

# PETROLEUM REFINING PROCESS WASTE LISTING DETERMINATION

# SUPPLEMENTAL BACKGROUND DOCUMENT

# LISTING SUPPORT ANALYSES

U.S. Environmental Protection Agency Office of Solid Waste Washington, D.C.

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#### **1. INTRODUCTION**

On November 20, 1995 (60 *FR* 57747), EPA published proposed listing decisions for fourteen petroleum residuals. The purpose of this document is to present additional analyses conducted since the date of the proposal. These analyses are discussed in the notice of data availability. Each section of this document discusses analyses that are used in the revised risk assessments or are otherwise referenced in the notice of data availability.

#### 2. ANALYSES REGARDING LEACHING OF OILY WASTE

Some commenters provided extensive arguments to the effect that the TCLP substantially understates the leachability of oily wastes by failing to capture much of the waste leaching potential and presuming the hazardous constituents are migrating in a dissolved rather than free phase flow. EPA conducted a number of analyses in response to the technical elements of the commenter's arguments that are described below. The policy elements of the commenter's arguments, as well as some of the technical arguments that did not result in new analyses, will be addressed in the response to comments for the final rule.

#### 2.1 Field and Laboratory Observations of Wastes

Commenters suggested that the wastes evaluated in the proposed listing determination are oily in nature, and have high levels of "free" oil. EPA contends that the residuals of concern are not oily in the manner anticipated by the commenter. For example, these materials differ dramatically from used oil which is essentially all oil. Crude oil tank sediment, the "oiliest" of all the residuals of concern, was never observed by the Agency during sampling and analysis to exhibit an oily phase. Table 1 of this response summarizes the Agency's field and laboratory observations of the listing residual samples. These materials were generally solid at room temperature, with a tarry or granular consistency. None were observed to exhibit immiscible phases. The samples were homogenous in nature, often quite solid, and did not generate filtrate during the initial filtration step of the TCLP. This table also contains the results of total oil and grease analyses (SW-846 Method 9071A) conducted by EPA on archived samples in the spring of 1996. For some samples, as indicated by "NA", insufficient sample remained to conduct this analysis.

#### 2.2 Reported Oil and Grease Levels Of Wastes Sent to Landfills

Commenters expressed concern that wastes with high levels of oil were sent to landfills, and that such waste would cause an oily phase to be released. EPA conducted additional analyses of the reported oil and grease content of landfilled wastes, based on data reported in Section VII of the questionnaire. See Appendix A: " Oil and Grease Content of Landfilled Refinery Wastes."

In assessing any waste that was disposed in an onsite nonhazardous landfill in 1992, the highest reported oil and grease concentration was 10 percent, with the median value less than 1 percent. For residuals disposed in offsite non-hazardous waste landfills in 1992, 8 individual wastes were reported to have oil and grease levels over 10 percent, but the median level was approximately 1 percent (oil and grease data were reported for only 120 out of the 621 residuals disposed in offsite nonhazardous waste landfills).

Sample ID	Sample Date	% Oil & Grease	Lab Preparation Sample Description <sup>1</sup>	Field Sampling Description		
Crude Oil Tank Sludge Sample Description						
R6B-CS-01	03/15/94	NA	Coarse texture, oily black appearance; colorless to yellow digestate.	Sludge within the tank was stratified. The upper layer was centrifuged to recover oil and remove water. The bottom layers passed the paint filter test and were placed directly into roll-off boxes. One centrifuged and two non-centrifuged roll-off boxes were available for sampling. A single core sample was collected from each of the three roll-off boxes and composited. Once composited the core samples were a thick black tarry, sandy sludge.		
R8C-CS-01	07/21/94	25	Black, tar-like sandy sludge; yellow digestate.	The sample was collected directly from the tank by refinery personnel prior to the de-oiling process and was described as black in color, relatively homogeneous with a small amount of free liquid. The refinery requested this sample to be filtered to remove the free liquid phase prior to analysis. The lab reported no free liquid present upon receipt.		
R4B-CS-01	08/25/94	15	Black sandy tar; yellow to orange digestate.	Tank sludge was sent through a heating coil system, blended with cutter stock and centrifuged to recover any oil. Centrifuged sludge was placed on storage pads prior to sampling. The sample was collected and composited from four storage pads. No sample appearance noted.		
R10-CS-01	08/26/94	41	Black, greasy medium texture; yellow digestate.	After removing the liquid layer, the tank sludge was vacuumed directly into bins. The sludge was described as black and oily with a consistency of cake icing. Compared to filter cakes or centrifuge cakes from other refineries this sludge was described as more fluid. Facility subsequently liquefied waste with hydrocarbon and recycled it to the refining process.		
R22-CS-01	09/21/94	4.9	Black, tar-like medium texture; yellow digestate.	Tank sludge contents were mostly rust and scale. The sludge was processed in a centrifuge and shaker to recover oil and remove heavy solids prior to disposal. No additional sample appearance information was noted.		
R19-CS-01	10/12/94	14	Black, tar-like medium texture; colorless to yellow digestate.	Filtered tank sludge available for sampling was described as brown-black, gritty, semi-solid with a small amount of water present.		

Table 1

Sample ID	Sample Date	% Oil & Grease	Lab Preparation Sample Description <sup>1</sup>	Field Sampling Description
Clarified Slur	ry Oil Tank	Sludge Samp	le Description	
R4-SO-01	11/16/93	NA	Black sandy coarse texture; yellow digestate.	The contents of the CSO tank after draining were air dried and removed to the facility's "stained soils pad". Contaminated soils were also stored and mixed with the CSO sludge in one area. Sampling was conducted from an area free of cross contamination. The CSO tank sludge had a higher accumulation of fines than normal due to a plugged line on the FCC. The sludge appearance was sandy to rock-like particles covered in a black tar-like oil. The sludge composition was hard and difficult to sample using an auger.
R9-SO-01	05/17/94	70	Black, oily fibrous filter material; petroleum odor; yellow to orange digestate.	Spent filter cartridge consisting of metal supported paper filter media. The metal portions of the filter cartridge were not sampled. The filter contained no free liquid, but oil seeped out of the filter if squeezed.
R1B-SO-01	08/26/94	16	Blackish-brown, greasy medium texture; yellow digestate.	CSO sludge from two tanks cleaned concurrently was stabilized with cement kiln dust. The CSO mixture was placed on a storage pad prior to sampling. The sludge sample appearance was fine and granular.
R20-SO-01	08/30/94	24	Black, medium texture; strong petroleum odor; yellow digestate.	The tank sludge was heated and centrifuged to recover oil from the solids. Sampling occurred after oil recovery. After de-oiling, the CSO sludge was reported to contain 20% oil and 80% solids. The sludge composition was described as fine and granular.
Unleaded Sto	rage Tank S	ludge Sample	Description	
R6B-US-01	03/30/94	NA	Wet, brown, muddy sludge; strong gasoline smell; yellow digestate.	Unleaded storage tank was water washed prior to screening to remove the solids. The screened solids consisted of large pieces of rust and metal. A total of 2 cubic yards of solids containing a small amount of free liquid were removed from the tank prior to sampling. The Shell personnel that collected the sample noted there was no odor present.

Sample ID	Sample Date	% Oil & Grease	Lab Preparation Sample Description <sup>1</sup>	Field Sampling Description	
R8A-US-01	04/14/94	0.09	Wet, black, sandy texture with some large solid pieces; strong gasoline smell; yellow digestate.	Grab samples were collected by Amoco personnel from four points directly inside the tank. This procedure was deemed necessary in order to prevent cross contamination from material present in the vacuum truck. The sample was homogenized prior to portioning in the sample containers. The sample was described as black in color with some areas of grey and orange. There was approximately one inch of free liquid on the surface and contained a mixture of "sludge" and scale solids ranging in size up to three inches in diameter. There was a hydrocarbon odor.	
R16-US-01	08/03/94	< 0.09	Brown, medium sandy texture; yellow digestate.	After draining and water washing the unleaded tank was allowed to air dry and the remaining solid residue was swept into two drums. Samples were composited from two drums. The sample collected was a uniform brown color, consisting of chips generally less than ½ inch, and was slightly moist. There was a moderate hydrocarbon odor.	
HF Alkylation	n Sludge Sar	nple Descript	ion		
R3-HS-01	11/18/93	NA	Black sludge; yellow digestate.	Grab samples where collected near the edge of the tank where most of the sludge settled. To evenly distribute the sludge to all the sample containers, the sample was constantly stirred to keep the solids suspended in the liquid. The sludge sample was black and oily with a high liquid content.	
R8B-HS-01	04/28/94	0.3	Whitish-yellow, opaque thick gelatinous substance; strong odor; colorless digestate.	Samples were obtained from the neutralization tank containing various HF alkylation streams. There was a yellowish oily emulsion floating on the surface of the liquid layer in the tank. The collected sludge exhibited an unusual organic odor, with a creamy white color and a viscous consistency.	
R9-HS-01	05/17/94	31	Brown, syrup-like substance; strong petroleum odor; colorless digestate.	Grab samples were collected from four 55-gallon drums. Each drum contained approximately 2 inches of water with oily solids suspended and settled below this level. The collected sludge was colored mustard yellow, with a stringy texture that appeared to have the consistency of an oil-in-water emulsion.	
R15-HS-01	08/02/94	6.8	Brown, fine texture sludge; colorless digestate.	Sludge samples were collected from the settling section of the pit. The sample was described as yellow with a consistency of wet oily sludge.	

Sample ID	Sample Date	% Oil & Grease	Lab Preparation Sample Description <sup>1</sup>	Field Sampling Description		
R7C-HS-01	10/13/94	0.08	Brown, medium texture; strong organic odor; colorless digestate.	Random samples were collected from centrifuged sludge stored on a concrete pad. The pile surfa appeared light grey and granular. The sludge in the pile's interior had the consistency of cookie dough: soft, wet, sticky, and tearable, with a yellow color.		
Sulfur Complex Sludge Sample Description						
R1-ME-01	10/20/93	1.0	Black, tar-like sludge; brown digestate.	Sludge was collected directly from all areas of the reclaimer unit and composited prior to containerization. The sludge was dark brown and contained no free liquid.		
R5-ME-02	02/07/94	NA	Brown, coarse filter paper; yellow digestate.	Spent cartridge filters approximately 2 inches in diameter and 20 inches long, containing dark solid scale on the exterior surface.		
R6-ME-01	02/09/94	NA	Black, coarse texture filter material; yellow digestate.	Spent DEA filter cartridges. No sample appearance was noted.		
R14-ME-01	06/07/94	0.2	Black, fine texture; wet, thick solid; yellow digestate.	Diatomaceous earth sludge was contained in a bin under a layer of water. Effort was made to exclude the water phase, however, the final sample collected contained a significant proportion of water. The sample was black (due to hydrocarbon content), had no odor, and consisted of particles in the shape of small balls and flakes.		
R18-ME-01	10/14/94	< 0.05	Blackish-brown oily solid, petroleum odor; yellow digestate.	Samples were collected from various points within the MEA kettle reboiler unit and homogenized prior to containerization. No sample appearance was noted.		

Sample ID	Sample Date	% Oil & Grease	Lab Preparation Sample Description <sup>1</sup>	Field Sampling Description			
Hydrotreating	Hydrotreating Catalyst Sample Description						
R1-TC-01	10/19/93	< 0.05	Black, coarse texture pellets; brown digestate.	Grab samples were obtained from four 55 gallon drum each containing recently unloaded spent catalyst. A small piece of dry ice was added to each filled sample container (except volatiles) due to the potential pyrophoricity. The catalyst was black, cylindrical pellets about 1/4 inch long. Samples were composited in the laboratory.			
R8A-TC-01	03/29/94	NA	Black, coarse texture; yellow digestate.	Grab samples were collected from four roll-off bins. The contents of each bin appeared, visually, to be homogeneous. The spent catalyst was described as black, rod shaped, with a significant oil coating. One roll-off bin selected for sampling contained a mound of catalyst located in the center with green tinted oil present on the uncovered floor bin. Due to the possible pyrophoric nature of the catalyst, the grab samples were not composited in the field.			
R11-TC-01	05/11/94	< 0.05	Black, coarse texture; colorless to yellow digestate.	Catalyst samples were collected by refinery personnel at the time of the reactor dump. The sample appearance was described as black and rod shaped (1 mm diameter and 5 cm long).			
R3B-TC-01	07/12/94	< 0.05	Black, coarse textured pellets; yellow digestate.	Since the spent catalyst was considered to be self-heating, the catalyst was collected directly into the sample containers and composited by the laboratory. No additional sample appearance information was noted.			
R22-TC-01	09/21/94	< 0.2	Black, coarse texture; brown digestate.	During the sample collection, small pieces of dry ice were collected with the spent catalyst (known to be pyrophoric) to maintain an inert atmosphere. The nickel molybdenum catalyst appeared to be small fine rice-shaped rods that were oil covered. Samples were composited in the laboratory prior to analysis.			
R18-TC-01	10/20/94	< 0.05	Black, coarse textured pellets; colorless digestate.	Grab samples were collected from four roll-off bins and homogenized in the field for the non-volatile constituents. According to refinery personnel the catalyst was not managed as hazardous or pyrophoric, therefore, compositing samples in the field was considered appropriate. No additional sample appearance information was noted .			

Sample ID	Sample Date	% Oil & Grease	Lab Preparation Sample Description <sup>1</sup>	Field Sampling Description		
Hydrorefining Catalyst Sample Description						
strips; yellow digestate. compositing at the laboratory. The catalyst was labeled for transport as a self heat				Spent catalyst from four randomly selected flowbins was collected directly into sample containers for compositing at the laboratory. The catalyst was labeled for transport as a self heating solid. No sample appearance information was noted.		
R7B-RC-01	03/14/94	NA	Black charcoal-like material; colorless digestate.	Samples were collected from four flowbins by refinery personnel due to potential high levels of arsenic. The catalyst appeared to be gray to black in color.		
R21-RC-01	08/31/94	0.08	Black, rod shaped; orange to pink digestate.	Samples were collected from four randomly selected drums. The catalyst appeared to be small rod shapes and covered with oil.		
Off-Spec Pro	duct and Fin	es from Ther	mal Processes Sample Description			
R6-TP-01	02/09/94	NA	Black, coarse textured sludge; yellow digestate.	Coke fines were present at the bottom of pit containing 3 feet of water and 1 foot of solid material. The water layer contained a black solid/liquid emulsion. Sampling attempts were made to exclude large coke chunks while minimizing water content. The sample was described as a black slurry.		
R8A-TP-01	03/29/94	NA	Black, sandy texture; colorless digestate.	Coke fines were collected at the fines pile using a front end loader. The sample exhibited no strong odor, and appeared moist, moderately homogeneous, and were easily compacted. There were specks of glistening material uniformly distributed in the coke fines.		
R12-TP-01	05/10/94	8.4	Black, sandy medium texture; strong petroleum odor; yellow digestate.	Dredged material from the coke pit containing the smallest available particle size was allowed to drain prior to sampling. The collected fines were described as moist, black, fine particles with little free liquid.		
R11-TP-01	05/11/94	0.6	Black, sandy coarse texture; colorless digestate.	The coke fines sample was collected from a yard bin used to gather fines as they fall from the conveyer. The fines appeared dry and black with a very fine particle size.		
R14-TP-01	06/07/94	0.03	Black, coarse texture; yellow digestate.	Samples were collected from a roll-off box containing spill material obtained in conjunction with the coke fines operation. The box contents included coke fines and larger coke material. The contents were black, powdery, and dry, but did not create a dust.		

	Table 1 (continued)								
NT	Sample IDSample Date% Oil & GreaseLab Preparation Sample Description 1				Field Sampling Description				
МΕ	R3B-TP-01	07/12/94	<0.05	Black fine particles; colorless digestate.	"Chunky" coke was dumped from the reactor into a bin where sample was collected. The sample was described as small, marble sized, black spheres.				
S	NA=not analyzed due to lack of sample availability.								
	All samples were classified by the laboratory as single-phased homogeneous wastes. Oily matrices were found to be non-filterable according to TCLP Method 1311 requirements and were considered as 100% solids for leaching purposes. There were no reported instances of sample free liquid (filtrate) that was not compatible or miscible with the associated leachate.								

- EPA conducted further verification of the 8 offsite landfill wastes disposed reported to have oil and grease levels above 10 percent. The two highest levels, for a crude oil tank sludge (80%) and a residual oil tank sludge (99%) appear to represent oil levels prior to deoiling (i.e., the residuals underwent an onsite removal step prior to being landfilled). Oil content following deoiling was not provided, however. The remaining 6 wastes had oil & grease levels ranging from 12 to 30 percent. Only one of these wastes was one of the 14 listing residuals (CSO sediment with 20 percent total oil & grease); the other 5 were study residuals. Two of these 5 residuals, both with 20 percent oil and grease levels, were accompanied by lab results. One sample was described as having no free liquids as determined by the paint filter test, and another was described as having 93 percent solids and 7 percent liquids (which indicates that most of the oil is bound to the solid matrix).
- Removing the 2 highest data points from the data set (because they do not reflect as disposed, de-oiled levels) reduced the average oil and grease level in these wastes to 19 percent. The median oil and grease content of all wastes landfilled remained approximately one percent.

#### 2.3 Alternative Leaching Methods

Some commenters stated that the TCLP method was not appropriate for "oily" wastes, and pointed out that EPA's Delisting program uses alternative methods, i.e., Method 1330, the Oily Waste Extraction Procedure (OWEP). The OWEP was developed by EPA for use in Delisting evaluations in an attempt to model the release of metals from an oily waste matrix after the oil degrades, and results in a release of the maximum leachable amount of metals. EPA did not include this method in its analytical protocols for the petroleum refining listing determination because EPA was concerned that it may over estimate the leaching potential of metals from wastes. This method uses strong organic solvents to leach out organic material, followed by extraction with an acidic aqueous solution. The mobile metal content is then calculated from metals measured in the organic and aqueous extraction. Such a procedure may cause drastic changes in the original waste matrix. However, in response to the commenter's concern, EPA retrieved 27 samples of eight listing residual categories from the laboratory archives and ran the OWEP for 7 metals to assess any differences in metals mobility between the TCLP and the OWEP (percent oil and grease was also measured for these samples). The results of the OWEP analyses are presented in Appendix B, "Comparison of the Toxicity Characteristic Leaching Procedure (TCLP) with the Modified Oily Waste Extraction Procedure (OWEP)," EPA, August 13, 1996. Of the 189 data pairs generated by this analysis, only 14 showed higher leaching rates using the OWEP when compared to the TCLP results and generally were within 1 order of magnitude of the TCLP results. Based on the results of this analysis, EPA concludes that oil content (as measured by total oil and grease) does not appear to impact the mobility of metals in the wastes relevant to this rulemaking.

#### 2.4 Analysis of Leaching Efficiency

Some comments indicated that EPA did not address the efficacy of the TCLP, or justify reliance on this method. EPA examined the existing analytical data for the petroleum wastes to see whether oil content significantly affected the leachability of a key organic constituent (benzene). EPA calculated the percentage of available benzene that the TCLP showed to be mobile, as summarized in the fourth column of Table 2. For the 27 samples for which the percentage of benzene leached could be calculated, the average sample leached 53 percent of the total mass of benzene contained in the residual. This leaching rate was fairly consistent regardless of whether the waste was oily (crude oil tank sludge, CSO sludge, and HF alkylation sludge: average leaching rate, 46 percent) or non-oily (all other listing residuals of concern with oil and grease content less than 1 percent: average leaching rate, 52.9 percent). These results indicate that the TCLP mobility of a typical organic constituent, benzene, is not adversely affected by the oil content in these wastes.

PETROLEUM REFINING RESIDUALS LEACHING POTENTIAL						
Sample ID	Total Benzene (µg/kg)	TCLP Benzene (µg/L)	% Benzene Leached <sup>1</sup>	% Oil & Grease		
	CRUD	E TANK SLUI	OGE			
R6B-CS-01	69,000	1,700	49	24		
R8C-CS-01	220,000	1,600	15	25		
R4B-CS-01	8,200	130	32	15		
R10-CS-01	52,000	560	22	41		
R19-CS-01	660	32	97	14		
R22-CS-01	< 2,500	< 50	NA	4.9		
τ	UNLEADED GA	ASOLINE TAN	NK SLUDGE			
R6B-US-01	43,000	600	28	NA		
R8A-US-01	110,000	1,600	29	0.09		
R16-US-01	2,700	55	41	< 0.09		
	С	SO SLUDGE				
R4-SO-01	< 1,250	< 50	NA	NA		
R9-SO-01	1,200	84	100	70		
R1B-SO-01	< 1,250	< 50	NA	16		
R20-SO-01	< 2,500	< 50	NA	24		
	HYDROTE	REATING CAT	TALYST			
R1-TC-01	500,000	39,000	100	< 0.05		
R8A-TC-01	9,400	170	36	NA		
R11-TC-01	24,000	3,700	100	< 0.05		
R3B-TC-01	2,000	48	48	< 0.05		
R18-TC-01	160,000	4,200	53	< 0.05		
R22-TC-01	2,900	250	100	< 0.2		

Table 2

PETROLEUM REFINING RESIDUALS LEACHING POTENTIAL						
Sample ID	Total Benzene (µg/kg)	Benzene Benzene Lea		% Oil & Grease		
	HYDRORI	EFINING CAT	ALYST	-		
R5-TC-01	4,200	110	52	NA		
R7B-RC-01	100,000	4,200	84	NA		
R21-RC-01	27,000	160	12	0.08		
	REFOR	MING CATAI	LYST			
R2-CR-01	< 25	< 50	NA	NA		
R5-CR-01	1,000	3,000	100	NA		
R7B-CR-01	2,300	86	75	NA		
R11-CR-01	430	42	100	NA		
R14-CR-01	570	< 50	0	NA		
R15-CR-01	26,000	NA	NA	NA		
	HF ALK	YLATION SLU	UDGE			
R3-HS-01	6,100	180	59	NA		
R8B-HS-01	14,000	< 50	0	0.3		
R9-HS-01	< 625	< 50	NA	31		
R15-HS-01	< 313	< 50	NA	6.8		
R7C-HS-01	< 650	< 50	NA	0.08		

PETROLEUM REFINING RESIDUALS LEACHING POTENTIAL						
Sample ID	Total Benzene (µg/kg)	TCLP Benzene (µg/L)	% Benzene Leached <sup>1</sup>	% Oil & Grease		
SULFUR COMPLEX SLUDGE						
R1-ME-01	< 2,500	< 50	NA	1.0		
R5-ME-01	96	< 50	0	NA		
R6-ME-01	R6-ME-01 < 1,250 < 50 NA NA					
R14-ME-01	< 625	< 50	NA	0.2		
R18-ME-01	420	26	100	< 0.05		

Percent benzene leached calculated based on a 20 to 1 ratio of leaching fluid to sample mass. The total concentration was multiplied by 0.05 to obtain the total theoretical leachate concentration. This value was divided into the reported TCLP concentration to obtain the percent leached. Calculated percentages greater than 100% are listed as 100% leached.

#### 3. POTENTIAL FOR ADDITIVE RISKS FROM MULTIPLE SOURCES

Commenters said that the Agency failed to sum risks across groundwater and non-groundwater pathways, and that correcting these deficiencies in the landfill modeling would raise the risk levels to the point where listing the waste would be warranted.

These risks correspond to those associated with land treatment (non-groundwater) and landfilling (groundwater), respectively. The Agency reviewed the site maps provided in the RCRA §3007 survey for those facilities with both on-site landfills and on-site land treatment units to determine whether the nearest residences could be impacted by both management units. The Agency eliminated those facilities with Part B permits for their land treatment units which require runoff controls. This narrowed the number of facilities to one and the geographic position of these waste management units (approximately 1 mile apart) appears to preclude exposures from both types of units to the near by residences. As a result, the risk assessment was not modified to address this concern. The Agency's detailed assessment follows.

The RCRA §3007 surveys for facilities reporting both an onsite <u>Subtitle D</u> landfill and a <u>non-hazardous</u> waste land treatment unit which are co-located in such a way that simultaneous exposure might be possible were reviewed.

There was only one facility that had both an onsite Subtitle D landfill and a <u>non-hazardous</u> waste land treatment unit: that facility was National Cooperative Refinery Corp. in McPherson, Kansas. However, the attached facility map shows the units are approximately 5,000 feet apart and therefore simultaneous exposure is not likely.

Fina Oil and Chemical Company, Big Spring, Texas is the only facility in which both the land treatment unit and landfill appear to be co-located such that simultaneous exposure might be possible. However, Fina has a Part B Permit for their hazardous waste land treatment unit. In addition, groundwater exposure would be to the residence 7,000 ft southwest of the landfill and non-groundwater exposure would be to the residence 9,000 ft southeast of the land treatment unit. (See attached map) Therefore, simultaneous exposure is not possible, even in their case.

A summary table for each facility which has both an onsite land treatment unit and landfill is attached.

Facilities with Both Onsite Land Treatment Units (LTU) and Landfills (LF)							
Name	Fac No	Unit No.	Unit type	Dist to well (ft)	Comments from Maps		
Nat. Coop,	58	2	LTU*	no well	Units on opposite sides		
McPherson		9	LTU*	no well	of refinery (>1 mile)		
		20	LF	no well			
Amerada Hess, Purvis	88	17	LTU	na	Units on opposite sides		
		20	LF	na	of refinery (`3600 ft)		
Giant, Gallup	103	30	LTU	26,400	Map unreadable		
		31	LF	26,800			
Conoco, Ponca City	110	4	LTU	1,000	~2500 ft appart		
		3	LF	1,000			
Fina, Big Springs	132	10	LTU	3,500	LTU & LF appear to be		
		13	LF	3,500	next to each other		
Star, Pt. Arthur	150	400	LTU	nr	Map not provided		
		401	LF	nr			
Dia. Sham., Sunray	153	230	LTU	9,000	GW appears to flow away		
		210	LF	9,000	from well		
		240	LF	9,000	Units not near each other		
Dia.Sham., 3 Rvrs	158	5	LTU	6,200	Map not provided		
		7	LF	6,200			
Hess, St. Croix	168	2	LTU	na	GW flows toward ocean		
		1	LF	na			

\* All LTUs were reported to be regulated with a hazardous waste permit ("Part B"), except the one facility as noted.

na - not applicable

nr - not reported

#### 4. THE POTENTIAL IMPACT OF OIL-BEARING RESIDUALS EXCLUSION ON COKE PRODUCT

In evaluating comments on the proposed rule, EPA realized it had omitted from the original docket the analysis it had completed concerning the impacts of recycling petroleum wastewater treatment sludge for coke production in an attempt to determine a "worst-case" scenario for metals loading in the coke product.

One commenter argued against the exclusion because, among other reasons, of the potential for unregulated disposal of toxicants. The purpose of this document is to provide the original analysis conducted in support of the proposed rule and how the Agency revised it to reflect more current data from literature sources that that provided during the public comment period.

In the proposed rule, the Agency noted that the coker is an integral part of the refining process, and "it is highly unlikely that refinery owners or operators would allow any incompatible materials to be inserted into the coker for fear of interfering with proper operation of the coker." In addition, EPA cited industry data "which supports industry's claim that oil-bearing sludges generated during the refining process are substantially similar to normal feedstock material."

#### 4.1 EPA's Analysis

EPA closely examined the potential for the recycling of secondary oil-bearing material to serve as a conduit for disposal for "toxics along for the ride" and has taken into consideration several steps, in crafting the exemption, to insure that toxics along for the ride do not present significant adverse environmental impacts:

- 1. The scope of the proposed exemption is limited to the petroleum refining, such that the oilbearing materials to be considered would be raw material-like and not contaminated prior to being recycled.
- 2. A limit is proposed on the amount of toxic constituents that may be accumulated in any coke product by making coke product derived from listed or characteristic hazardous waste subject to the TC rule.
- 3. A prohibition on speculative accumulation or land placement of secondary materials prior to being recycled is proposed.
- 4. EPA has assessed available data to identify the significance of potential exposure to toxics carried through to the fuels produced to evaluate the need for limitations the commenter suggests are needed.

One possible pathway of environmental concern is the increase in toxic metals contained in petroleum coke products. Because anode-grade petroleum coke must meet rigorous specifications on ash content, silica content, and hardness and is of significantly greater economic value than fuel grade coke, market constraints

would work to limit any degradation of product quality. In the case of fuel grade coke, while there are fewer stringent product specifications, there are nevertheless standards on the ash, sulfur, nitrogen and volatile combustible material content, and as noted in the proposed rule (60 FR 57755), the limited data EPA obtained does not indicate a significant change in the composition of fuel grade coke.

To determine the highest level of metals in coke product derived from F and K listed sludges, EPA constructed a worst case scenario. The scenario assumed that 100 % of the F and K sludge volumes generated during 1992 would be recycled to produce the total quantity of product coke on a national basis. The hypothetical coke product with sludge added concentration was calculated using a weighted-average of the F/K sludge metal concentration and the non-derived coke product concentration and their respective volumes of 1,026,000 MT (metric tons) and 39,634,000 MT. The concentrations used for the sludge and the coke product were based on several EPA and literature references. The results of the calculations are shown in Table 1 of the attachment.

The concentrations for most metals projected for the hypothetical sludge-derived coke are similar to the metal concentrations reported for coke product. The results of the EPA worst-case calculation are compared (Table 2 in attachment) with data from two literature references on coke product composition and with data provided by Mobil Oil Corporation for coke product with and without F/K sludge being added. The comparison indicates that the coke product with sludge added metals concentrations are within at least one of the ranges of coke product found in the literature. The sludge-derived coke shows a somewhat higher concentration of chromium compared to most literature values for coke product.

The level of chromium projected, however, appears well below any level of concern. For example, even assuming the direct ingestion of material with 5 ppm of chromium, the amount of chromium ingested would be far below the RfD.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>Using ingestion rates for soil of 100 mg/day, for an adult, this would result in the ingestion of about 0.001 mg of chromium per day. The RfD for chromium (assuming it is the more toxic hexavalent form) is 0.005 mg/kg-day; for a 70 kg adult this is equivalent to 0.35 mg/day. Therefore, the risks due to chromium in coke products are projected to be negligible.

#### ATTACHMENT

#### Impacts of Recycling All Petroleum Sludge to Coke Production

The total quantity of coke produced in the United States in 1992<sup>2</sup> was 39,634,000 MT. The number of facilities reported having cokers in the §3007 Survey was 54 (29%) out of a total of 187 refineries in 1992.

The sludge volume generated in 1992 was 1,026,000 MT (2.6% of the total coke produced).<sup>3</sup> To calculate the metals concentration in the coke product with sludge added, the following table uses three published data sources. In calculating the worst-case metals loading in the coke product, EPA used total constituent concentration data developed for the EPA F037/38 rulemaking, unless a concentration was not available; in this case the highest concentration found from other sources was used. See Table 1 for the results of the weighted-average calculation showing the calculated total constituent concentrations in the coke product with sludge added.

Results of the calculations comparing calculated metals concentrations from the metals loadings of the F/K sludges in petroleum coke with actual metals concentrations found in coke are presented in Table 2. Mobil Oil Corporation provided data for the coke product before and after they inserted F037/38 sludge with their feedstock.

<sup>&</sup>lt;sup>2</sup>DOE. <u>Petroleum Supply Annual 1992, Volume 1</u>. May 1993.

<sup>&</sup>lt;sup>3</sup>API. <u>Generation and Management of Residual Materials 1992-1993</u>. February 1995.

Metal Constituent	1992 Coke Product <sup>1</sup> (ppm)	F/K Sludge <sup>2</sup> ppm	New Calculated (ppm)
As	3.5 <sup>3</sup>	4.8	3.5
Cd	0.8 <sup>3</sup>	0.6 <sup>3</sup>	0.8
Cr	1.3	150	5.1
Pb	1.5	50.8	2.8
Ni	39.3	6.1	38.4
Hg	0.06	$0.4^{-4}$	0.07
Volume, MT	39,634,000.00	1,026,000.00	40,660,000.00

#### Table 1. Calculated Increase of Metals in Coke Derived from F and K Sludges

References:

<sup>1</sup>EPA. <u>Listing Background Document for the 1992-1996 Petroleum Refining Listing Determination</u>. SAIC. October 31, 1995. Average concentrations from Table 3.7.6 were used, if available.

<sup>2</sup>EPA. <u>Regulatory Impact Analysis for the Listings of Primary and Secondary Oil/Water/Solids Separation</u> <u>Sludges from the Treatment of Petroleum Refinery Wastewaters</u>. DPRA. September 1990. Table 4.1 using the geometric mean.

<sup>4</sup> ERM Southwest, Inc. <u>Fate of Selected Trace Metals in the Petroleum Refining Industry</u>. API. June 5, 1985. Table 2-1 and Table 3-3.

<sup>5</sup> Jacobs Engineering Co. <u>Assessment of Hazardous Waste Practices in the Petroleum Industry</u>. June 1976. PB-259 0997. Table 39.

# Table 2. Comparison of EPA's Calculated Coke Product Concentrations withLiterature and API Data

Metal Constituent	New Calculated Conc. (ppm)	ERM Literature Range (ppm)			Mobil Coke with Sludge Added (ppm)
As	3.5	<2-108	0.07-4.1	<25	<25
Cd	0.8	< 0.15-2	nd-0.64	<2.5	<2.5
Cr	5.1	<2-7.5	0.02-1.8	<5	11
Pb	2.8	<5-29	<0.01-7.7	<5	<5
Ni	38.4	nr	nr	104	97
Hg	0.06	nr	nr	nd	nd

nr - not reported

nd - non-detect

References:

ERM Southwest, Inc. <u>Fate of Selected Trace Metals in the Petroleum Refining Industry</u>. API. June 5, 1985. Appendices. ERM data developed from a literature search and API data for metals concentration in coke product.

Mobil. "Petroleum Coking Process Operations Briefing Materials from API/EPA Meeting on May 5, 1995." F-95-PRLP-S0084

#### 5. COMPARISON OF PRODUCT COKE TO OFF-SPEC PRODUCT AND FINES FROM THERMAL PROCESSES

The Agency did not evaluate the management practice consisting of placing off-spec product and fines on product piles since they are not within the jurisdiction of the proposed rulemaking. One commenter on this action stated that the proposal did not adequately explain the statutory or regulatory basis for the lack of jurisdiction over coke fines managed on a pile.

The information the Agency collected information via the 1992 RCRA 3007 questionnaire shows that the majority of off-spec product and fines from thermal processes are sold as coke product, are managed as coke product, and have physical and chemical properties that are very similar to typical coke product as reported by various sources. Generation of offspec product and fines from thermal processes are further discribed in the listing background document.<sup>4</sup>

Table 1 shows a comparison of the mean physical properties of the 6 off-spec product and fines samples collected during the 1992 industry study for the listing determination and 4 individual coke product samples from industry and the Electric Power Research Institute. As presented in the data, off-spec coke and fines are very similar in composition to product coke.

Table 2 shows a comparison between the chemical composition for metals of off-specification product and fines from thermal processes and product coke. Comparison of the individual chemical composition for each metal also confirms the similarity between the off-spec product and fines and typical product petroleum coke.

<sup>&</sup>lt;sup>4</sup> EPA. <u>Listing Background Document for the 1992-1996 Petroluem Refining Listing Determination</u>. October 31, 1995. F-95-PRLP-S0003.

Table 1. Comparison of Physical Properties of Off-spec Product/Fines from Thermal      Processes and Product Coke							
Properties	Off-spec Coke/fines1	EPRI <sup>2</sup> "Green" Coke	Unocal <sup>3</sup> Typical Coke	Mobil⁴ Typical Fuel- grade Coke	Mobil⁴ Typical Anode-grade Coke		
рН	7.2	NA	7.7	NA	NA		
Reactive CN, ppm	4.5	NA	<0.25	NA	NA		
Reactive S, ppm	18	NA	<100	NA	NA		
Flash Point, C	125	NA	>100	NA	NA		
Ash, %	NT	0.1	0.27	0.5	0.25		
Total Organic Carbon, vol%	53	82	88.78	NA	NA		
Specific Gravity	1.26	NA	1.8	NA	NA		
BTU Content, BTU/lb	18,200	14,500	15,403	NA	NA		

NT - not tested

NA - not available

Sources:

<sup>1</sup>EPA. <u>Listing Background Document for the 1992-1996 Petroleum Refining Listing Determination</u>. SAIC. October 31, 1995.

<sup>2</sup> Electric Power Research Institute. <u>Petroleum Coke Outlook</u>. July 1984.

<sup>3</sup>Unocal letter - from Mark Smith, Unocal to James Berlow, EPA, regarding analytical information on petroleum coke product, dated October 13, 1993.

<sup>4</sup>Mobil letter - from C.F. Berster, Mobil to Michaelle Wilson, EPA dated February 2, 1993.

Table 2. Comparison of Total Metal Concentrations of Off-spec Product/Fines from Thermal Processes and Product    Coke									
Metals, ppm	Off-Spec Coke/Fines <sup>1</sup>	Unocal Typical Coke <sup>2</sup>	Mobil Typical Fuel-grade Coke <sup>3</sup>	1985 ERM Report <sup>4</sup> - Coke (average)	1985 API Survey <sup>4</sup> - Coke (average)	1976 Jacobs Report <sup>5</sup> - Coke Fines (maximum)			
Arsenic	ND	1.9	2	3.5	2.1	2.0			
Barium	ND	27	NA	NA	NA	NA			
Beryllium	ND	0.34	NA	NA	NA	0.005			
Cadmium	ND	<0.06	NA	0.83	0.37	1.0			
Chromium	1.3	5.9	NA	2.43	0.97	0.02			
Cobalt	ND	2.4	NA	NA	NA	4.0			
Copper	4.7	9.2	NA	NA	NA	4.0			
Iron	275	NA	7	NA	NA	NA			
Lead	1.5	5.6	1	11.4	5.3	13			
Manganese	2.4	NA	NA	NA	NA	NA			
Mercury	0.06	< 0.17	NA	NA	NA	0.04			
Molybdenum	ND	2.3	1	NA	NA	0.1			
Nickel	39.3	6.6	62	NA	NA	580			
Selenium	0.7	< 0.25	1	NA	NA	0.01			
Silicon	ND	NA	2	NA	NA	NA			
Silver	ND	<0.2	<1	NA	NA	0.01			
Vanadium	109.5	22	186	NA	NA	455			

Table 2. Comparison of Total Metal Concentrations of Off-spec Product/Fines from Thermal Processes and Product    Coke							
Zinc	9.5	42	1	NA	NA	14	
from Table 3.7.6 w <sup>2</sup> Unocal letter - fro <sup>3</sup> Mobil letter - fron <sup>4</sup> ERM Southwest, Table 3-3 and in th	kground Document for the 1992 ere used, if available. m Mark Smith, Unocal to James n C.F. Berster, Mobil to Michae Inc. <u>Fate of Selected Trace Me</u>	s Berlow, EPA, regard lle Wilson, EPA date tals in the Petroleum	ding analytical inform d February 2, 1993. <u>Refining Industry</u> . 4	nation on petroleum c API. June 5, 1985. T	oke product, dated O able 3-3. API Surve	ctober 13, 1993.	

#### 6. ACTIVE LIVES OF LANDFILLS USED FOR DISPOSAL OF PETROLEUM REFINING WASTES

EPA proposed hazardous waste listing determinations for 14 residuals generated by the petroleum refining industry on November 20, 1995 (60 *Federal Register* 57747). As documented in the proposed rule, EPA conducted ground water modeling for wastes that were reported to be disposed in nonhazardous landfills in 1992. In public comments on this proposed rule, one commenter argued that the assumed active life for landfills used in the model (20 years) was too short. The purpose of this report is to document the results of new analyses regarding the calculation of active lives for onsite refinery landfills.

#### 6.1 Results

Number of landfills accepting any of nine petroleum wastes<sup>5</sup> in any year: 33 Number of landfills for which sufficient data are available to calculate the active life: 26

10th percentile active life: 10 years 50th percentile active life: 21.5 years 90th percentile active life: 56 years

Attachment 1 presents the raw data extracted from the 1992 RCRA 3007 questionnaire responses, as well as the results of the landfill-by-landfill calculations described in this report.

#### 6.2 Methods to Calculate Active Life

An active life was determined for 26 landfills. In most cases these landfills are still active and therefore estimation methods were required for determining its lifetime. Three different methods were used, identified in Attachment 1 and below as Method 1, Method 2, and Method 3. All three methods rely on data obtained from the RCRA 3007 questionnaire response. Table 1 describes the data used by each method.

<sup>&</sup>lt;sup>5</sup> The nine wastes for which onsite landfill modeling was conducted are as follows: CSO sediment, FCC catalyst and fines, hydrotreating catalyst, hydrorefining catalyst, Claus and SCOT catalyst, unleaded gasoline tank sludge, off-spec product and fines from thermal processes, HF alkylation sludge, and sulfur sludge (*Listing Background Document*, October 1995).

Table 1. Data Requirements In Calculating Active Lives for Landfills								
Parameter	Method 1	Method 2	Method 3	Source				
Date opened	х	X	X	Table VIII-1 of				
Expected closure date	Х			questionnaire				
Total capacity			X					
Remaining capacity as of 1/92			X					
% Remaining capacity used in 1992		Х						

As Table 1 shows, each method uses different data to calculate an end date but each requires knowing the start date. Method 1 was used for 22 landfills, and Methods 2 and 3 were each used for 2 units, to yield estimates for a total of 26 landfills. Active lives could not be calculated for seven landfills, either because the start date was unknown, or because the other required data specified in Table 1 were missing.

### 6.2.1 <u>Method 1</u>

This is the simplest method of calculating active life and was therefore used preferentially, when the data were available. This method simply assumed that active life equaled the projected end date minus the start date. For example, if a refinery stated that its landfill was opened in 1980 and it was expected to be closed in 2002, its calculated active life is 2002 minus 1980=22 years.

Attachment 1 presents the results of these calculations for each landfill. This method was used for estimating the active lives for 22 landfills.

### 6.2.2 <u>Method 2</u>

As shown in Table 1, the respondent was requested to estimate how much of the remaining landfill capacity was used in 1992. This disposal rate was assumed to hold true for the future. For example, if the refinery reported that 25% of the remaining capacity was used in 1992, EPA assumed the landfill would receive equal quantities of waste in 1993, 1994, and 1995 when it would reach capacity. The algorithm used to calculate active life is:

Active life = 1992 - start date + 100 / (% remaining capacity used in 1992).

For the previously mentioned example, if the landfill was opened in 1980, then the calculated active life is: 1992 - 1980 + 100/25 = 16 years.

This method makes the following assumptions: (1) the disposal pattern for a single year (i.e., 1992) predicts future disposal patterns, and (2) a landfill will not close until it reaches capacity. Attachment 1 presents the results of these calculations for each landfill where data are available. This method was used for estimating the active lives for two landfills.

#### Method 3 6.2.3

In Method 3, the history of landfill disposal (not just 1992 activity) was used for calculating the active life. This method relies on the respondent's accurate estimation of two quantities: (1) total capacity, and (2) remaining capacity. In using these data, it is assumed that the ratio of the past life to the future life is proportional to the ratio of capacity used in the past to the capacity to be used in the future. The algorithm is:

Active life = 1992 - starting date + (capacity remaining in 1992) x (1992 - starting date) / (total capacity - capacity remaining in 1992)

For example, if a refinery reported its landfill was opened in 1980, had a total capacity of 50,000 cubic yards,

This method makes the following assumptions: (1) past disposal patterns will predict future disposal patterns, and (2) a landfill will not close until it reaches capacity. This method was used for calculating active lives for

The first of the first As stated previously, Method 1 was used preferentially due to its simplicity and was used to calculate lives using both methods. In two cases (landfills at facilities numbered 56 and 98 in Attachment 1) the active lives calculated using Method 2 appear unreasonably long (110 and 442 years, respectively). This is supported landfills with sufficient data is 74 years. Therefore, Method 3 was used to calculate active lives for these two

From the 26 data points, the median (50th percentile) active life was calculated to be 21.5 years. The

					Attachment	1. All Facilitie	es with Onsite	Landfills Used in S	tatistics			
	Facility Number	Landfill Numbe	Year Opene	Year Closed	Calculated Active Life,	Calculation Method	Capacity, cubic yards	Capacity Remaining in	% Remaining Capacity Used	Calcula	ted Active Life	(years)
		r	d		years			1992, cubic yards	in 1992	Method 1	Method 2	Method 3
	035	1	NA	NA		-						
	039	1	1955	2011	56	1	430000	296000	7.5	56	50.3	118.7
	056	801	1982	NA	40	3	564000	423000	1		110.0	40.0
1	058	20	1991	1992	1	1	3183	3077	40	1	3.5	30.0
	060	4	1976	2050	74	1	800000	6500000	0.7	74	158.9	85.3
	060	9	1983	2050	67	1	10200000	9100000	1.1	67	99.9	83.5
	063	R2	1971	2005	34	1	81100	62800	7	34	35.3	93.1
	076	2 20	1981	1995	14	1	225000	80000	25	14	15.0	17.1
1	088	20	1985 1983	NA 2000	15 17	2 1	57000	12540	13	17	14.7	9.0
	096 098	06	1983	2000 NA	23	3	85000 75325	50000 3631	13 0.25	17	16.7 422.0	21.9 23.1
	102	101	1970	2013	23 30	3 1	23000	22000	0.25	30	209.0	207.0
	102	31	1983	2013 NA	15	2	25000	15000	0.5 10	30	209.0	12.5
١	103	2	1987	2005	22	2	10500000	6440000	7	22	23.3	23.3
	103	3	1986	1995	9	1	38238	18000	44	9	8.3	11.3
	132	13	1989	2004	15	1	85500	70500	10	15	13.0	17.1
	133	45	1991	2030	39	1	840000	838000	2	39	51.0	420.0
	138	9	1974	2013	39	1	7348	3674	0.25	39	418.0	36.0
1	140	3	1977	1991	14	1	53000	0	NA	14		15.0
	140	4	1991	2006	15	1	338000	320000	6	15	17.7	18.8
1	141	501	NA	NA		-						
	141	504	NA	NA		-						
L	148	503	1937	NA		-	NA	NA	NA			
1	148	502	1937	NA		-	NA	NA	NA			
	150	401	1992	NA		-	88400	NA	NA			
	153	240	1978	1999	21	1	12100	3025	2	21	64.0	18.7
	153	210	1985	2012	27	1	400	280	9	27	18.1	23.3
	154	512	1984	1994	10	1	112900	25088	12	10	16.3	10.3
	158	007	1993	2003	10	1	NA	NA	<5	10		
	167	5	1983	2013	30	1	25000	20000	2.5	30	49.0	45.0
	168	1	1969	2000	31	1	240000	NA	100	31	24.0	23.0
	182	511	NA	NA	40	-	00000	0070		40	40.0	40.4
	182	502	1980	1993	13	1	82300	6970	80	13	13.3	13.1

NA: Data not available; Calculation could not be performed.

RESULTS	
Number of landfills with data	26
10th%tile 50th%tile	10 21.5
90th%tile	56

#### 7. CHARACTERIZATION OF ON-SITE LAND TREATMENT UNITS

Central tendency and high end values of onsite land treatment unit areas were calculated for each of seven wastes<sup>6</sup> evaluated. The population of land treatment units was limited to those that were determined to be nonhazardous and that were reported to have managed any of these seven wastes in any year. Only the six land treatment units listed in Table 1 meet these criteria.

Managing Datualaum Lighing Dagiduala	Table 1. Non-hazardous La	and Treatment Units
Managing Petroleum Listing Residuals	Managing Petroleum L	isting Residuals

Texaco, El Dorado Kansas (Reference 057-2). Surface area 7 acres

National Cooperative Refinery Association, McPherson Kansas (Reference 058-2). Surface area 0.6 acres

Navajo Refining Company, Artesia New Mexico (Reference 101-12). Surface area 3 acres

Lyondell-Citgo, Houston Texas (Reference 143-103). Surface area 5 acres

Texaco, Anacortes Washington (Reference 170-5). Surface area of non-hazardous section 15.76 acres

ARCO, Blaine Washington (Reference 171-3). Surface area 7.5 acres

Land treatment units were initially identified from the 1992 RCRA §3007 questionnaire. Most units were reported to have RCRA Part B permits, and are regulated as hazardous waste units. Units were inferred to be nonhazardous from the following information presented in the questionnaire: (1) if they were permitted as a solid waste management unit or had no associated permit (as indicated in Table VIII-1 of the questionnaire), and (2) if no hazardous wastes were managed in the unit (determined from cross referencing Sections VI and VII of the questionnaire). Engineering site visits were conducted at two of these sites (numbers 170-5 and 171-3), providing a second data source to confirm permitting information.

Each of the six facilities were investigated to determine which of these seven wastes were reported to be managed in their units in any year (based on questionnaire data). In every case except sulfuric acid alkylation sludge, at least one facility reported managing each waste. For these six wastes, the areas of the relevant land treatment units were arrayed and 10th, 50th, and 90th percentiles were calculated. For sulfuric acid alkylation sludge, EPA determined that one of the six facilities had a sulfuric acid alkylation unit and assumed that this facility could potentially generate sludge and manage it onsite in its land treatment unit. For this one waste,

<sup>&</sup>lt;sup>6</sup> These seven wastes are crude oil tank sediment, clarified slurry oil (CSO) sediment, unleaded gasoline tank sludge, sulfur complex sludge, hydrofluoric acid alkylation sludge, sulfuric acid alkylation sludge, and off-spec products and fines from thermal processes.

10th, 50th, and 90th percentiles were calculated from this single unit. The results of these analyses are presented in Table 2.

Table 2. Distribution of Areas for Onsite Land Treatment Units							
Waste	10 <sup>th</sup> %ile Area (acres)	50 <sup>th</sup> %ile Area (acres)	90 <sup>th</sup> %ile Area (acres)				
Crude oil storage tank sediment	3	6.3	15.8				
CSO sediment	15.8	15.8	15.8				
Unleaded gasoline tank sediment	0.6	5	15.8				
Sulfur complex sludge	3	7	7.5				
HF alkylation sludge	0.6	3	7				
Sulfuric acid alkylation sludge	15.8	15.8	15.8				
Off-spec product and fines	0.6	7.5	15.8				

#### 8. ANALYSIS OF POTENTIAL IMPACT OF THE HEADWORKS EXEMPTION FOR CSO SEDIMENT

EPA proposed to modify the definition of hazardous waste on November 20, 1995 with respect to certain wastes generated by the petroleum refining industry. One of the three wastes proposed for listing as hazardous waste was sediment from the storage or filtration of clarified slurry oil. During storage tank turnaround, EPA observed water washing of the tank, resulting in a wastewater stream that contains sediment proposed to be listed as K170. Industry also reported through the §3007 survey one case of flushing the entire storage tank sludge volume to wastewater treatment. EPA proposed to cover these discharges under the existing headworks exemption (60 FR 57781), in a manner comparable to the tube bundle cleaning (K050) exemption at §261.3(a)(2)(iv)(C) as follows:

One of the following wastes listed in §261.32, provided that the wastes are discharged to the refinery oil recovery sewer before primary oil/water/solids separation -- heat exchanger bundle cleaning sludge from the petroleum refining industry (EPA Hazardous Waste No. K050), and clarified slurry oil tank sediment and/or inline filter/separation solids from petroleum refining operations (EPA Hazardous Waste No. K170); ...

Public comment was submitted regarding the appropriateness of the proposed headworks exemption. One specific complaint was that EPA did not consider the potential risks associated with the discharge of CSO sediment to on-site wastewater treatment. EPA notes that the proposed rule does, in fact, discuss why waste discharge to wastewater treatment systems was not explicitly modeled (60 FR 57759). As noted in the proposal, exposure pathways associated with this type of disposal are largely covered by regulation under the NPDES or air programs. Further, sludges that separate out in oil/water separators and primary treatment units are already regulated as listed hazardous wastes (K048, K051, F037, F038). Finally, the dilution and treatment that occurs in these wastewater treatment systems also reduce any potential risks. The purpose of this document is to describe the Agency's analysis of the worst case scenario of direct discharge to wastewater treatment of K170, as reported by one facility in the 1992 §3007 survey.

EPA assessed the impact of discharging CSO sediment to a refinery wastewater treatment plant on both the wastewater reaching an aggressive biological treatment (ABT) surface impoundment/equalization pond, and the ABT sludge generated in such a unit. The primary constituents of concern in this residual are PAHs and benzene, as determined by the risk assessment conducted in support of the proposed rule and NODA. Volatilization pathways were not considered due to the low volatility of the PAHs of concern and the low benzene levels which likely would be subject to Benzene NESHAPS controls.

#### 8.1 Description of Management Practice

Of the 172 refineries that responded to §3007 Survey sent by EPA, only one facility reported discharging its CSO sediment to its on-site wastewater treatment plant in 1992 (note that 42 of these facilities reported generating any CSO sediment in that year). The sludge volume was reported to be 250 metric tons. The facility reported that this practice has not been repeated because of the expense associated with increased hazardous wastewater treatment sludge generation. To assess the potential impact on the wastewater treatment system, some estimate of wastewater generated at the facility was needed. The facility reported in the 1983 §3007 survey that it typically treated 1.5 million gallons per day of wastewater. The CSO discharge time period was assumed to be 6 weeks, a typical tank turnaround period.

Attachment 1 to this analysis reproduces a table from the July 1996 Office of Water study entitled, "Preliminary Data Summary for the Petroleum Refining Category". This attachment describes the wastewater treatment units found at 27 refineries surveyed by the Office of Air and Radiation in 1992. Consistent with these data, EPA assumed the wastewater treatment system consists of primary treatment (i.e., API separators and DAFs), secondary treatment (i.e., aggressive biological treatment) and polishing. The secondary and polishing units are assumed to be surface impoundments, while the primary treatment units are tanks. This profile of wastewater treatment was essentially confirmed by an API survey in 1994, as reproduced in Attachment 2.

The disposition of the CSO sediment in the wastewater treatment system is assumed to consist of the following steps:

Primary treatment in the API separator and DAF units. DAF removal of solids is estimated to be 70 to 90 percent without polymer addition, and averaging 97 percent with polymer addition.<sup>7</sup> EPA was unable to identify a reference for solids removal for the API separator. It was assumed that the solids removal rate of the two units would be comparable to the high end effectiveness of the DAF alone.

Aggressive biological treatment (ABT) and clarification in surface impoundments, achieving PAHspecific biodegradation and sedimentation rates predicted in a mass balance analysis conducted by ERM-Southwest.<sup>8</sup>

<sup>&</sup>lt;sup>7</sup>Warren Viessman, Jr. and Mark J. Hammer. "Water Supply and Pollution Control". Fifth Edition. Section 13.8 Description of Dissolved-Air Flotation, "Without polymer addition, solids capture is 70-90%. However removal efficiency increases to a mean of 97%, with a polymer dosage of approximately 10 lb/ton of dry suspended solids."

<sup>&</sup>lt;sup>8</sup>Letter from Robert E. Robinson, P.E., ERM-Southwest, to Kyle B. Isakower, American Petroleum Institute, dated November 13, 1995.

### 8.2 Estimates of Wastewater Concentrations

EPA conducted sampling and analysis of 4 samples of CSO sediment. The analyses included total and TCLP characterization for a broad array of volatile and semi-volatile organics and toxic metals. The risk assessment for the November 20, 1995 proposed rule found risk to be associated with 7 polyaromatic hydrocarbons (PAHs). Table 1 summarizes the analytical results for these contaminants.

The Agency's analytical results show that many of the toxicants of concern in CSO sediment appear to be highly immobile, with none of the PAHs being detected in the TCLP leachate samples. The solubilities of these contaminants are generally well below the TCLP method's quantitation limits.<sup>9</sup> The average benzene leachate concentration was 59 ug/L.

Table 1. CSO Sediment Characterization				
Constituent	Average Total Constituent Concentration (mg/kg)	Solubility (mg/L)		
Benz(a)pyrene	132	0.00194		
Dibenz(a,h)anthracene	37.0	0.00067		
3-Methylchloranthrene	23.8	0.00019		
Benz(a)anthracene	203	0.00128		
7,12- Dimethylbenz(a)anthracene	331	0.050		
Benzo(b)fluoranthene <sup>1</sup>	38.4	0.0043		
Benzo(k)fluoranthene	38.4	0.00094		
Benzene	1.2	1,780		

The average total benzofluoranthene concentration was divided by two to estimate the concentrations of the b and k isomers.

The PAHs are relatively insoluble in water and are not expected in the aqueous phase--this is consistent with the lack of detection in the TCLP tests (down to 10 ppb). These compounds are unlikely to be a threat in groundwater due to their insolubility and their propensity to adsorb to any organic material. However, as a

<sup>&</sup>lt;sup>9</sup> Quantitation limits in the 1995 Listing Background Document were reported to be 100 ug/L. Because the GC/MS instrumentation used for Method 8270B TCLP analysis is sufficiently sensitive to detect on-column concentration of 1 ng, or 10 ug/L in the leachate, it is reasonable to state that the actual TCLP PAH detection limits more closely resemble the method detection limits (MDLs) of 10 ug/L. The MDLs represent the minimum concentration of a substance that can be measured and reported with 99% confidence the analyte concentration is greater than zero. Thus, all PAH detection limits can be reported as <10 ug/L.

worst case, EPA assumed that the PAHs are in solubility equilibrium with the tank wash water. This analysis may overstate tank wash water concentrations due to the presence of oils and oily sludges, to which the PAHs may be preferentially drawn, resulting in wastewater concentrations somewhat below solubility levels. Use of solubility for benzene to estimate wastewater concentration would violate mass balance requirements, i.e., there is not enough benzene present in the waste to reach the solubility limit. Instead, the TCLP results were used to estimate the equilibrium state between benzene in the CSO sediment and the water column.

Table 2 presents the wastewater analysis. The third column shows the solubility limits assumed to be reached in the wash water. The wash water volume<sup>10</sup> is then diluted with other process wastewaters at the headworks as predicted in column four of Table 2. (PAH contributions from other sources are ignored as a means of isolating the impact associated with CSO dumping).

The ABT unit is assumed to provide PAH removal from influent wastewater at levels comparable to those observed by API and documented by ERM (see Attachment 3). Benzene removal is assumed to be comparable to levels observed by API (see Attachment 6). The calculated results are presented in column five of Table 2.

The last two columns of Table 2 present cancer slope factors and calculated risk levels. As a worst case bounding analysis, the risk levels assume migration of the ABT effluent through the subsurface of the ABT and equalization impoundments to a nearby drinking water well with no intervening dilution. The risk levels were calculated from the appropriate cancer-slope factors (CSF) using the following equation and assumptions:

 $Risk = (I \times ED \times EF \times CSF) / (BW \times AT \times 365), where$ 

I = consumption rate, 1.4 L/day x concentration in media (mg/L) ED = exposure duration = 9 years EF = frequency, 6 weeks/year<sup>11</sup>, one tank turnaround and sediment dumping per year BW = 70 kg adult AT = averaging time, 70 years.

The results of this analysis shows that none of the PAHs or benzene are likely to exceed their associated health-based number (HBNs) for ground-water ingestion.

<sup>&</sup>lt;sup>10</sup> EPA's contractor (DPRA) conducted a phone survey of 12 refineries regarding typical tank wash water volumes in January 1997. Of the nine responsive refineries, three facilities reported generation of CSO tank wash waters, with a median of 27,500 gal/tank.

<sup>&</sup>lt;sup>11</sup> 350 days/year is the standard assumption used in the full risk assessment. Six weeks reflects the assumed tank turnaround period.

Constituent	Average Total Constituent Conc. (mg/kg)	Solubility as Wash Water Conc. (ug/L)	Headworks Conc. (ug/L) <sup>1</sup>	ABT Effluent Conc. $(ug/L)^2$	Cancer Slope factor (mg/kg/day) <sup>-1</sup>	Ground- water Risk (ug/L)
Benz(a)pyrene	132	1.94	8.47e-04	1.21e-05	7.30	2.61e-11
Dibenz(a,h)anthracene	37.0	0.67	2.92e-04	1.75e-05	8.10	4.21e-11
3- Methylchloranthrene	23.8	1.9	8.29e-04	1.85e-05	26.00	1.42e-10
Benz(a)anthracene	203	12.8	5.59e-03	1.54e-05	1.10	5.00e-12
7,12-Dimethyl benz(a)anthracene	331	50	2.18e-02	4.87e-04	25.00	3.60e-09
Benzo(b)fluoranthene	38.4	4.3	1.88e-03	1.88e-05	1.20	6.66e-12
Benzo(k)fluoranthene	38.4	0.94	4.10e-04	1.01e-05	0.15	4.46e-13
Benzene	1.2	59	2.58e-02	9.91e-05	0.03	8.50e-13
Total Risk						3.82e-09

#### 8.3 Estimates of Sludge Concentrations

This portion of the analysis attempts to evaluate the potential impact of discharging CSO sediment on wastewater treatment sludges generated downstream of regulated K048, K050, F037 and F038 sludges. In particular, the goal of this section is to compare the concentrations of PAHs in the initial CSO sediment with the PAH concentrations potentially remaining in the sludge removed from an aggressive biological treatment unit. As a worst case analysis, EPA estimated the potential impact the one known discharge of CSO sediment (250 MT) might have on ABT sludge composition.

The analysis for the one known discharge that occurred in 1992, presented in Table 3, consists of the following steps and assumptions:

- The API separator and DAF units remove the majority of the CSO sediment from the wastewater. The effective solids removal rate is assumed to be 90 percent. PAHs are assumed to be evenly distributed on the solids particles, allowing for calculation of PAH-specific loadings to the ABT.
  - Using the average adsorption rates reported by ERM (Table 9, partially reproduced in this analysis as Attachment 4), PAH-specific loadings to the ABT sludge were calculated.
  - The ABT unit generates sludge at an estimated rate of 12,500 gal/day<sup>12</sup>.
  - The average TSS value reported for ABT sludges at 4 refineries, as reported by ERM (Refineries 1, 2, and 3) and API (Refinery 8), was 10,850 mg/L. This was assumed to be the solids content of the wasted sludge in this analysis.
  - The reduction in PAH concentrations from the CSO tank sediment to the ABT sludge was calculated as a ratio.

Table 3 shows that the concentrations in the ABT sludge are reduced from the original CSO sediment concentrations by factors ranging from 800 to 79,000. Based on data from API, ABT sludge removed from the ABT units is often sent to land treatment.<sup>13</sup> It is assumed that the sludge is land farmed without further processing (e.g., dewatering). PAHs levels would be

<sup>&</sup>lt;sup>12</sup>ERM reported flow data for influents and waste sludges for 3 refineries. API reported these data for 4 refineries (#1, 3, 7, and 8). These data are summarized in Attachment 5. The median ratio of influent to sludge rates was 120. This median was divided into the modeled refinery's influent rate of 1.5 million gal/d to estimate the ABT sludge rate or 12,500 gal/d.

<sup>&</sup>lt;sup>13</sup>American Petroleum Institute. Management of Residual Materials: 1994. Petroleum Refining Performance. API Publication Number 336. September 1996. Page 37.

Constituents	Average Total Conc. (mg/kg)	Loading to WWT Headworks (g/day) <sup>1</sup>	Loading to ABT Influent (g/day) <sup>2</sup>	Loading to ABT Sludge (g/day) <sup>3</sup>	Conc. In ABT Sludge (mg/kg) <sup>4</sup>	Ratio of CSO to ABT Sludge Conc.
Benz(a)pyrene	132	786	79	5.55	0.117	1,124
Dibenz(a,h)anthracene	37	220	22	2.15	0.046	812
3- Methylchloranthrene	24	142	14	0.58	0.012	1,946
Benz(a)anthracene	203	1,208	121	0.42	0.009	22,680
7,12-Dimethyl benz(a)anthracene	331	1,970	197	8.04	0.170	1,946
Benzo(b)fluoranthene	38	228	23	0.71	0.015	2,557
Benzo(k)fluoranthene	38	228	23	0.02	0.000	79,380
Benzene	1	7	1	0.003	0.000	20,889
daily PAH loading to Headworks were est water treatment system over 6 week; for e g x <u>250,000 kg x g x week</u> = 6 weeks 1000mg 7 days ing to ABT Influent = 10 percent of head ling to ABT sludge = Influent loading tim	xample, for Ben 786 g/day vorks loading, as	zo(a)pyrene, the ssuming 90% sol	calculation was: lids removal in A		uming the entire	waste was discl

Sludge Concentration = Sludge loading in  $\underline{g} \times \underline{day} \times \underline{gal} \times \underline{1e+03 \text{ mg}}$ day 12,500 gal 3.78 L g

somewhat higher if the wet sludge was dewatered for landfilling, e.g., if dewatered to 20% solids, the PAHs levels might increase 18-fold. However, the *untreated* CSO sediment exhibited minimal risk when sent to a landfill<sup>14</sup>, thus EPA does not believe any remaining constituents from CSO sediment in the dewatered ABT sludge would be of concern. EPA notes that the risk analysis for landfilling CSO sediment showed that benzene (not PAHs) was the constituent of concern.

<sup>&</sup>lt;sup>14</sup>U.S. Environmental Protection Agency, <u>Assessment of Risks from the Management of Petroleum</u> <u>Refining Waste: Background Document</u>, Volume II, draft report, October 1995a.

	Treatment Type	Direct Discharge Refineries (total 20)	Indirect Discharge Refineries (total 7)
In-Plant Controls	Oil-Water Separator	15	4
	Stripper	16	5
	Oxidizer	2	0
	Activated Carbon	1	1
Primary Treatment	API Separator	9	5
	Air Flotation	5	1
	Coagulation	1	0
	Chemical Precipitation	1	0
	Dissolved Air Flotation	10	1
	Equalization	16	4
	Flocculation	1	1
	Grit Chamber	0	1
	Gas Flotation	0	1
	Induced Air Flotation	4	2
	Settling & Skimming	0	1
Secondary	Activated Sludge Unit	11	0
Treatment	Bio Treatment Ponds	6	2
	PAC Bio-treatment	1	0
	RBCs	1	1
	Secondary Clarifier	12	0
	Lagoons	3	0
	Filtration (media & sand)	3	1
	Aeration & Other Biological Treatment	5	0

WASTEWATER TREATMENT COMPONENT	# REFINERIES
PRIMARY OIL/WATER SEPARATION (n=80)	
Oil/Water Separator (e.g., API separator; corrugated plate, etc.)	76
Other	3
SECONDARY OIL/WATER SEPARATION (n=60)	
Gas Flotation (Dissolved or Induced Gas)	52
Filtration	2
Other	6
SECONDARY BIOLOGICAL TREATMENT (n=64)	
Aerated Lagoon	11
Trickling Filter	4
Activated Sludge	52
Rotating Biological Contactor	4
Other	1
Anaerobic Filters or Contactors	0
Other	3
TERTIARY/POLISHING TREATMENT (n=34)	
Filtration	17
Carbon Adsorbers	6
Biological Denitrifaction	3
Metals Removal Processes	3
Other	11

PERCENT PAH REMOVAL FROM WASTEWATER IN ABT UNITS							
Constituent	Refinery 1	Refinery 2	Refinery 3	Refinery 4	Average		
Benz(a)pyrene	99.8	99.3	99.9	95.3	98.6		
Dibenz(a,h)anthracene	99.4	99.3	98.5	78.8	94.0		
3-Methyl chloranthrene	NA	NA	NA	NA	0.0		
Benz(a)anthracene	99.9	99.8	99.8	99.4	99.7		
7,12-Dimethyl benz(a)anthracene	NA	NA	NA	NA	0.0		
Benzo(b)fluoranthene	99.5	99.6	99.5	97.4	99.0		
Benzo(k)fluoranthene	97.4	97.7	NA	NA	97.6		
Average PAH Removal					97.8		

Note: Detection limits appear to be 0.01 ug/L. Percentages represent differences between influent and effluent concentrations at the ABT unit. Reductions are due to biodegradation (primary) and settling (secondary). In cases where effluent concentrations were not detected, ERM used ½ the detection limits to calculate removal rates. Where data were not available to allow calculation of removal rates, EPA used the average PAH removal rate of 97.8 percent.

Source: Letter from Robert E. Robinson, P.E., ERM-Southwest, to Kyle B. Isakower, American Petroleum Institute, dated November 13, 1995. Derived from Table 2.

<b>ATTACHMENT 4</b>	ŀ
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PERCENTAGE OF ABT INFLUENT PAH LOADING DEPOSITED IN ABT SLUDGE				
Constituent	Low Value	High Value	Average	
Benz(a)pyrene	2.83%	11.3%	7.07%	
Dibenz(a,h)anthracene	5.45%	14.10%	9.78%	
3-Methyl chloranthrene	NA	NA		
Benz(a)anthracene	<0.1%	0.6%	0.35%	
7,12-Dimethyl benz(a)anthracene	NA	NA		
Benzo(b)fluoranthene	1.31%	4.9%	3.11%	
Benzo(k)fluoranthene	<0.1%	<0.1%	0.10%	
Average PAH Sludge De	position	•	4.08%	

Note: Where data were not available to allow calculation of removal rates, EPA used the average PAH removal rate of 97.8 percent.

Source: Letter from Robert E. Robinson, P.E., ERM-Southwest, to Kyle B. Isakower, American Petroleum Institute, dated November 13, 1995. Derived from Table 9.

Refinery	Influent flow (gal/day)	Sludge wasting rate (gal/day)	Influent to Sludge Ratio
ERM #1	9,227,520	112,320	82
ERM #2	16,731,360	67,680	247
ERM #3	6,222,240	64,800	96
API #1	13,000,000	108,000	120
API #2	35,000,000	NA	
API #3	3,170,000	11,983	265
API #4	5,200,000	519	10,013
API #5	34,000,000	NA	
API #6	NA	NA	
API #7	6,700,000	129,600	52
API #8	19,400,000	300,000	65
API #9	350,000	NA	
API #10	3,600,000	23	157,200
Median	7,963,760	67,680	120
	ert E. Robinson, P.E., ERM-Southwes	,	
3, 1995.	Aggressive Biological Treatment Sys	tems". American Petrole	ım Institute. September

Sources: Letter from Robert E. Robinson, P.E., ERM-Southwest, to Kyle B. Isakower, American Petroleum Institute, dated November

Wastewater Concentrations of Benzene (ug/L)						
	Minimum	Median	Maximum	Number of Samples	%>DL	
Wastewater Influent	13	650	30,000	32	97	
Biological Influent	<5	<5	12	25	14	
Final Influent	<5	<5	<5	23	0	
Percent Reduction in ABT Unit	80.77%	99.62%	99.96%			

Source: "Performance of Refinery Aggressive Biological Treatment Systems". American Petroleum Institute. September, 1996. Table 20. Calculated percentage reduction assumes ½ detection limit. Median used in analysis.

### 9. ANALYSIS OF POTENTIAL IMPACT OF THE HEADWORKS EXEMPTION FOR K171/K172 WASHWATERS

EPA proposed to modify the definition of hazardous waste on November 20, 1995 with respect to certain wastes generated by the petroleum refining industry. Two of the three wastes proposed for listing as hazardous wastes were spent hydrotreating and hydrorefining catalysts (EPA Hazardous Waste Nos. K171 and K172, respectively). In public comments to this proposal, some refineries stated that water is sometimes used during the removal of spent catalyst from the hydrotreating and hydrorefining process reactor vessels (often referred to as "drill water"). This drill water and another similar stream, wastewater from the drainage pad, are sent to the onsite wastewater treatment system. The commenters state that, if the spent catalysts are listed, then the "derived from" rule (40 CFR §261.3(c)(2)(i)) would result in the hazardous waste designation of these washwaters. The commenters argue that the washwaters should be exempted from hazardous waste regulations if managed in a refinery's onsite wastewater treatment system.

The purpose of this document is to describe the Agency's analysis of the discharge of these washwaters to onsite wastewater treatment systems, as described by several commenters. EPA assessed the following impacts of discharging spent catalyst washwaters to a refinery wastewater treatment plant: (a) impacts on wastewater that might emanate from an aggressive biological treatment (ABT) surface impoundment and equalization ponds, and (b) impacts on ABT sludge from the unit. The primary constituents of concern in these washwaters are volatile organics and metals, based on sampling data provided during the public comment period. This is consistent with EPA's analytical results from record samples of K171/K172. Volatilization pathways were not considered due to the low volatility of the metals of concern, and low concentrations of other volatile organic compounds. Furthermore, any releases of the most toxic volatile chemical, benzene, would likely be subject to regulations under the Clean Air Act (benzene NESHAP).

#### 9.1 Description of Management Practice

Refineries that commented on the proposed rule stated that they use washwater during the removal of spent catalyst from their hydrotreating and hydrorefining reactors. In one case (Chevron), the wash water is reportedly treated further prior to discharge to the wastewater treatment plant. However, for this analysis EPA did not consider such pretreatment. In an effort to determine the population of refineries that use water during catalyst removal, EPA contacted nine corporations with hydrotreating or hydrorefining reactors in January 1997. These nine corporations were selected to achieve a representative mix based on geography, refinery size, and reported catalyst dumping practice (i.e., both facilities reporting water use and not reporting water use were contacted). Seven of nine corporations, providing data for 12 refineries, reported using at least occasional use of water during spent catalyst removal (the other two companies reported that washwater is typically not generated). Water in the form of steam, soda ash solution, or rinsewater is reported. Based on data collected by EPA

(1995b), 92 refineries reported generating spent hydrotreating catalyst and 38 refineries reported generating spent hydrorefining catalyst in 1992. EPA does not have complete data of the frequency of spent catalyst washwater generation from the 1992 RCRA §3007 responses.

EPA has data from several facilities characterizing the quantity of K171/K172 washwater discharged to wastewater treatment. These data are summarized in Table 1. For comparison, Table 1 also lists the typical discharge rate of all refinery wastewaters.

Table 1. Quantities of Spent Catalyst Washwater Generated at Refineries				
Facility/Source	Quantity	Data Source		
Chevron (site not specified)	0.4 MG from a single unit, 2.0 MGY.	А		
Chevron Richmond, CA	0.5 MGY.	В		
	0.03-0.23 MG from a single unit. EPA estimates 0.25 MGY. See footnote C.	С		
Refinery A	0.08 MG from a single unit. EPA estimates 0.16 MGY. See footnote C.	С		
Corporation B (represents 4 refineries)	Together, the four refineries generate a total of 0.64 MG over a period of 3 years. (EPA estimates 0.053 MGY for each of the four refineries)	В		
Refinery C	0.24 MGY.	В		
Refinery D	Total of 0.05 MG over a period of 3 years. (EPA estimates 0.02 MGY).	В		
Average refinery: catalyst dump	0.33 MGY	Calculated from above. See footnote E		
Average refinery: total wastewater discharge	3.3 MGD. EPA estimates 1,200 MGY based on 365 days of discharge.	D		

MG: Million gallons. MGY: Million gallons per year. MGD: Million gallons per day.

A Each spent catalyst dumping generates 0.4 million gallons of washwater. Total annual generation of catalyst waters is 2 million gallons or less. From public comment PRLP-00050 (Chevron).

B Based on follow-up phone calls by EPA to nine corporations in January 1997. Note that four of nine estimated washwater volume.

C Based on data supplied in 1992 RCRA §3007 surveys. Refinery A and Chevron Richmond CA each reported a total of four hydrotreating and hydrorefining reactors. The typical K171 and K172 generation frequency is 2.5 and 3.5 years, respectively (EPA, 1995c). Therefore, EPA estimates that the total annual washwater volume is generated from two units.

D Source: American Petroleum Institute, Management of Residual Materials: 1994, Publication Number 336, September 1996.

E Calculated from the annual generation of the nine unique refineries presented in the table.

approximately 0.33 million gallons per year from the data presented in Table 1, and used this value in subsequent calculations. Consistent with the EPA report titled, "Analysis of Potential Impact of the Headworks Exemption for CSO Sediment," also prepared for the Notice of Data Availability, EPA

assumes that the catalyst washwater will enter a refinery wastewater treatment system consisting of primary treatment (i.e., API separators and DAFs), secondary treatment (i.e., aggressive biological treatment) and polishing. The secondary and polishing units are assumed to be surface impoundments, while the primary treatment units are tanks. The previously mentioned docket report justifies the appropriateness of this treatment train; this treatment train was derived from data presented by API (1996a) and EPA (1996). Pretreatment of the catalyst washwaters (e.g., as Chevron has done) is assumed to be absent.

EPA calculated the average refinery's volume of catalyst washwater to be

### 9.2 Estimate of Spent Catalyst Washwater Concentrations

In public comments to the proposed rule, Chevron Corporation (1996) provided data for its drill and pad drainage water. Characterization data for the drill and pad water are summarized in Table 2. This is the only data available to EPA to characterize these waters (no useful characterization data were found from RCRA 3007 responses for any refinery). For comparison, total and TCLP analyses of these constituents in K171 and K172 are also presented. These were calculated from all data points presented in EPA (1995b). A total of nine data points were available for all constituents except nickel. Due to CBI constraints, EPA (1995b) only presented nickel data from eight samples.

The risk assessment for the November 20, 1995 proposed rule found risks of the spent catalysts to be associated with landfilling. There were two constituents of concern (benzene and arsenic). Note, however, that levels of these two constituents in catalyst washwaters are much lower than the concentrations in the spent catalyst record samples. As a worst case analysis, EPA used the compositions from the drill water because they are higher than corresponding concentrations in the pad runoff for all constituents (except for nickel--however, the values for nickel are within 20 percent, thus use of either concentration will give similar results).

	Con	istituent	Co mg
			-
	Ben	zene	
	Ethy ben	yl zene	
	Tol	uene	
L.	Xyl	enes <sup>B</sup>	
z			
Ξ	Ars	enic	
Σ	Nic	kel	
n	Var	adium	
DOQ	are fro A Onl	e: drill and p om EPA (199 y detected c evron data is	95b). onstit
VE	9.3	Potenti	al In
IH	as fo	The ass llows:	umpt
$\approx$	•	As a wo	
		inorgan convers	
		washwa	ater c
A		dissolve Most of	
Ш		As a bo and una	undi

Tε	Table 2. Composition of Spent Catalysts and Their Washwaters							
Constituent <sup>A</sup>	Drill Water Concentration, mg/l	Pad Water Concentration, mg/l	Average TCLP Level in K171/ K172, mg/l	Average Total Level in K171/ K172, mg/kg				
		Organi	cs					
Benzene	0.0093	< 0.005	5.8	92				
Ethyl benzene	0.0074	<0.005	0.5	51				
Toluene	0.011	< 0.005	5.6	190				
Xylenes <sup>B</sup>	0.14	0.007	1.9	76				
		Inorgan	ics					
Arsenic	0.018	0.0072	4	430				
Nickel	280	334	110	11,000				
Vanadium	7.7	4.6	1.3	4,100				

ashwater data are from Chevron (PRLP-00050). K171/K172 waste characterization data

tuents are listed.

otal xylenes; K171/K172 total and TCLP data are for m- and p-xylenes.

# npact on Wastewater Concentrations

tions used to assess this pathway, and the bases for these assumptions, are

case for wastewater loadings, EPA assumed that measured values of onstituents represent dissolved concentrations. Follow-up telephone ns by EPA in January 1997 with several refineries indicate that the contains some catalyst fines, therefore, assuming these metals are in the ate is likely to overestimate the dissolved concentrations in wastewater. solids (likely at least 90 percent) are removed during primary treatment. ng case analysis, the organic constituents are assumed to be water soluble ted by primary treatment.

- Catalyst washwaters are diluted with other refinery wastewaters in the wastewater treatment system. The dilution factor is  $3x10^{-4}$  over the course of a year. EPA assumes, from Table 2, the average annual quantity of spent catalyst washwater to be 0.33 million gallons and the average annual quantity of refinery wastewater to be 1,200 million gallons. This provides the given dilution factor. Even though the washwaters are discharged to wastewater treatment over a short period of time, EPA made a steady-state assumption that a constant quantity of contaminant reaches a receptor over the course of a year, every year.
- As a worst case, EPA assessed potential risks presented by the direct ingestion of these diluted wastewaters, without any further dilution or attenuation in the subsurface.

Table 3 shows the results of using the above assumptions to estimate potential risks presented by diluted washwaters.

	Table 3. Calculated Concentrations ofWastewaters Impacted by Spent Catalyst Drill Water									
Constituent	Concentration in Drill Water, mg/l	Dilution Factor <sup>A</sup>	Impoundment Concentration, mg/L <sup>A</sup>	Carcinogeni c Risk <sup>B</sup>	Hazard Quotient <sup>C</sup>					
		Orga	anics							
Benzene	0.0093	3x10 <sup>-4</sup>	3x10 <sup>-6</sup>	$2x10^{-10}$	NA					
Ethyl benzene	0.0074	3x10 <sup>-4</sup>	2x10 <sup>-6</sup>	NA	< 0.0001					
Toluene	0.011	3x10 <sup>-4</sup>	3x10 <sup>-6</sup>	NA	< 0.0001					
Xylenes	0.14	3x10 <sup>-4</sup>	4x10 <sup>-5</sup>	NA	< 0.0001					
		Inorg	anics							
Arsenic	0.018	3x10 <sup>-4</sup>	5x10 <sup>-6</sup>	2x10 <sup>-8</sup>	0.0003					
Nickel	280	3x10 <sup>-4</sup>	8x10 <sup>-2</sup>	NA	0.08					
Vanadium	7.7	3x10 <sup>-4</sup>	2x10 <sup>-3</sup>	NA	0.006					

NA: CSF or RfD is unavailable for conducting calculations.

A Concentrations of inorganic and organic constituents were calculated by using a dilution factor of 0.0003, which is the annual K171/K172 discharged (0.33 MGY) divided by the annual quantity of wastewaters generated (1200 MGY).

B For carcinogens, risk={IxEDxEFxCSF}/{BWxATx365}, where:

I=consumption rate, 1.4 L/day x concentration in media (mg/L)

ED=exposure duration=9 years

EF=Frequency=365 days/year BW=70 kg adult AT=averaging time, 70 years CSF=cancer slope factor, (mg/kg/day)<sup>-1</sup> = 0.029 for benzene, 1.5 for arsenic (Source: EPA, 1995a)

C For noncarcinogens, hazard quotient=I/{BWxRfD}, where:

I=consumption rate, 1.4 L/day x concentration in media (mg/L) BW=70 kg adult RfD= Reference Dose, mg/kg/day = 0.1 for ethyl benzene, 0.2 for toluene, 2.0 for xylenes, 0.0003 for arsenic, 0.02 for nickel, 0.007 for vanadium (Source: EPA, 1995a)

Table 3 shows that none of the constituents exceed a risk of 10<sup>-6</sup> for carcinogens or exceed a hazard quotient of 1 for noncarcinogens. Therefore, EPA concludes that the discharge of spent catalyst washwaters to wastewater treatment presents a negligible risk.

#### 9.4 Potential Impact on ABT Sludge

This portion of the analysis attempts to evaluate the potential impact of discharging K171/K172 washwater on wastewater treatment sludges generated downstream of regulated K048, K050, F037 and F038 sludges. In particular, the goal of this section is to compare the concentrations of metals and organics in the initial K171/K172 wastes with the corresponding concentrations potentially remaining in the sludge removed from an aggressive biological treatment unit. Assumptions made in this portion of the analysis are as follows:

- The API separator and DAF units remove the majority of the CSO sediment from the wastewater. The effective solids removal rate is assumed to be 90 percent. It is assumed that inorganic constituents are present as solids. As a bounding case analysis, the organic constituents are assumed to be unaffected by primary treatment. The basis for 90 percent removal is as follows. DAF removal of solids is estimated to be between 70 and 90 percent without polymer addition, and averaging 97 percent with polymer addition (Viessman, undated). EPA was unable to identify a reference for solids removal for the API separator. It was assumed that the solids removal rate of the two units would be comparable to the high end effectiveness of the DAF alone. Therefore, it is assumed that the concentration of inorganics in the DAF effluent is 10-fold lower than the concentration influent to the API separator (i.e., the headworks).
  - The ABT unit generates sludge at an estimated rate of 39,000 MT year. See Attachment 1.
- The average TSS value reported for ABT sludges at 4 refineries, as reported by ERM (Refineries 1, 2, and 3) and API (Refinery 8), was 10,850 mg/L. This was assumed to be the solids content of the wasted sludge in this analysis.

The ABT unit removes 78 percent of the inorganics and 100 percent of the organics as ABT sludge. The calculations for solids removal are shown in Attachment 1, using data from API (1996b). This assumption is valid when the inorganics are assumed to be present as solids, which is the case here. As a bounding case, the organics are assumed to be completely transferred to ABT sludge with no biodegradation.

Table 4 shows the calculations of ABT sludge levels and compares them to average levels in the original wastes.

Table 4.	Table 4. Calculated Concentrations of Ground Water Impacted by ABT Sludge									
Constituen t	Concen- tration in Drill Water, mg/l <sup>A</sup>	ABT Sludge Loading, kg/yr <sup>B</sup>	ABT Sludge Concen- tration, mg/kg <sup>c</sup>	Average K171/K172 Concentration, mg/kg <sup>A</sup>	Ratio of K171/172 to ABT sludge Concentration					
			Organics							
Benzene	0.0093	0.012	3.1x10 <sup>-4</sup>	92	3x10 <sup>5</sup>					
Ethyl benzene	0.0074	0.0093	2.4x10 <sup>-4</sup>	51	2x10 <sup>5</sup>					
Toluene	0.011	0.014	3.6x10 <sup>-4</sup>	190	5x10 <sup>5</sup>					
Xylenes	0.14	0.18	4.6x10 <sup>-3</sup>	76	$2x10^{4}$					
			Inorganics							
Arsenic	0.018	0.0018	4.6x10 <sup>-5</sup>	430	9x10 <sup>6</sup>					
Nickel	280	27	0.69	11,100	$2x10^{4}$					
Vanadium	7.7	0.75	0.019	4,100	2x10 <sup>5</sup>					

A From Table 2.

B Sludge loadings calculated by assuming 0.33 million gallons/year of drill water, with composition shown in table. All of the organics are assumed to be transferred to the sludge. Ninety percent of the inorganics are assumed to be captured in primary treatment, while 78 percent of the remaining solids are assumed to settle as ABT sludge.

C Total sludge concentrations are assumed to be equal to the total mass of constituent in the sludge, divided by the quantity of generated sludge (i.e., 39,000 MT/yr).

Table 4 shows that the concentrations in the ABT sludge are reduced from the original K171/K172 waste concentrations by factors ranging from 20 thousand to 9 million. Levels would be somewhat higher if the wet sludge was dewatered for landfilling, e.g., if dewatered

to 20 percent solids, the levels might increase 18-fold. EPA concludes that all of the constituents are diluted to levels far below those present in the original waste, and that none of the constituents found in spent catalyst washwater and transferred to ABT sludge are expected to present a significant risk.

## **Bibliography**

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U.S. Environmental Protection Agency, Assessment of Risks from the Management of Petroleum Refining Wastes: Background Document, volume II, draft report, October 1995a.

U.S. Environmental Protection Agency, *Listing Background Document for the 1992-1996 Petroleum Refining Listing Determination*, October 1995b.

U.S. Environmental Protection Agency, *Cost and Economic Impact Analysis of Listing Hazardous Wastes from the Petroleum Refining Industry*, September 21, 1995c.

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#### ATTACHMENT 1. MISCELLANEOUS CALCULATIONS

#### Solids Removal in ABT Systems

The average removal rate of solids in ABT systems is 78 percent. This is based on the average of the six positive values presented in Table A-1. The negative removal rate calculated for Plant No. 4 was not included based on the plant's operating conditions as described in the API report.

Table A-1.	Solids Removal Data	from API S	tudy of AB'	Г Systems
Plant #	TSS ABT Influent (mg/L)	TSS ABT Effluent (mg/L)	TSS Outfall (mg/L)	Removal Rate
1	86	20	2	97.67%
2	93	110	44	52.69%
3	NA	NA	8	NA
4	6	109	19	-216.67%
5	82	27	10	87.80%
6	NA	NA	NA	NA
7	43	8	3	93.02%
8	102	2850 <sup>1</sup>	46	54.90%
9	40	105	7	82.50%
10	NA	NA	NA	NA

1. Before clarification and removal of biological solids.

Source: "Performance of Refinery Aggressive Biological Treatment Systems". American Petroleum Institute. September, 1996.

#### **ABT Sludge Volume**

ERM reported flow data for influents and waste sludges for 3 refineries. API reported these data for six additional refineries. These data are summarized in Table A-2. The median ratio of influent to sludge rates was 120. This value, 120 gallons influent/1 gallon sludge, was used in conjunction with the average wastewater flow of 3.3 million gallons/day listed in Table 1 to estimate an ABT sludge generation rate of 28,000 gal/d. This corresponds to an

annual generation rate of 39,000 MT/year of wet sludge. The average TSS value reported for ABT sludges at four refineries, as reported by ERM (Refineries 1, 2, and 3) and API (Refinery 8) is 10,850 mg/L, or approximately 1.1 percent solids. This is assumed to be the solids content of the ABT sludges described in Table A-2.

Table A-2. ABT Sludge Generation							
Refinery	Influent flow (gal/day)	Sludge wasting rate (gal/day)	Influent to Sludge Ratio				
ERM #1	9,227,520	112,320	82				
ERM #2	16,731,360	67,680	247				
ERM #3	6,222,240	64,800	96				
API #1	13,000,000	108,000	120				
API #3	3,170,000	11,983	265				
API #4	5,200,000	519	10,013				
API #7	6,700,000	129,600	52				
API #8	19,400,000	300,000	65				
API #10	3,600,000	23	157,200				
Median	7,963,760	67,680	120				

Sources: Letter from Robert E. Robinson, P.E., ERM-Southwest, to Kyle B. Isakower, American Petroleum Institute, dated November 13, 1995.

"Performance of Refinery Aggressive Biological Treatment Systems". American Petroleum Institute. September, 1996.

## **10. TELEPHONE CONTACTS WITH REFINERY PERSONNEL**

Date: December 4, 1996

From: Kristy Allman, SAIC

To: Mike Donnelly, ARCO Products Blaine Washington, 360-371-1340

Purpose: ARCO's RCRA §3007 questionnaire response did not include an estimate of the quantity of coke fines placed in their land treatment unit in 1992.

Discussion: Mike Donnelly estimated the quantity to be approximately 1 cubic yard per year, or less than 1 MT. It is placed on their permitted non-hazardous waste land treatment unit. Mike said these fines are contaminated with silica which doesn't allow them to be processed to the calciner with the rest of the coke fines.

Relevance to NODA: This quantity is used in the co-disposal scenario for the non-ground water risk assessment.

Date: Approximately Summer 1995

From: Gwen de Poix (presently Gwen DiPietro), Kristy Allman, SAIC

To: Stephen Cohrs, Farmland Industries, Coffeyville Kansas, 316-251-4000

Purpose: Verify costs of certain management practices

Discussion: Mr. Cohrs verified that RIN 42, CSO sludge, was managed at the wastewater treatment plant in the API separator. The reported cost included disposing of the K051 sludge. It was very expensive and the refinery has no plans to do this again.

Relevance to NODA: This information was used in conducting further analysis for the proposed headworks exemption. [Additional information from this phone conversation is recorded in the facility's file. However, it was not used in conducting any additional analyses for the NODA.]

### **APPENDIX A**

#### **Oil and Grease Content of Landfilled Refining Wastes**

EPA reported the 1992 management practices of 29 petroleum refining residuals in two documents: *Listing Background Document for the 1992-1996 Petroleum Refining Listing Determination*, October 31, 1995 and *Study of Selected Petroleum Refining Residuals*, August 1996. The management method for many residuals included landfilling in an onsite or offsite nonhazardous waste disposal unit. EPA also presented oil and grease contents of these 29 residuals in these two documents. This analysis uses the available data to determine the oil and grease content of residuals that were actually landfilled. The source of all information in this analysis is the completed surveys and resulting database from the 1992 petroleum refining questionnaire, discussed in detail in the two documents mentioned above.

#### **Offsite Landfill Disposal**

Based on the two documents cited above, the following 23 residuals (of the 29 residuals) were disposed in offsite Subtitle D landfills in 1992:

- Desalting sludge Residual oil tank sludge Treating clay from clay filtering Treating clay from isomerization/extraction Hydrocracking catalyst Process sludge from residual upgrading Off-spec sulfur Treating clay from lube oil processing Spent treating solution from sulfur removal processes Catalyst from polymerization Treating clay from alkylation CSO sediment Crude oil tank sediment
- Catalyst from hydrotreating Catalyst from hydrorefining Sulfur complex sludge Off-spec product and fines from thermal processes Reforming catalyst Unleaded gasoline tank sludge FCC catalyst and fines Catalyst from sulfur removal (all processes) HF alkylation sludge Sulfuric acid alkylation sludge

The oil and grease content, as reported by the survey respondents, was extracted from the database for every residual disposed in this manner in 1992. Unfortunately, this parameter was not always reported. Of the approximately 621 residuals reported to be disposed in offsite landfills in 1992, 120 reported oil and grease content.

The median reported level of oil and grease content from these 120 residuals was approximately 1 percent. EPA more closely investigated all residuals reporting an oil and

grease level greater than 10 percent (a value 10 times the median). There were 8 such residuals, as follows:

Crude oil tank sediment, 80% oil and grease, 632 MT Residual oil tank sludge, 99% oil and grease, 50 MT Residual oil tank sludge, 28% oil and grease, quantity CBI CSO sediment, 20% oil and grease, 309 MT Desalting sludge, 12.5% oil and grease, 0.4 MT Desalting sludge, 20% oil and grease, 0.2 MT Treating clay from clay filtering, 18% oil and grease, 100 MT Treating clay from clay filtering, 13% oil and grease, 2.2 MT

In verifying these values by reviewing the facilities' RCRA 3007 survey responses, EPA found that the two highest levels, for the crude oil tank sediment (80%) and the residual oil tank sludge (99%), appear to represent oil levels prior to deoiling based on the way the facility presented information in its completed survey. Oil content following deoiling was not provided, however.

Two other residuals were accompanied by lab results. The CSO sediment (20% oil and grease) was described as having no free liquids as determined by the paint filter test. One of the desalting sludges (20% oil and grease) was described as having 93 percent solids and 7 percent liquids; however, the liquid was not identified as either aqueous or organic. In any case, EPA concluded from its record analyses that all samples analyzed for oil and grease and by the TCLP did not contain free or filterable liquid (see Appendix B: "Comparison of the Toxicity Characteristic Leaching Procedure (TCLP) with the Modified Oily Waste Extraction Procedure (OWEP)"). EPA found no information regarding the other four samples.

In conclusion, EPA found that approximately 621 residuals were disposed in offsite nonhazardous landfills in 1992 and that oil and grease content was reported for 120 of them. Six of these 120 residuals had oil and grease contents greater than 10 percent and only one of the six corresponds to a listing residual (CSO sediment); the remaining five residuals were study residuals.

### **Onsite Landfill Disposal**

EPA also assessed the reported oil and grease content of wastes disposed in onsite Subtitle D landfills in 1992 in a similar way. Of the 149 residuals reported to be disposed in onsite landfills in 1992, oil and grease data were reported for 57 streams. Oil and grease data for the remaining streams were not reported. The highest reported oil and grease concentration was 10 percent, with the median value less than 1 percent.

#### **APPENDIX B**

## COMPARISON OF THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) WITH THE MODIFIED OILY WASTE EXTRACTION PROCEDURE (OWEP)

#### 1. Introduction

Commenters suggested that EPA should use Oily Waste Extraction Procedure (OWEP) to characterize the refinery residuals with an oil and grease content greater than 1 percent. The OWEP was designed for the Delisting Program to quantitate the mobile metals concentration in oily waste. Although the Agency did not observe any problems such as unusually low leachability with the existing TCLP data, the Agency used a modified OWEP on those samples believed to contain oil and grease greater than 1 percent in order to compare the results with the data obtained using the TCLP.

#### 2. Sample Selection

The following eight petroleum refining residual categories with an oil and grease concentration greater than one percent as reported in the Background Document, were identified for additional laboratory analyses to better estimate the metals groundwater mobility from oily wastes.

- Crude tank sludge
- CSO sludge
- HF alkylation sludge
- Sulfur complex sludge
- Hydrotreating catalyst
- Hydrorefining catalyst
- Off-Spec product and fines from thermal process
- Unleaded tank sludge

A total of 38 samples of the eight residual categories were originally collected from October 19, 1993, through October 20, 1994. The samples have remained in storage under ambient temperature conditions at EPA's contract laboratory. The laboratory identified 27 samples for which sufficient volume remained (minimum 100 grams) to perform the waste extraction procedure outlined in SW 846, Method 1330A. At least one sample from each category was available for analysis.

## 3. **OWEP Analytical Protocol**

The Oily Waste Extraction Procedure (OWEP) Method 1330A was modified using TCLP Method 1311 instead of EP Toxicity Method 1310A. The TCLP technique was utilized

since it is the most current methodology for assessing constituent mobility in leachate. There were no other deviations from the procedures as outlined in OWEP Method 1330A.

As with the original TCLP analyses, the samples available for OWEP analyses contain no free or filterable liquid. Prior to leaching, the samples were extracted using tetrahydrofuran and toluene to remove the organic phase. The solvent extracts were concentrated to near dryness, diluted with water, and acid digested according to Method 3010A. The remaining solvent extracted solids were leached according to Method 1311, and the resulting leachate acid digested according to Method 3010A.

The solvent and TCLP digestates were analyzed for all RCRA metals (arsenic, barium, cadmium, chromium, lead, selenium, and silver) except mercury. The analysis of mercury was not possible since the solvent extracts were concentrated to near dryness and consumed in the digestion for ICP metals. Analytical procedures included ICP-MS Method 6020 for all leachate metals and arsenic, lead, and selenium for the solvent extracts. All other analyses were performed using ICP-trace Method 6010A. The analytical methods used in the new analyses resulted in somewhat lower quantification levels.

## 4. **OWEP Results**

The solvent and leachate concentrations for each metal were mathematically combined according to the partial volume present with each phase in order to obtain the OWEP result. The OWEP values were compared directly to the original TCLP data and are presented Tables 1 through 7. Each table includes five columns of data, percent oil and grease, OWEP, solvent, leachate, and the original TCLP concentration.

Overall the OWEP results are consistent with the original TCLP data; only 14 out of 189 OWEP values were greater than the original TCLP concentrations. All of these 14 values were within one order of magnitude of the TCLP concentration. Additionally, 8 of the 14 OWEP values were associated with residuals that contained less than one percent oil and grease as determined by Method 9071A. Any differences are more likely due to sample composition variability rather than the leaching technique. Based on the consistency of the OWEP and TCLP data, there is no evidence that the oil content present in the petroleum refining listing residuals significantly affected the leachable levels of the metals in the original TCLP analyses.

		% Oil &		Arsenio	c mg/L	
Residual	Sample ID	% Oll & Grease	OWEP	Solvent	Leachate	TCLP
Crude Sludge	R8C-CS-01 R4B-CS-01 R10-CS-01 R22-CS-01 R19-CS-01	25 15 41 4.9 14	0.03 <0.02 <0.02 <0.02 <0.02	0.014 0.007 0.007 0.029 0.004	0.03 <0.02 <0.02 <0.02 <0.02	<0.10 <0.10 <0.10 <0.10 <0.10
CSO Sludge	R9-SO-01 R1B-SO-01 R20-SO-01	70 16 24	0.11 <0.02 0.04	0.011 <0.002 <0.002	0.21 <0.02 0.06	<0.10 <0.10 <0.10
Unleaded Sludge	R8A-US-01 R16-US-01	0.09 <0.09	0.09 0.02	0.147 0.011	0.07 0.02	<0.10 <0.10
HF Alkylation Sludge	R8B-HS-01 R9-HS-01 R15-HS-01 R7C-HS-01	0.3 31 6.8 0.08	<0.02 <0.02 <0.02 <0.02	0.003 0.003 <0.002 0.003	<0.02 <0.02 <0.02 <0.02	<0.10 <0.10 <0.10 <0.10
Sulfur Complex Sludge	R1-ME-01 R14-ME-01 R18-ME-01	1.0 0.2 <0.05	<0.02 <0.02 0.02	<0.002 <0.002 0.006	<0.02 <0.02 0.03	<0.10 <0.10 <0.10
Hydrotreating Catalyst	R18-TC-01 R1-TC-01 R11-TC-01 R3B-TC-01 R22-TC-01	<0.05 <0.05 <0.05 <0.05 <0.2	0.24 0.37 0.04 0.02 6.69	<0.002 0.003 <0.002 0.003 <0.002	0.31 0.49 0.05 0.03 8.70	<0.10 <0.10 <0.10 <0.10 1.5
Hydrorefining Catalyst	R21-RC-01	0.08	0.04	<0.002	0.05	6.9
Off-Spec Product and Fines from Thermal Processes	R12-TP-01 R11-TP-01 R14-TP-01 R3B-TP-01	8.4 0.6 0.03 <0.05	<0.02 <0.02 <0.02 <0.02	<0.002 <0.002 <0.002 <0.002	<0.02 <0.02 <0.02 <0.02	<0.10 <0.10 <0.10 <0.10

# Table 1 - OWEP / Original TCLP Data Comparison

				Barium mg/L			
Residual	Sample ID	% Oil & Grease	OWEP	Solvent	Leachate	TCLP	
Crude Sludge	R8C-CS-01 R4B-CS-01 R10-CS-01 R22-CS-01 R19-CS-01	25 15 41 4.9 14	3.33 0.22 0.88 0.38 0.64	0.036 0.016 0.462 0.024 0.154	4.85 0.30 1.13 0.51 0.80	2.4 <2.0 <2.0 <2.0 2.7	
CSO Sludge	R9-SO-01 R1B-SO-01 R20-SO-01	70 16 24	0.33 0.70 0.39	0.045 0.006 0.010	0.64 0.99 0.62	<2.0 <2.0 <2.0	
Unleaded Sludge	R8A-US-01 R16-US-01	0.09 <0.09	0.09 0.36	0.013 0.066	0.13 0.45	<2.0 <2.0	
HF Alkylation Sludge	R8B-HS-01 R9-HS-01 R15-HS-01 R7C-HS-01	0.3 31 6.8 0.08	2.67 0.29 0.08 0.44	0.009 0.010 0.007 0.010	4.34 0.59 0.13 0.63	<2.0 <2.0 <2.0 <2.0	
Sulfur Complex Sludge	R1-ME-01 R14-ME-01 R18-ME-01	1.0 0.2 <0.05	0.11 0.27 0.12	<0.005 0.006 <0.005	0.15 0.42 0.17	<2.0 <2.0 <2.0	
Hydrotreating Catalyst	R18-TC-01 R1-TC-01 R11-TC-01 R3B-TC-01 R22-TC-01	<0.05 <0.05 <0.05 <0.05 <0.2	0.11 0.15 0.15 0.10 0.13	<0.005 <0.005 <0.005 <0.005 <0.005	0.14 0.20 0.20 0.13 0.17	<2.0 <2.0 <2.0 <2.0 <2.0	
Hydrorefining Catalyst	R21-RC-01	0.08	0.13	0.013	0.17	<2.0	
Off-Spec Product and Fines from Thermal Processes	R12-TP-01 R11-TP-01 R14-TP-01 R3B-TP-01	8.4 0.6 0.03 <0.05	0.64 0.60 0.53 0.45	0.011 <0.005 0.005 <0.005	0.95 0.81 0.85 0.72	<2.0 <2.0 <2.0 <2.0	

# Table 2 - OWEP / Original TCLP Data Comparison

		% Oil &		Cadmium mg/L			
Residual	Sample ID	Grease	OWEP	Solvent	Leachate	TCLP	
Crude Sludge	R8C-CS-01 R4B-CS-01 R10-CS-01 R22-CS-01 R19-CS-01	25 15 41 4.9 14	<0.01 <0.01 <0.01 <0.01 <0.01	<0.005 <0.005 <0.005 <0.005 <0.005	<0.01 <0.01 <0.01 <0.01 <0.01	<0.05 <0.05 <0.05 <0.05 <0.05	
CSO Sludge	R9-SO-01 R1B-SO-01 R20-SO-01	70 16 24	<0.01 <0.01 <0.01	<0.005 <0.005 <0.005	<0.01 <0.01 <0.01	<0.05 <0.05 <0.05	
Unleaded Sludge	R8A-US-01 R16-US-01	0.09 <0.09	<0.01 <0.01	<0.005 <0.005	<0.01 <0.01	<0.05 <0.05	
HF Alkylation Sludge	R8B-HS-01 R9-HS-01 R15-HS-01 R7C-HS-01	0.3 31 6.8 0.08	<0.01 <0.01 <0.01 <0.01	<0.005 <0.005 <0.005 <0.005	<0.01 <0.01 <0.01 <0.01	<0.05 <0.05 <0.05 <0.05	
Sulfur Complex Sludge	R1-ME-01 R14-ME-01 R18-ME-01	1.0 0.2 <0.05	<0.01 <0.01 <0.01	<0.005 <0.005 <0.005	<0.01 <0.01 <0.01	<0.05 <0.05 <0.05	
Hydrotreating Catalyst	R18-TC-01 R1-TC-01 R11-TC-01 R3B-TC-01 R22-TC-01	<0.05 <0.05 <0.05 <0.05 <0.2	0.01 <0.01 <0.01 0.02 0.07	<0.005 <0.005 <0.005 <0.005 <0.005	0.02 <0.01 <0.01 0.03 0.09	<0.05 0.08 <0.05 <0.05 <0.05	
Hydrorefining Catalyst	R21-RC-01	0.08	<0.01	<0.005	<0.01	<0.05	
Off-Spec Product and Fines from Thermal Processes	R12-TP-01 R11-TP-01 R14-TP-01 R3B-TP-01	8.4 0.6 0.03 <0.05	<0.01 <0.01 <0.01 <0.01	<0.005 <0.005 <0.005 <0.005	<0.01 <0.01 <0.01 <0.01	<0.05 <0.05 <0.05 <0.05	

# Table 3 - OWEP / Original TCLP Data Comparison

				Chromium mg/L			
Residual	Sample ID	% Oil & Grease	OWEP	Solvent	Leachate	TCLP	
Crude Sludge	R8C-CS-01 R4B-CS-01 R10-CS-01 R22-CS-01 R19-CS-01	25 15 41 4.9 14	0.89 0.02 0.01 0.01 0.06	0.184 <0.006 <0.006 0.010 0.072	1.21 0.03 0.02 0.01 0.05	<0.10 <0.10 <0.10 <0.10 <0.10	
CSO Sludge	R9-SO-01 R1B-SO-01 R20-SO-01	70 16 24	0.01 0.04 0.03	0.007 <0.006 <0.006	0.02 0.05 0.04	<0.10 <0.10 <0.10	
Unleaded Sludge	R8A-US-01 R16-US-01	0.09 <0.09	0.18 0.04	0.022 0.009	0.24 0.05	<0.10 <0.10	
HF Alkylation Sludge	R8B-HS-01 R9-HS-01 R15-HS-01 R7C-HS-01	0.3 31 6.8 0.08	0.01 0.02 0.06 0.01	<0.006 <0.006 <0.006 <0.006	0.02 0.04 0.11 0.02	<0.10 <0.10 <0.10 <0.10	
Sulfur Complex Sludge	R1-ME-01 R14-ME-01 R18-ME-01	1.0 0.2 <0.05	0.02 0.05 0.03	<0.006 0.008 <0.006	0.03 0.08 0.04	<0.10 <0.10 0.11	
Hydrotreating Catalyst	R18-TC-01 R1-TC-01 R11-TC-01 R3B-TC-01 R22-TC-01	<0.05 <0.05 <0.05 <0.05 <0.2	0.02 0.04 0.02 0.02 0.04	<0.006 <0.006 <0.006 <0.006 <0.006	0.03 0.05 0.03 0.03 0.05	<0.10 <0.10 <0.10 <0.10 <0.10	
Hydrorefining Catalyst	R21-RC-01	0.08	0.02	0.035	0.02	<0.10	
Off-Spec Product and Fines from Thermal Processes	R12-TP-01 R11-TP-01 R14-TP-01 R3B-TP-01	8.4 0.6 0.03 <0.05	0.01 0.01 0.01 0.03	<0.006 <0.006 <0.006 <0.006	0.02 0.02 0.02 0.05	<0.10 <0.10 <0.10 <0.10	

# Table 4 - OWEP / Original TCLP Data Comparison

		% Oil &		Lead mg/L			
Residual	Sample ID	% Oll & Grease	OWEP	Solvent	Leachate	TCLP	
Crude Sludge	R8C-CS-01 R4B-CS-01 R10-CS-01 R22-CS-01 R19-CS-01	25 15 41 4.9 14	<0.01 0.07 0.03 0.01 0.30	0.010 0.019 0.057 0.028 0.095	<0.01 0.08 0.01 <0.01 0.37	<0.03 <0.03 <0.03 <0.03 <0.03	
CSO Sludge	R9-SO-01 R1B-SO-01 R20-SO-01	70 16 24	0.01 0.01 <0.01	0.014 0.019 0.004	<0.01 <0.01 <0.01	<0.03 <0.03 <0.03	
Unleaded Sludge	R8A-US-01 R16-US-01	0.09 <0.09	0.11 0.02	0.121 0.043	0.11 0.02	0.07 <0.03	
HF Alkylation Sludge	R8B-HS-01 R9-HS-01 R15-HS-01 R7C-HS-01	0.3 31 6.8 0.08	0.01 <0.01 <0.01 <0.01	0.002 0.004 0.001 0.002	0.02 <0.01 <0.01 <0.01	<0.03 <0.03 <0.03 <0.03	
Sulfur Complex Sludge	R1-ME-01 R14-ME-01 R18-ME-01	1.0 0.2 <0.05	<0.01 <0.01 <0.01	0.001 0.002 0.001	<0.01 <0.01 <0.01	<0.03 <0.03 <0.03	
Hydrotreating Catalyst	R18-TC-01 R1-TC-01 R11-TC-01 R3B-TC-01 R22-TC-01	<0.05 <0.05 <0.05 <0.05 <0.2	<0.01 <0.01 <0.01 0.01 0.01	0.003 0.001 0.002 0.001 0.002	<0.01 <0.01 <0.01 0.01 0.02	<0.03 <0.03 <0.03 <0.03 <0.03	
Hydrorefining Catalyst	R21-RC-01	0.08	<0.01	0.003	<0.01	<0.03	
Off-Spec Product and Fines from Thermal Processes	R12-TP-01 R11-TP-01 R14-TP-01 R3B-TP-01	8.4 0.6 0.03 <0.05	<0.01 <0.01 0.03 <0.01	0.002 0.003 0.002 0.001	<0.01 <0.01 0.05 <0.01	<0.03 <0.03 0.03 <0.03	

# Table 5 - OWEP / Original TCLP Data Comparison

		% Oil &		Seleniu	m mg/L	
Residual	Sample ID	% Oll & Grease	OWEP	Solvent	Leachate	TCLP
Crude Sludge	R8C-CS-01 R4B-CS-01 R10-CS-01 R22-CS-01 R19-CS-01	25 15 41 4.9 14	<0.03 <0.03 <0.03 <0.03 <0.03	<0.003 <0.003 <0.003 0.005 <0.003	<0.03 <0.03 <0.03 <0.03 <0.03	<0.05 <0.05 <0.05 <0.05 <0.05
CSO Sludge	R9-SO-01 R1B-SO-01 R20-SO-01	70 16 24	<0.03 <0.03 <0.03	<0.003 <0.003 <0.003	<0.03 <0.03 <0.03	<0.05 <0.05 <0.05
Unleaded Sludge	R8A-US-01 R16-US-01	0.09 <0.09	<0.03 <0.03	<0.003 <0.003	<0.03 <0.03	<0.05 <0.05
HF Alkylation Sludge	R8B-HS-01 R9-HS-01 R15-HS-01 R7C-HS-01	0.3 31 6.8 0.08	<0.03 <0.03 <0.03 <0.03	<0.003 <0.003 <0.003 <0.003	<0.03 <0.03 <0.03 <0.03	<0.05 <0.05 <0.05 <0.05
Sulfur Complex Sludge	R1-ME-01 R14-ME-01 R18-ME-01	1.0 0.2 <0.05	0.11 <0.03 0.35	0.225 0.031 1.120	0.07 <0.03 0.08	<0.05 <0.05 0.12
Hydrotreating Catalyst	R18-TC-01 R1-TC-01 R11-TC-01 R3B-TC-01 R22-TC-01	<0.05 <0.05 <0.05 <0.05 <0.2	<0.03 <0.03 <0.03 0.03 <0.03	0.005 <0.003 <0.003 0.113 <0.003	<0.03 <0.03 <0.03 <0.03 <0.03	<0.05 <0.05 <0.05 <0.05 <0.05
Hydrorefining Catalyst	R21-RC-01	0.08	<0.03	0.004	<0.03	<0.05
Off-Spec Product and Fines from Thermal Processes	R12-TP-01 R11-TP-01 R14-TP-01 R3B-TP-01	8.4 0.6 0.03 <0.05	<0.03 <0.03 <0.03 <0.03	<0.003 <0.003 <0.003 <0.003	<0.03 <0.03 <0.03 <0.03	<0.05 <0.05 <0.05 <0.05

# Table 6 - OWEP / Original TCLP Data Comparison

		% Oil &		Silver	mg/L	
Residual	Sample ID	% Oll & Grease	OWEP	Solvent	Leachate	TCLP
Crude Sludge	R8C-CS-01 R4B-CS-01 R10-CS-01 R22-CS-01 R19-CS-01	25 15 41 4.9 14	<0.01 <0.01 <0.01 <0.01 <0.01	<0.007 <0.007 <0.007 <0.007 <0.007	<0.01 <0.01 <0.01 <0.01 <0.01	<0.10 <0.10 <0.10 <0.10 <0.10
CSO Sludge	R9-SO-01 R1B-SO-01 R20-SO-01	70 16 24	<0.01 <0.01 <0.01	<0.007 <0.007 <0.007	<0.01 <0.01 <0.01	<0.10 <0.10 <0.10
Unleaded Sludge	R8A-US-01 R16-US-01	0.09 <0.09	<0.01 <0.01	<0.007 <0.007	<0.01 <0.01	<0.10 <0.10
HF Alkylation Sludge	R8B-HS-01 R9-HS-01 R15-HS-01 R7C-HS-01	0.3 31 6.8 0.08	<0.01 <0.01 <0.01 <0.01	<0.007 <0.007 <0.007 <0.007	<0.01 <0.01 <0.01 <0.01	<0.10 <0.10 <0.10 <0.10
Sulfur Complex Sludge	R1-ME-01 R14-ME-01 R18-ME-01	1.0 0.2 <0.05	<0.01 <0.01 <0.01	<0.007 <0.007 <0.007	<0.01 <0.01 <0.01	<0.10 <0.10 <0.10
Hydrotreating Catalyst	R18-TC-01 R1-TC-01 R11-TC-01 R3B-TC-01 R22-TC-01	<0.05 <0.05 <0.05 <0.05 <0.2	<0.01 <0.01 <0.01 <0.01 <0.01	<0.007 <0.007 <0.007 <0.007 <0.007	<0.01 <0.01 <0.01 <0.01 <0.01	<0.10 <0.10 <0.10 <0.10 <0.10
Hydrorefining Catalyst	R21-RC-01	0.08	<0.01	<0.007	<0.01	<0.10
Off-Spec Product and Fines from Thermal Processes	R12-TP-01 R11-TP-01 R14-TP-01 R3B-TP-01	8.4 0.6 0.03 <0.05	<0.01 <0.01 <0.01 <0.01	<0.007 <0.007 <0.007 <0.007	<0.01 <0.01 <0.01 <0.01	<0.10 <0.10 <0.10 <0.10

# Table 7 - OWEP / Original TCLP Data Comparison