TSD - APPENDIX C

RESPONSE TO USEPA OBJECTIONS RE: COKER EMISSIONS

Introduction:

As a part of the Whiting Refinery Modernization Project (WRMP) BP Products North America, Inc. (BPP) will replace its existing 4 drum Delayed Coker, Coker 11B, with a new 6-drum Delayed Coker designated as Coker 2. In an effort to more thoroughly evaluate the emissions impact of this change, BPP developed methods to estimate emissions from each coker during (a) depressurization or venting of the drums; cutting the coke from the drum, and water handling/recirculation of the coker quench/cutting water. The calculations for these emission estimates are presented in the Appendix to this report. The following provides a description of the calculations and their technical bases.

Coker Operations

Both Coker 11B and Coker 2 are Delayed Cokers. Coke drums in Delayed Cokers operate in pairs, with one drum in coking service and the other drum being cooled, decoked and re-warmed in preparation to go back into coking service. This allows the unit to operate continuously while the drums operate in a batch basis.

Once a coke drum is full, feed is switched to the alternate drum of the pair. The coke in the drum is then cooled, first with steam and then with water to the point where it can be safely handled once it is cut out of the drum. For most of this period the steam generated by the hot coke is directed first to the fractionator and then to a closed blow down system. Water is added to the bottom of the coke drum, so the coke is cooled from the bottom up. As the temperature of the coke bed at the bottom of the drum drops below the boiling point of water, liquid water begins to fill the drum. Water continues to be added until the water in the drum completely covers the coke bed. At that point the operations of the two cokers diverge.

In the case of the existing 11B coker, once water reaches a point in the drum at which the coke is known to be covered, the water addition is temporarily stopped and the drum overhead vapor line is routed from the blowdown scrubber to a stack that is remote from the coke drum. Water is then restarted into the drum until the drum is completely full and over flows out the overhead vapor line to the stack. Water continues to be added to the drum until the water temperature leaving the drum is below 175 deg F. Steam and other vapors generated during this overflow process are vented to the atmosphere through this stack. Because of the short cycle time on the existing 11B Coker, the coke drum pressure is at approximately 12 psig when the drum is vented to this stack.

In the case of the new coker there will be no overflow. Rather, once the coke is covered, water additions stop and the coke is allowed to soak for 30 minutes or until the internal drum pressure drops below 5 psig, the highest pressure at which the new coke drum may be vented to atmosphere under EPA new source performance standards.

In both cases, following these steps, valves at the bottom of the drums are opened to allow the water in the drum to drain out into the coke pit, and the coke is then cut out of the drum using high pressure water lances. This water is collected and reused as quench and cutting water for the next cycle.

Emissions from Venting

The emissions of gaseous pollutants from the initial venting of the coke drum are a function of two variables: the amount of water vaporized and the concentration of pollutants in the vent stream. The mass of water vaporized per venting event was calculated thermodynamically from known variables specific to each coker. Estimates of the concentration of various compounds of interest in this vapor were based on the results of tests conducted by the South Coast Air Quality Management District (SCAQMD) on several of the cokers in the Los Angles area and compared to testing done by URS on cokers at the Hovensa, Virgin Islands and Citgo Corpus Christi refineries as a check on the validity of the concentrations used. .

The first of these variables is a function of the volume of water in the drum and the temperature of the water/coke mixture at the time the drum is vented to the atmosphere. Given the volumes of water used during the cooling process it is reasonable to assume that the water and coke have reached thermal equilibrium. Thus, the temperature of both the water and coke at that point will be equal to the boiling point of water at the drum pressure. When the drum is vented and the pressure reduced, a portion of the water in the drum vaporizes generating the vent stream. Using the volume of the coke drum, the amount of coke in the drum, the coke void fraction and the amount of water over the top of the coke bed, the total amount of water in the drum can be calculated. Flashing the water in the drum from the conditions just prior to opening the vent down to atmospheric conditions, the amount of water vented each cycle can be calculated. Additionally, there is a portion of the drum that is not filled with liquid water when the drum is vented, but contains water vapor that also contributes to the vent stream. The amount vapor generated from depressurizing this portion of the drum was calculated using the Ideal Gas Law assuming the vapor was all steam.

Once the total quantity of the water vented is calculated, it is then necessary to estimate the concentration (in ppm) of the compounds of interest in that water. Industry data on these concentrations has been collected in coker vent tests done by the SCAQMD on several of the Cokers in the Los Angeles area and by URS Corp for at the Hovensa Virgin Islands and Citgo Corpus Christi refineries. The data from these tests show appreciable quantities of hydrocarbons in the vent stream as the drum is being depressurized. These hydrocarbons are predominantly methane and ethane, but heavier hydrocarbons are also present. This is a very difficult stream to measure as it is mostly water vapor and the rate that this stream exits the vent pipe is very high initially and decreases over time as the drum depressurizes. As a result, the data from the source tests have a large degree of variation. Additionally, the test methods used and the way the data was reported from these tests also had a great deal of variation. To compensate for this variability, the highest concentration of the six credible Los Angeles area tests were used to estimate emissions for methane, ethane, non-methane non-ethane VOC and CO. The source test for Valero Wilmington was not credible as there was a valve leak that resulted in extremely high readings for hydrocarbons and H2S that were not representative of the operation of that Coker. Only one of the source tests had a credible result for H2S, so that concentration was used. The average of all thirteen available data sets was taken to estimate particulate emissions due to the significant challenges associated with getting accurate data for particulates on this stream. The values selected are similar to the data collected at Hovensa, which is the most recent testing.

Using these same test data, a molecular weight of the non-methane non-ethane VOC's could be calculated. Using that molecular weight the mass emissions during each venting event could be calculated.

The concentrations of the compounds of interest (non-methane non-ethane VOC, H2S, CO and particulates) used in the calculations are listed below:

Non-methane non-ethane VOC	500 ppm
H2S	200 ppm
CO	100 ppm
Particulates	20 gr/DSCF

The non-methane non-ethane VOC emissions at Hovensa ranged from 180 ppm to 2589 ppm. However, one test run appears unrepresentative both because one period during that run showed a negative NMNE VOC value, while the values for other periods were outliers compared to the other runs. The time-weighted concentration of NMNE VOC measured in the other three runs averaged 510 ppm, consistent with what was measured in the SCAQMD tests.

Finally, the total annual emissions were calculated by multiplying the emissions per venting event by the number of venting events per year. Each coke drum is vented once per cycle of the pair of drums. For the existing Coker, annual emissions were based on the actual two-year annual average number of venting events during the appropriate baseline periods: 1999-2000 for CO, 2000-2001 for H2S, and 20001-2002 for VOC and PM10/2.5. The new Coker 2 is designed to operate on an 18 hour fill cycle, so each drum will be vented once per 36 hour cycle. The maximum number of venting events for this 6 drum Coker is 1460 times.

The calculations described above are presented in detail in the spreadsheet labeled "Coker Venting and Cutting Emissions.xls". The results are summarized in the following table:

Coker Venting Emissions

	Baseline				Future			Change
	Years	Events Per Year	Pounds Per Event	Tons Per year	Events Per Year	Pounds Per Event	Tons Per year	

VOC	2001-2002	1793	40.8	36.5	1460	62.3	45.5	8.9
H2S / TRS	2000 - 2001	1785	8.2	7.3	1460	12.1	8.9	1.6
CO	1999 - 2000	1817	3.3	3.0	1460	5.0	3.6	0.7
PM10 / 2.5	2001-2002	1793	22.7	20.4	1460	34.7	25.3	5.0

Emissions from Coke Cutting

Emissions associated with cutting the coke out of the drum were calculated in much the same manner as those associated with venting. As with venting emissions, cutting emissions are a function of the amount of water vaporized during the cutting process and the concentration of the compounds of interest in that vapor. The stored energy was used to estimate the quantity of water vaporized during cutting the coke from the drum. As there is no measured data available for the emissions generated during cutting, the concentration of those compounds were assumed to be the same as during the venting stage.

Stored energy in the coke was used to heat the cutting water to boiling temperature and to vaporize this water until the coke was cool enough that it would not generate steam at atmospheric conditions. The assumed initial temperature of the coke was the same temperature as the equilibrium temperature of water at the drum pressure just prior to venting the drum. Additionally, there is energy stored in the metal of the coke drum that can vaporize water. The drum was assumed to be at the same initial temperature as the coke bed. The vapor stream generated by the vaporization of the cutting water was assumed to contain the same concentrations of non-methane non-ethane VOCs, H2S, and CO as during the venting stage. Because the coke is being inundated with water during the cutting process, particulate emissions are negligible.

The calculations described above are also presented in the spreadsheet labeled “Coker Venting and Cutting Emissions.xls”. The results are summarized in the following table.

Coke Cutting Emissions

	Baseline				Future			Change
	Years	Events Per Year	Pounds Per Event	Tons Per year	Events Per Year	Pounds Per Event	Tons Per year	
VOC	2001-2002	1793	11.2	10.0	1460	24.9	18.2	8.1
H2S / TRS	2000 - 2001	1785	2.5	2.2	1460	4.8	3.5	1.4
CO	1999 - 2000	1817	1.0	0.9	1460	2.1	1.5	0.5

Water Handling Emissions

Emissions from the coker water handling system were estimated by performing a material balance around the existing and proposed new water handling systems. In doing this, the mass of pollutants in the various input streams was compared to the mass of the pollutants in the output streams. The difference was assumed to be the amount emitted to the atmosphere.

The concentrations of the pollutants of interest (VOC, sulfides and CO) were determined by collecting and analyzing water samples from various locations. The Coker 11B material balance used sampling data collected at that coker. The Coker 2 material balance used samples collected at the BP-Husky Toledo Refinery Coker 3. Coker 3 at Toledo was deemed to be representative of Coker #2 both because it operates in a manner very similar to the way Coker #2 will operate (e.g. with no water overflow) and because its feed is derived from a heavy Canadian crude very similar to what Coker #2 will process

A copy of the sampling plans for both cokers as well as the sampling results are attached hereto. The following table describes the sampling locations:

Input Streams:	Whiting Coker 11B	Toledo Coker 3	Comments
Coke Drum Overflow Water	Sampled until there was not enough pressure to collect a sample. Three composite samples in December and 5 composite samples in January.	NA	Toledo does not overflow coke drums. Toledo Coker sludge injection was discontinued for 2 days prior to the test and during the test, since the Whiting No 2 Coker will not process sludge.

Input Streams:	Whiting Coker 11B	Toledo Coker 3	Comments
Coke Drum Drainage Water	Sampled until there was not enough pressure to collect a sample, which resulted in two composite samples.	Sampled five times with an improved sampling technique.	
Coke Drum Drilling Water	Sampled four times as the water drains into the sluiceway. Drainage lasts for about 60 minutes	Sampled four times as the water drains into the sluiceway. Drainage lasts for about 90 minutes	It is not safe to sample the drilling water directly as it flows from the coke drum with large quantities of coke.
Output Streams:			
Water from cutting water Tank.	Sampled seven times over several hours after the coke drum was drained.	NA: Coker 3 shares the water tank with Coker 2 so water tank not included.	
Water from the coke pit	NA: The cutting water tank was part of the mass balance.	Sampled eight times over several hours after the coke drum was drained.	The water is pumped from the maze to the cutting water tank.

The Whiting Coker 11B was tested on December, 9, 2009, and the "Coke Drum Overflow Water" was re-sampled on Jan 14, 2010, with an improved sampling technique. The same improved sampling technique was used at the Toledo No 3 Coker on January, 15, 2010. Two URS teams performed all sampling, one team for Whiting, and another at Toledo, but both followed a similar sampling plan. TestAmerica, performed all the analysis of the water samples at its labs in University Park, IL, for the Whiting samples, and in New Canton, OH, for the Toledo water samples.

For the December Whiting samples (except the Coke Drum Drilling Water), sample tubing was connected to the process piping, and 10 gallons of sample was collected per sample event into a stainless steel container which was continuously cooled in an ice bath to minimize evaporation. The ice cooling was necessary since the "Coke Drum Overflow Water" and the "Coke Drum Drainage Water" could be 180 degF and 200 degF, respectively. Since it was not safe to collect the "Coke Drum Drilling Water" directly, the water was collected in buckets from the sluiceway and then cooled in an ice bath. After sampling, all water containers were cooled further and then inspected to determine if an oil sheen was visible on the surface. The cooled water was then transferred through a 0.45 micron filter (to remove coke fines) and directly into the laboratory sample bottles with a peristaltic pump.

Since one of the three Whiting "Coke Drum Overflow Water" samples had an oil sheen on the surface, it was decided to modify the sample plan, and resample the "Coke Drum Overflow

Water". The improved sample plan consisted of collecting a hot sample directly into sample bottles so that a total, unfiltered Oil & Grease analysis could be performed. This was necessary since the overflow water sample had substantial coke fines suspended in the water which may have absorbed liquid hydrocarbon droplets. Afterwards, a 10 gallon stainless steel container was filled as before, except that 10 pounds of ice was added to the inside of the container to facilitate flash cooling. The final lab analysis was corrected for the ice dilution.

The Toledo sampling utilized the same improved sampling technique described above, except a separate sample cooler was used rather than using direct contact of the sample water with ice. (The Whiting sample points did not have enough process pressure to flow through a sample coil.)

For the purpose of these tests, the VOC concentration was a sum of the results from following tests, corrected for possible double accounting:

- 8260B Constituents from the Test America's Default list and Appendix IX list
- Indiana Gasoline Range Organics (IN GRA C6-C12)
- Indiana Extended Range Organics (IN ERO C8-C36)

The above sum was compared to oil & grease by hexane extraction result on the unfiltered samples. If the extraction Oil & Grease for the unfiltered sample was greater than the Oil & Grease for the filtered sample, then the ratio was used to increase VOC concentration. This replacement was used for the Whiting "Coke Drum Overflow" water samples where the extraction test on the unfiltered samples averaged 13.6 mg/L while the filtered extraction test averaged 3.6mg/L. The same method was used for the Toledo coke drum drainage water, but the unfiltered and filtered Oil & Grease results were the same.

Since the coke drum cooling, drilling and coke handling operation of the new Whiting #2 Coker will be similar to the existing Toledo No 3 Coker, most of the design water concentrations for the new coker were based upon the Toledo test as described below.

VOC Concentrations
The major input compositions for the Whiting #2 Coker were derived by doubling the concentrations measured in the Toledo Test to be conservative since the measured concentrations were low.

		Coker 11 B	Toledo No 3 Coker Measured Values	Values used in Whiting No 2 Coker Material Balance
Test Dates		12/9/2009 and 1/14/2010	1/15/2010	
Coke Drum Drainage Water	mg/L	9.6	1.4	3.0
Coke Drum Overflow Water	mg/L	53.4	NA (1)	NA (1)
Coke Drum Drilling Water	mg/L	1.4	0.8	1.4
Water From the Coke Pit	mg/L	4.9	0.7	0.7

Sulfide Concentrations

The major input compositions for the Whiting No 2 Coker were derived by rounding up the concentrations measured in the Toledo Test to be conservative.

		Coker 11 B	Toledo No 3 Coker Measured Values	Values used in Whiting No 2 Coker Material Balance
Test Dates		12/9/2009 and 1/14/2010	1/15/2010	
Coke Drum Drainage Water	mg/L	5.5	15.2	16
Coke Drum Overflow Water	mg/L	11.4	NA (1)	NA (1)
Coke Drum Drilling Water	mg/L	1.0	5.9	6
Water From the Coke Pit	mg/L	1.0	5.5	5

CO Concentrations

All CO test values at both cokers were below the detection limits (50 ug/l at Whiting and 13 ug/l at Toledo. To be conservative, the CO concentration was assumed to be equal to the higher of the two detection limits for both cokers.

		Coker 11 B	Toledo No 3 Coker Measured Values	Values used in Whiting No 2 Coker Material Balance
Test Dates		12/9/2009 and 1/14/2010	1/15/2010	
Coke Drum Drainage Water	ug/L	50	13	50
Coke Drum Overflow Water	ug/L	50	NA (1)	50
Coke Drum Drilling Water	ug/L	50	13	50
Water From the Coke Pit	ug/L	50	13	50

(1) Neither "Toledo No 3 Coker" nor "Whiting No 2 Coker" have "Coke drum overflow water"

The following describes how the mass of water per coker water stream was estimated.

1. Coke Drum Drainage Water. (Mass Balance Input)

The mass of water in the coke drum for the Whiting Coker 11B was estimated as follows: After the coke drum was overflowed with water, the coke drum was full of coke and water. The level of coke was determined from unit data (Coke Drum Outage). The coke level was converted to a mass of coke based upon the cokes bulk density in the coke drum (50 LB/cuft) and the coke drum dimensions. The total water in the coke drum was estimated from: water in the coke bed (50wt%), and the volume of water above the coke bed, assuming the elliptical head was 90% full of water. The sum of the water above the coke bed and the water in the coke bed was equal to the mass of water drained from the coke drum. The VOCs in the water were directly measured from sample connections to the process piping. The product of the drained mass of water and the VOC content in the water was the VOC input into the component mass balance.

The mass of water for the new Whiting No 2 Coker was determined similarly except the water level in the coke drum was set at 10 ft above the coke bed. A bulk coke density of 55 lb/cuft was used, and the 50wt% water in the coke bed was used. The mass of water in the coke drum was reduced by the small percentage of water that flashed when the vent to the atmosphere was opened at 2psig. The estimated mass of water in the coke drum was equal to the mass of water drained from the coke drum.

2. Coke drum drilling water (Mass Balance Input)

The mass of coke drum drilling water drained from the coke drum was set equal to the volume of drilling water added to the coke drum, minus any water that evaporated in the coke drum. The mass of water added to the coke drum was equal to the design flow rate of the coke cutting pump times the duration of the pumps operation. The mass of water evaporated from the coke drum was estimated by assuming the coke was at the same temperature as the water prior to draining the coke drum, and that the drilling water cooled the coke, and in the process generated a small portion of steam, as calculated in a heat balance. The VOCs and other constituents in the water were directly measured from the drilling water after it drained from the coke drum. The product of the drained mass of water and the VOC content in the water was the VOC input into the component mass balance.

3. Coke Drum Overflow Water for Coker 11B (Mass Balance Input)

The new Coker No 2 does not have a water overflow stream, and this estimate only applies to Coker 11B. After the coke drum has been depressured to the blowdown stack, the water pump is restarted, and cooling water is added again to the bottom of the coke drum. The empty space at the top of the coke drum is filled with water, which then overflows to D-105 vapor-liquid separation drum, where additional quench water is added. The vapor is vented to the blowdown stack, and the quenched water from D-105 (which is called "Coke Drum Overflow Water") is drained to the sluiceway. The water flow rate to the coke drum is continuously measured. The volume of water that feeds D-105 from the coke drum is the sum of all water added to the coke drum (after the pump is restarted) minus the volume of water necessary to fill the empty portion of the coke drum. This mass of water is then increased from a heat balance around D-105 as quench water is added. The resultant mass of quenched water from D-105 is called "Coke Drum Overflow Water" and was sampled repeatedly for VOCs and other constituents. The product of the drained mass of water and the VOC content in the water was the VOC input into the component mass balance.

4. Fresh Water Makeup (Mass Balance Input)

The mass of this stream was set equal to the total coke drum water losses during the coke drum cooling, cutting, handling (evaporation from the sluiceway/pad/pit), and venting operations. Water losses during the cooling operation, where cooling water that was added to the coke drum is vaporized and routed to the scrubber, is estimated from the difference between the water metered into the coke drum minus water drained from the coke drum, with corrections for other minor effects. The VOC, sulfide, and CO contents of this fresh water stream were set equal to zero. Therefore the pollutants this stream is 0.0 LBs/drum.

5. Drainage Water from Kinder Morgan (Mass Balance Input for Coker No 2)

Kinder Morgan provided a drainage water estimate of 90 GPM. The daily volume was converted to mass by dividing by the number of coke drums filled per day. The constituent concentration was assumed to be the same as the water pumped from the coke pit (Item 7 below).

6. Water evaporation (Mass Balance Output)

The water evaporation rate was assumed to be equal to 2wt% of the hot water streams ("Coke Drum Overflow" and "Coke Drum Drainage"). The mass difference between the VOC/Constituent inputs and outputs, is assumed to be losses due to evaporation.

7. Water Leaving with the Coke (Mass Balance Output)

The water leaving with the coke was assumed to be 10wt% of the coke make per drum. The VOC/constituent concentrations for Coker 11B was set equal to the concentration measured in the coke cutting tank.

8. Water from cutting water Tank/ Water from the coke pit (Mass Balance Output)

The water mass was determined by difference between water input and the sum of other outputs. The VOC/constituent concentrations were measured.

The material balance calculations are presented in the spreadsheet labeled "Coker Water Handling Emissions.xls" The results are summarized below:

Water Handling Emissions

	Baseline				Future			
	Years	Events Per Year	Pounds Per Event	Tons Per year	Events Per Year	Pounds Per Event	Tons Per year	Change
VOC	2001-2002	1793	21.1	18.9	1460	5.2	3.8	-15.1
H2S / TRS	2000 - 2001	1785	7.1	6.4	1460	18.5	13.5	7.1
CO	1999 - 2000	1817	0	0	1460	0	0	0

The sulfide emissions may be over-reported in the pollutant balances. The balances assumed that the loss of a pollutant was an emission. An alternate explanation is that the pollutant (sulfides for example), reacted with another constituent in the water, such as calcium or iron, and became an insoluble compound that was removed when the sample was filtered. TestAmerica used the Iodometric titration method with sodium thiosulfate to determine the total dissolved sulfide concentration in the filtered water samples. Dissolved sulfides that were in the input streams, may have reacted with other dissolved substances in the water sluiceway, such as iron or calcium, and formed insoluble compounds that were removed when the sample for the output stream was filtered. For this reason, the sulfide emissions may have been over-reported.

In its objections, USEPA referred to a study performed in the early 1990s of VOC emissions from a coker quench water pond at what was then the Amoco Yorktown Refinery. That study showed significant emissions from that pond, but those emissions are not representative of what emissions will be from Coker 2, or even from Coker 11B. In fact, they are not even representative of current emissions at Yorktown

The procedure used for taking a coke drum offline at the Yorktown Coker is different from the 11B Coker and #2 Coker procedures in one key way. For a typical coker, taking a coke drum offline after it is full of hot coke involves a few key steps: (1) steam strip the coke to recover volatile hydrocarbons (normally routed to the main fractionator), (2) steam strip the coke to recover additional volatile hydrocarbons (normally routed to the closed blowdown system), and (3) water quench the coke to both recover volatile hydrocarbons and cool the coke (normally routed to the closed blowdown system). It is this last step that the Yorktown Coker did differently. During this step, the coke drum overhead vapor, that is full of both heavy and volatile hydrocarbons, was instead routed to a water circulated blowdown stack. In the process of condensing the coke drum overhead vapor for the purpose of re-using the condensate for quenching another coke drum, the heavy hydrocarbons would accumulate on top of the recycled water storage and contribute to quench water evaporative emissions. Because blowdown stacks are not closed systems, this also implies that any non-condensable light hydrocarbons in the coke drum overhead vapor would be released to the atmosphere during the quench cycle. These differences mean that the evaporative emissions from the coke drum quench water would be significantly greater at the Yorktown Coker.

Conclusion:

The table below summarizes the results of these calculations:

		Venting	**Cutting**	**Water Handling**	**Total**
		TPY	TPY	TPY	TPY
Baseline	**H2S**	7.3	2.2	6.4	15.9
	VOC	36.5	10.0	18.9	65.4
	CO	3.0	0.9	0	3.9
	PM	20.4			20.4
# 2 Coker PTE	**H2S**	8.9	3.5	13.5	25.9
	VOC	45.5	18.2	3.8	67.5
	CO	3.6	1.5	0	5.1
	PM	25.3			25.3
Change	**H2S**	1.6	1.4	7.1	10.0
	VOC	8.9	8.1	-15.1	2.0
	CO	0.7	0.5	0	1.2
	PM	5.0			5.0

January 7, 2010

Test Plan to estimate emissions for coke drum drainage. (Rev Jan-7-2010)

Purpose:
Estimate VOC emissions from the Whiting Coker and the Toledo Coker 3 from the combined coker pad, sluiceway, maze, and cutting water tank by performing an overall VOC material balance. (Toledo's estimate will not include the cutting water tank.) Emissions from the mass balance volume will be estimated from the difference between VOC inputs and VOC output. The flow rates for the inputs and outputs will be estimated, and major input/output streams will be sampled for VOCs. Sludge injection should be discontinued for 2 days prior to the test and during the test for the Toledo Coker.

Material Balance
An example material balance is shown in the file "VOC pit balance rev1.xls". The input and output streams are:

Input Streams	Whiting	Toledo Coker 3	Comments
D-105 coke drum overflow water	Sample multiple times from the drainage line. Drainage lasts for 105 minutes	NA	Toledo does not overflow coke drums. Sludge injection should be discontinued for 2 days prior to the test and during the test for the Toledo Coker.
Coke drum drainage water	Sample multiple times from the drainage line. Drainage lasts for about 15 minutes	Sample multiple times. Drainage lasts for about 100 minutes	
Coke drum drilling water from coke drum.	Sample multiple times as the water drains into the sluiceway. Drainage lasts for about 60 minutes	Sample multiple times as the water drains into the sluiceway. Drainage lasts for about 90(?) minutes	It is not possible to sample the drilling water as it flows from the coke drum with large quantities of coke. Samples are taken for informational purposes.
Output Streams			
Water from cutting water Tank.	Sample for multiple times for 4 hrs and 15 minutes after the coke drum was drained.	NA Coker 3 shares the water tank with Coker 2 so water tank not included.	This assumes the Whiting Coker is on 8.5 hr. =2*(cycle time)/(Nos of drums)
Water pumped from the Maze to the cutting water tank.	NA The tank will be park of the mass balance.	Sample from the maze pumps when they run for 16 hours.	This assumes the Toledo Coker on 16 hr cycles. =2*(cycle time)/(Nos of drums)

The balance will ignore the contribution of rain water. Drainage to the sewer for the Whiting coker will be assumed to be the same concentration as the water in the tank. Also the VOCs in the water leaving with the coke from the pad (or pit) will be assumed to have the same concentration as the water in the tank.

The Whiting Coker is expected to be on 8.5 hr cycles and the Toledo coker will be on 16 hr cycles.

A refinery Sample Coordinator should be assigned to:

1. Tag all sample points for the sample team to insure that the correct location is being used.

2. Agree to the sample date and be available for its duration.
3. Point out the designated sample locations to the sample team and insure that they are following safe procedures.
4. Provide an estimated time to the sample team when samples should be started and when they should end.
5. Inform the sample team when it is safe to actually begin sampling.
6. Inform the sample team that sampling should stop for a sample point.
7. Submit to the Refinery Lab hydrocarbon samples if a sampled stream has a separate hydrocarbon layer. Assuming that there is enough hydrocarbon to sample, submit the sample for simulated distillation, liquid GC for C1 thru C5, and specific gravity. URS will also send a sample to Test America for Method 8260 speciation.
8. Collect unit data in spreadsheet format during the test with one minute averages. Include the time period when the coke drum was cooled, drained, drilled, and 4.5hrs after coke drum draining **for Whiting and 16hrs for Toledo.**

The Toledo sample team will:

1. Coordinate their watches with refinery time. This is necessary to match process variables to samples.
2. Follow all instructions from the Refinery Sample Coordinator.
3. Take digital pictures of the sample apparatus including sample coolers.
4. For the "Coke Drum Drain", digital pictures should be taken of the water flowing from the drain line at beginning, middle, and near the end.
5. Take multiple samples as required in the Sample Plan.
6. Record the exact time each 5 gallon sample container was filled, and insure this time is recorded with the sample results. **Record start/stop time for each sample.** **<u>Measure and record final container water temperature when the container is full.</u>**
7. Samples should be cooled to within the 40 – 100 degF range. **Cool samples using one of the 2 techniques. Each method will vent the sample container to a safe location to avoid the risk of the samplers being sprayed with hot/boiling water:**
   - 7.1. **Preferred Method: Use a cooling coil submerged in an ice bath.** The water from the cooling coil will fill the 5 gallon container (located in an ice bath) to about the 80% level, **do not overfill. Fill the container from the bottom up**. Add ice to ice bath as it melts. Roughly 35-45LBs of ice will be needed per container if the inlet water is 220 degF. There is a significant risk that the cooling coil will plug when used on the coke drum draining sample, if so use the Alternate Method.
   - 7.2. **Alternate Method: Directly contact the hot water with ice inside the 5 gallon container.**
     - 7.2.1. **All weights accurate to within 0.1 LBs.**
     - 7.2.2. **Weigh each empty container with caps in place (roughly 10LBs)**
     - 7.2.3. **<u>Add 12-14LBs of ice into each container. Remove roughly 4 LB of ice from the container for composited lab analysis on the ice</u> (Do this for each container). Weight container with caps in place. (roughly 18-20 LBs)**
     - 7.2.4. **Fill the container from the bottom up (to about the 80% level) so that the hot water directly contacts the ice for a flash cooling effect. This occurs while the container is in a separate ice bath. Add ice to the ice bath as it melts. Roughly 25-35LBs of ice will be needed for the ice bath if the inlet water is about 220degF. After the container is 80% full, stop water flow and tightly cap the container as it continues to cool.**
     - 7.2.5. **Weigh the filled container with caps in place (roughly 44 LBs), and record all 3 weights for each container.**
8. **After each sample container is cooled to 35-45 degF,** the hydrocarbon and water levels for each container must be measured and recorded. If there is just an oil sheen, record "Oil sheen". If there is enough hydrocarbon to sample, send:
   - 8.1. One sample to Test America for 8260 Speciation.
   - 8.2. One sample should be submitted to the Refinery Lab for simulated distillation, liquid GC for C1 thru C5, and specific gravity

9. **After each sample container is cooled to 35-45 degF**, the sample team will pump the sampled water from the **cooled 5 gallon containers, through a 0.45** micron filter, and into the sample bottles, which were provided by Test America. Oil samples will not be filtered.
10. Afterwards, record an estimate of how much coke settled to the bottom of the 5 gallon containers. If possible, the coke should be removed and weighed per container.

The Whiting sample team will:

1. Coordinate their watches with refinery time. This is necessary to match process variables to samples.
2. Follow all instructions from the Refinery Sample Coordinator.
3. Take digital pictures of the sample apparatus including sample coolers.
4. For the "D-105 coke drum overflow" and the "Coke Drum Drain", digital pictures should be taken of the water flowing from the drain line at beginning, middle, and near the end.
5. Take multiple samples as required in the Sample Plan.
6. Record the exact time each 10 gallon sample container was filled, and insure this time is recorded with the sample results.
7. Samples should be cooled to within the 40 – 100 degF range.
8. Current plans include collecting the water in cooled 10 gallon containers. Each sample container should be flushed by overflowing through its vent for roughly twice the sample volume. The hydrocarbon and water levels for each container must be measured and recorded. If there is enough hydrocarbon to sample, send:
   8.1. One sample to Test America for 8260 Speciation.
   8.2. One sample should be submitted to the Refinery Lab for simulated distillation, liquid GC for C1 thru C5, and specific gravity
9. The sample team will pump the sampled water from the cooled 10 gallon containers, through a 45 micron filter, and into the sample bottles, which were provided by Test America. Oil samples will not be filtered.
10. Afterwards, record an estimate of how much coke settled to the bottom of the 10 gallon containers. The coke should be removed and weighed per container.

Special Instructions to the Lab

1. If coke fines may influence test results, filter samples as necessary to remove coke fines. For example, for all TOC tests, the water MUST be filtered again by lab with a 1-2 um filter. URS will filter all water samples with a 0.45 micron filter, so additional filtering by the lab should not be necessary.
2. All water samples will be speciated for 8260B compounds. In addition, the following tests will be run: dissolved gas test (methane, ethane, ethane, CO, CO2), gasoline range test **for Indiana** (C5-C12), and extended range test **for Indiana**(C8-C36), TOC, Oil & Grease by hexane extraction. Other miscellaneous tests are listed in the attached table.
3. For a water sample, if a hydrocarbon layer is present, only test the water layer.
4. For a hydrocarbon sample, if a water level is present, only test the oil layer. Perform 8260 speciation, GRO test, and ERO test on the hydrocarbon samples.
5. QA/QC reporting will be Level 4 for the 8260/8260B tests. All other tests will be Level 2.
6. The 8260/8260B speciation will include all of Test America's "Default List" and Appendix IX" compounds.

Whiting Coker Sample Plan, rev 12-7-2009

	D-105 coke drum overflow water	Coke drum drainage water	Coke drum drilling water from coke drum.	Water from TK 813 cutting water Tank.	Comments
Type of stream for Mass Balance	Input	Input	Input	Output	
Sample Start Time	When water from D-105 drain significantly increases to the sluiceway.	When water starts to drain from coke drum.	After the pilot hole is cut in the coke bed, and it is safe to sample.	After coke drum was drained.	
Sample Finish Time	When water flow significantly decreases	When very little water drains from the pipe.	When water and coke stop falling from coke drum.	4.25 hours after start of sampling.	
Approximate duration of water flow and sampling.	105 minutes	15 minutes	60 minutes	4.25 hours.	
Temperature of stream (approx), degF	140 to 180	90 to 200	90-120	60-70	These are rough estimates and indicate that the temperature of the sample will change with time.
Estimated water quality	Varies with time. Initially may have a separate oil phase. Hydrocarbon content and flow rate will decrease with time. Coke fines will be present, and their concentration will be high for the earlier samples.	Varies with time. Initially there is a remote possibility that a separate oil phase will be present. Hydrocarbon content and flow rate will decrease with time. We expect very low hydrocarbon content. Coke fines will be present, and their concentration will be high for the earlier samples.	Low hydrocarbon content with significant coke fines.	Lowest hydrocarbon content and the lowest coke fines concentration.	URS will filter all water samples with a 0.45 micron filter. Water tests are performed on the water phase. Hydrocarbon tests (including 8260) performed separately on the oil layer.
Sample cooler required	Yes	Yes	No, since a bucket will be used. Just cool the sample after it is collected.	No	Used to cool the water to 40-100 degF before taking a sample
Samples times from start. Try to take all samples within these time windows.	1- 15 minute (high flow rate)	1-5 minute	1 - 10 minute	1 -20 minute	
	16-30 minute (high flow)	6-10 minute	11 - 20 minute	21 - 45 minute	
	30-45 minute (high flow)	11-15 minute	21 - 30 minute	One every 45 minutes there after	
	46-75 minute (medium flow)	Every 10 minutes if continues	31-60 minute		
	76-105 minute (low flow)	Take as many samples as possible.			
Method 8260/8260B Speciation on "Default List" and Appendix IX"; Dissolved Gas Test, Gasoline Range Test, Extended Range Test,	Separate tests on all water and oil samples	Separate tests on all water and oil samples	Separate tests on all water and oil samples	Separate tests on all water and oil samples	-Lab: Filter samples as necessary to remove coke fines. URS will pre-filter all samples. -The TOC test MUST be filtered first.

TOC test (water only).					-Includes hydrocarbon samples. (TOC test not run on oil samples).
Total sulfides (includes H2S) and NH3 .	All water samples	All water samples	All water samples	All water samples	
pH	All water samples	All water samples	All water samples	All water samples	
Oil & Grease by Hexane Extraction	All water samples	All water samples	All water samples	All water samples	
Water hardness, Na, K, Ca, Mg, inorganic chlorides, sulfates	All water samples.	All water samples	All water samples	All water samples	All water samples

Toledo Sample Plan rev Jan-7-2010

	Coke drum drainage water	Coke drum drilling water from coke drum.	Water from maze pumps	**Water surge tank PR500-310.**	Comments
Type of stream for Mass Balance	Input	Input	Output	**Comparison**	
Sample Start Time	When water starts to drain from coke drum.	After the pilot hole is cut in the coke bed, and it is safe to sample.	After coke drum was drained.	**At the end of coke drum cooling.**	
Sample Finish Time	When very little water drains from the pipe.	When water and coke stop falling from coke drum.	**8 hours after start of sampling or LCV-5349 stays closed for 2 hours.**	**2.0 hours after start of sampling.**	
Approximate duration of water flow and sampling.	**150 minutes, but expect that there is enough pressure for only 75 minutes**	**2-3 hours**	16 hours.	**Nearly continuous**	
Temperature of stream (approx), degF	**212-220**	90-120	**80-200**	**80-100**	These are rough estimates and indicate that the temperature of the sample will change with time.
Estimated water quality	Varies with time **with some water flashing to steam.** Initially there is a remote possibility that a separate oil phase will be present. Hydrocarbon content and flow rate will decrease with time. We expect very low hydrocarbon content. Coke fines will be present, and their concentration will be higher for the earlier samples.	Low hydrocarbon content with significant coke fines.	Lowest hydrocarbon content and the lowest coke fines concentration.	Lowest hydrocarbon content and the lowest coke fines concentration.	**URS will filter all water samples with a 0.45 micron** filter. Water tests are performed on the water phase. Hydrocarbon tests (including 8260) performed separately on the oil layer.
Sample cooler required	Yes. **Use either the Preferred or Alternate method.**	No, since a bucket will be used. Just cool the sample after it is collected.	Yes. **Use the Preferred method.**	No. **Directly fill the 5 gallon sample container.**	Used to cool the water to 40-100 degF before taking a sample
Samples times from start. Try to take all samples within these time windows.	**1-10 minute**	**Just take 4 samples, one every 25-30 minutes**	1 -20 minute	**1 -30 minute**	
	11-20 minute		21 - 45 minute	**31-60 minute (wait at least 30 minutes after first sample)**	
	30-40 minute		**Sample if level control valve LCV-5349 is open, every 45 minutes. Stop sampling if the level control valve stays closed for 2 hours.**	**No additional samples needed**	

	50-60 minute				
	60-70 minutes (if flow continues)				
Method 8260/8260B Speciation on "Default List" and Appendix IX"; Dissolved Gas Test, Gasoline Range Test, Extended Range Test, TOC test (water only).	Separate tests on all water and oil samples. **If an oil layer is found, URS will try to sample so that it can be analyzed separately**.	Separate tests on all water and oil samples	Separate tests on all water and oil samples	Separate tests on all water and oil samples	-Lab: Filter samples as necessary to remove coke fines. URS will pre-filter all samples. -The TOC test MUST be filtered first. **-Includes hydrocarbon samples.** (TOC test not run on oil samples).
Total sulfides (includes H2S) and NH3 .	All water samples	**All water samples**	All water samples	All water samples	
pH	All water samples	**All water samples**	All water samples	All water samples	
Oil & Grease by Hexane Extraction	All water samples	All water samples	All water samples	All water samples	
Water hardness, Na, K, Ca, Mg, inorganic chlorides, sulfates	**All water samples**.	**All water samples**	**All water samples**	**All water samples**	Sample composites were eliminated.