
- d. Physically picking small quantities of fine floating biphenyl particles which weighed <120 mg (with over half of the tests <10 mg) in all the tests.
- e. Biphenyl has the tendency to sublime and it is possible some biphenyl may have been lost during pouring of the treated slurry from the autoclave.

Off-Gas Generation

Tables VIII and IX show the off-gas data for all the tests except test 16. The concentration of the permanent gases (oxygen, nitrogen, carbon monoxide, carbon dioxide, and hydrogen) and methane are all at expected levels. The carbon dioxide concentration in the off-gas is low even though it is the major gas product that is expected to be produced during the destruction of the organics. This is because carbon dioxide dissolves in the highly alkaline slurry to form presumably sodium carbonate compounds. In general, high oxygen uptake or consumption leads to low levels of oxygen in the off-gas. Comparison of the test with and without copper catalyst indicates catalyst generally leads to low THC values. There is variability in the THC data when tests with similar conditions are compared (e.g., Tests 4 and 13). The variability stems from the same reasons given earlier.

Table VIII. Off-Gas Data for the Screening Tests (Series 1)

	Units	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 9	Test 10	Test 11
Off-Gas Volume	L	13.3	11.0	11.4	10.2	12.0	11.1	14.0	12.2	13.1	10.3
Off-Gas Temp.	°C	19.3	18.9	19.3	18.3	18.6	18.5	19.8	18.3	20.0	18.3
CO ₂	vol%	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
O ₂	vol%	14.4	7.1	12.7	2.9	11.4	7.1	10.8	7.3	8.3	5.3
N ₂	vol%	82.9	89.7	84.3	96.1	86.7	93.2	90.4	92.1	89.8	92.9
CO	vol%	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
THC (as ethane - C ₂ H ₆)	ppmv	3,000	3,160	3,390	860	870	1,390	1,170	720	880	1,250
Methane (CH ₄)	ppmv	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
H ₂	vol%	0.054	<0.05	0.052	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
O ₂ Uptake	g/L ^a	17.8	31.5	22.0	38.3	23.2	33.4	26.3	33.8	31.0	37.4

^a This is the mass of oxygen consumed by the oxidation of constituents in the slurry. The units are grams of oxygen per liter of slurry treated in the autoclave.

Table IX. Off-Gas Data for the Optimization Tests (Series 2)

	Units	Test 12	Test 13	Test 14	Test 15
Off-Gas Volume	L	11.4	11.9	11.0	14.2
Off-Gas Temperature	°C	17.3	17.9	62	19.3
CO ₂	vol%	<0.5	<0.5	<0.5	<0.5
O ₂	vol%	12.3	11.4	12.4	13.1
N ₂	vol%	89.6	90.5	88.0	87.9
CO	vol%	<0.1	<0.1	<0.1	<0.1
THC (as ethane - C ₂ H ₆)	ppmv	2,250	2,255	2,290	1,370
Methane (CH ₄)	ppmv	<50	<50	<50	<50
H ₂	vol%	0.054	<0.05	0.052	<0.05
O ₂ Uptake	g/L ^a	23.5	25.1	24.2	21.1

^a This is the mass of oxygen consumed by the oxidation of constituents in the slurry. The units are grams of oxygen per liter of slurry treated in the autoclave.

Test 3 generated the maximum THC value (3,390 ppmv or 0.34 vol%). Again, assuming all the off-gas THC is benzene, this is about 24% of the lower flammability limit of benzene (1.4 vol% at 25 °C). Flammability of benzene appears potentially resolvable based on the off-gas to THC data bearing in mind that more realistic off-gas data need to be gathered with a continuous flow system.

Note that the off-gas temperature (62 °C) for test 14 was considerably higher than the values for the remaining tests (about 19 °C on the average). The off-gas temperature is the temperature of the gas during venting. It was postulated that because of biphenyl's propensity to sublime, it moves to the gas phase or headspace of the autoclave and therefore was not oxidized. To test this postulate, for test 14, the autoclave was cooled to 62 °C before the off-gas was released, analyzed and metered. Thus, the increased levels of gaseous biphenyl would in turn increase the THC in the off-gas. The temperature of

62 °C was close to the melting point of biphenyl (68-70 °C) such that a substantial portion of the gaseous biphenyl would not solidify at this temperature compared to 19 °C.

Tests 12 and 14 had similar conditions except the feed slurry dilutions were 1:1 and 1:2, respectively. This means that the initial organic concentration of the diluted feed slurry of test 12 is 1.5 times that of test 14. Even though the THC value of test 14 was expected to be 1.5 times lower than that of test 12, Table IX shows that the THC values for tests 12 and 14 are roughly the same. The implication is that test 14 had increased levels of THC from biphenyl which had not yet solidified at 62 °C. Along the same lines, the ratio of THC values of tests 13 and 15 (which were cooled to approximately the same temperature) is about 1.6. This ratio is roughly equal to the ratio of their initial organic concentrations of their respective diluted feed slurries i.e., 1:1 for test 13 and 1:2 for test 15.

These results support the hypothesis that some biphenyl transfers to the autoclave headspace (gas phase) and therefore does not take part in the oxidation reaction. This also is potentially one way of resolving the floating residual biphenyl issue in a continuous flow process at the separation stage following depressurization. Considering the fact that biphenyl is a liquid above 68-70 °C, temperatures higher than the 62 °C used here may drive even more biphenyl into the gas phase to allow further treatment by an appropriate process such as thermal/catalytic oxidizers.

General Observations

Based on the foregoing, the following general observations are made.

- a. Destruction of biphenyl requires more aggressive conditions than TPB, 3PB, 2PB, 1PB and phenol.
- b. High temperatures lead to low residual biphenyl in the treated slurry.
- c. Increasing reaction time results in low residual biphenyl in the treated slurry.
- d. Copper catalyst improves residual biphenyl destruction and lowers THC in the off-gas.
- e. The catalytic effect of copper diminishes at copper concentrations of 750 mg/L and higher. There is a possibility that good catalytic effect may be achieved at copper concentrations less than 500 mg/L.
- f. Diluting the feed slurry with 2M NaOH solution (instead of 4M) leads to adequate slurry pH levels to render copper catalyst soluble..
- g. Increasing feed slurry dilution seems to decrease residual biphenyl in the treated slurry. There is also a possibility that dilutions less than 1:1 may be adequate.
- h. Antifoam appears to enhance residual biphenyl destruction.

Confirmation (Series 3) Tests

A review of all the test data indicated test 13 or 4 conditions were best for additional testing:

1. temperature of 300 °C
2. reaction time of 3 hours
3. 1:1 feed slurry dilution with 2M NaOH solution
4. addition of 500 mg/L copper catalyst
5. addition of 2000 mL/L of antifoam

Hence, for the confirmation (series 3) tests, four runs were conducted at the above conditions. Tables X and XI give the data for the treated slurry simulant. As can be seen, the analyses performed were more extensive than the prior tests. Again TPB, 3PB, 2PB, 1PB and phenol were destroyed to below their respective detection limits. The floating residual biphenyl values attest to the reproducibility issues mentioned earlier.

The only SVOC and VOC detected by GC-MS are low levels of biphenyl and benzene. The free hydroxide values agree roughly with the pH data. The TOC data indicate virtually all the organics are destroyed if the floating residual biphenyl is excluded. The carbonate in the treated slurry increased because almost all the carbon dioxide produced from the oxidation reaction dissolved in the highly alkaline slurry as alluded to earlier. All the organic acids were below detection limits. Typically, WAO does not destroy the low molecular weight carboxylic acids. It looks as if the copper catalyst may have aided in their destruction. Since the TPB is present as insoluble solids (KTPB and CsTPB), the amount of the remaining insoluble solids in the treated slurry lends an indirect support to the fact that the virtually all the TPB is destroyed. The boron and potassium data in the treated slurry again imply feed slurry sampling was more or less representative of the original feed slurry. The nitrite and nitrate data show that about 40% of the nitrite was converted or oxidized to nitrate.

Table XII shows the off-gas data for test 16. The deductions made earlier on the off-gas data from the screening and optimization tests still hold here. The variation in the THC data is narrower. Unlike the previous tests, the off-gas was analyzed for VOC by GC-MS. The only VOC identified in the off-gas was benzene. It seems that any biphenyl in the off-gas may have solidified prior to analysis. The benzene data for Tests 16A and B, when converted to an ethane basis using molecular weights, give 902 and 3232 ppmv respectively. This result indicates approximately 62% of the THC in the Test 16A off-gas was benzene. The benzene concentration measured in Test 16B was twice the THC value, which is not possible. It seems the benzene data is suspect since the THC data for all four tests are reasonably close. On the other hand, if the off-gas is mainly benzene, then the THC data may be suspect since the error associated with using THC analyzers to measure aromatics are typically large. However, it can still be deduced that a greater portion of the THC in the off-gas is benzene, but as stated earlier it is well below the lower flammability limit of benzene or biphenyl.

Table X. Treated Slurry Simulant Data for the Confirmation Tests (Series 3)

	Units	Diluted Feed Slurry Conc. (Calculated)	Test 16A	Test 16B	Test 16C	Test 16D
TPB	mg/L	9,186	<0.8	<1.0	<0.8	<1.0
3PB	mg/L	<5	<10	<10	<10	<10
2PB	mg/L	<5	<10	<10	<10	<10
1PB	mg/L	<5	<10	<10	<10	<10
Phenol	mg/L	476	<10	<10	<10	<10
Soluble Biphenyl ^a	mg/L	---	<10	<10	<10	<10
Floating Biphenyl	mg/L	309	127 ^b	144	51 ^b	214
pH	---	---	13.8	13.8	13.8	13.8
Biphenyl ^c	mg/L	309	1.1	---	0.71	---
Benzene ^c	mg/L	27.5	1.1	---	0.53	---
TOC	mg/L	8,951 (excludes antifoam)	< 10	---	< 10	---
TIC	mg/L	2,739	6,780	---	7,270	---
Formate	mg/L	None	< 10	---	< 10	---
Oxalate	mg/L	None	< 10	---	< 10	---
Acetate	mg/L	None	< 100	---	< 100	---
Acetic Acid	mg/L	None	---	<153	---	---
Acrylic Acid	mg/L	None	---	<2.50	---	---
Butyric Acid	mg/L	None	---	<130	---	---
Formic Acid	mg/L	None	---	<97.0	---	---
Fumaric Acid	mg/L	None	---	<1.00	---	---
Isobutyric Acid	mg/L	None	---	<104	---	---
Maleic Acid	mg/L	None	---	<2.00	---	---
Malonic Acid	mg/L	None	---	<153	---	---
Propionic Acid	mg/L	None	---	<103	---	---
Succinic Acid	mg/L	None	---	<175	---	---
Oxalic Acid	mg/L	None	---	<14	---	---
Glyoxalic Acid	mg/L	None	---	<176	---	---

^a Soluble biphenyl is biphenyl dissolved in the aqueous phase.

^b The floating biphenyl was not physically removed initially. Hence, values may have skewed to the low side.

^c This is from SVOC/VOC analysis of the treated slurry.

Table XI. Continuation of Treated Slurry Simulant Data for the Confirmation Tests (Series 3)

	Units	Diluted Feed Slurry Conc. (Calculated)	Test 16A	Test 16B	Test 16C	Test 16D
Free OH ⁻	mg/L	1.799 M (includes 2M NaOH as diluent)	0.229	---	0.271	---
Carbonate	mg/L	13,681	33,874	---	36,322	---
Nitrite	mg/L	10,469	6,310	---	6,300	---
Nitrate	mg/L	6,541	10,600	---	10,800	---
Phosphate	mg/L	252	158	---	146	---
Sulfate	mg/L	889 (includes catalyst)	1,080	---	1,050	---
Chloride	mg/L	111	143	---	103	---
Fluoride	mg/L	8.7	< 2	---	< 2	---
Insoluble Solids	wt %	1.01	0.01	---	0.01	---
Al	mg/L	992	813	---	807	---
B	mg/L	311	262	---	270	---
Cs	mg/L	7.4	17.5	---	16.8	---
Cu ^a	mg/L	501.3 (includes catalyst)	241	---	256	---
K	mg/L	1,260	1,227	---	1,327	---
Na	mg/L	60,572 (includes 2M NaOH as diluent)	50,630	---	46,010	---
P	mg/L	82	< 169	---	< 122	---
S	mg/L	296 (includes catalyst)	<286	---	297	---
Ti ^a	mg/L	380	87.1	---	57.5	---

^a Cu and Ti have lower than expected values. Possible explanation is that they could have formed phases under WAO conditions that may not have dissolved in the analytical preparation method.

Table XII. Off-Gas Data for the Confirmation Tests (Series 3)

	Units	Test 16A	Test 16B	Test 16C	Test 16D
Off-Gas Volume	L	12.8	11.0	13.6	12.4
Off-Gas Temperature	°C	18.3	17.3	21.2	25.2
CO ₂	vol %	<0.5	<0.5	<0.5	<0.5
O ₂	vol%	7.9	6.5	9.0	7.8
N ₂	vol%	90.6	92.1	89.8	91.6
CO	vol%	<0.1	<0.1	<0.1	<0.1
THC (as ethane - C ₂ H ₆)	ppmv	1,460	1,612	1,140	1,180
Methane (CH ₄)	ppmv	<50	<50	<50	<50
H ₂	vol%	<0.05	<0.05	<0.05	<0.05
Benzene (C ₆ H ₆)	ppmv	347	1,243	---	---
O ₂ Uptake	g/L ^a	32.0	34.4	29.2	32.5

^a This is the mass of oxygen consumed by the oxidation of constituents in the slurry. The units are grams of oxygen per liter of slurry treated in the autoclave.

CONCLUSIONS

The bench-scale autoclave testing results indicate WAO is effective in destroying TPB, its primary daughter compounds (3PB, 2PB, and 1PB), phenol and a large portion of the biphenyl byproduct in SRS's Tank 48H simulated slurry. Destruction of biphenyl requires more aggressive conditions than the above remaining compounds.

Although the batch autoclave tests demonstrate the conduciveness of WAO to the destruction of organics in Tank 48H simulated slurry and the quality of treated product that can be expected, they do not entirely portray the expectations of a steady-state continuous flow system. Hence, future studies will focus on assessing the impact of treating the Tank 48H slurry simulatant in a continuous flow system to (a) optimize the identified bench-scale conditions (b) obtain more realistic off-gas data, and (c) get a good handle on the biphenyl destruction.

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