

US EPA ARCHIVE DOCUMENT

**STUDY OF SELECTED
PETROLEUM REFINING RESIDUALS

INDUSTRY STUDY**

Part 1

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U.S. ENVIRONMENTAL PROTECTION AGENCY
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1.0 INTRODUCTION

1.1 BACKGROUND

The U.S. Environmental Protection Agency (EPA) is directed in section 3001(e)(2) of the Resource Conservation and Recovery Act (RCRA) (42 U.S.C. §6921 (e)(2)) to determine whether to list as hazardous wastes a number of different wastes including those of the petroleum refining industry. A lawsuit by the Environmental Defense Fund (EDF) in 1989 resulted in a consent decree approved by the court, that sets out an extensive series of deadlines for making the listing determinations required by Section 3001 (e)(2). The deadlines include those for making final listing determinations as well as for concluding various related studies or reports on the industries of concern. With respect to the refining industry, the consent decree identifies 14 specific residuals for which the Agency must make listing determinations and an additional 15 residuals for which the Agency must conduct a study. These 29 residuals, subsequently referred to as the Residuals of Concern (RCs), are listed in Table 1.1. As a result of the consent decree, the Agency embarked on a project to determine whether these 29 RCs pose a threat to human health and the environment and to develop a basis for making such a determination. As a result of the preliminary evaluation of the waste subject to the listing determination, EPA proposed a rule in which eleven wastes were not to be listed and three wastes were to be listed as hazardous wastes: K169, K170, and K171 (clarified slurry oil storage tank sediments and/or filter/separation solids from catalytic cracking, catalyst from hydrotreating, and catalyst from hydrorefining, respectively) (60 *FR* 57747, November 20, 1995). The final determination will be issued under the applicable terms of the consent decree. This report is the result of the Agency's study of the remaining 15 residuals.

The Petroleum Refining Industry was previously studied by OSW in the 1980s. This original effort involved sampling and analysis of a number of residuals at 19 sites, distribution of a RCRA §3007 questionnaire to 180 refineries (characterizing the industry as of 1983), and, ultimately, a listing determination effort focused on wastewater treatment sludges, culminating in the promulgation of hazardous waste listings F037 and F038 (respectively, primary and secondary oil/water/solids separation sludges from petroleum refining).

As part of the Agency's current investigation of residuals from petroleum refining, the Agency conducted engineering site visits at 20 refineries to gain an understanding of the present state of the industry. These 20 refineries were randomly selected from the 185 refineries operating in the continental United States in 1992. Familiarization samples of various residuals were collected at 3 of the 20 refineries to obtain data on the nature of the RCs and to identify potential problems with respect to future analysis. The Agency then conducted record sampling and analysis of the RCs. During the record sampling timeframe, an additional 6 facilities were randomly selected to increase sample availability. Approximately 100 record samples were collected and analyzed. Concurrently, the Agency developed, distributed and evaluated a RCRA §3007 survey to the 180 refineries in the U.S.

Table 1.1. Petroleum Refining Residuals Identified in the EDF/EPA Consent Decree**Listing Residuals**

Clarified slurry oil sludge from catalytic cracking
 Unleaded storage tank sludge
 Crude storage tank sludge
 Process sludge from sulfur complex and H₂S removal facilities (sulfur complex sludge)
 Sludge from HF alkylation
 Sludge from H₂SO₄ alkylation
 Catalyst from catalytic hydrotreating
 Catalyst from catalytic reforming
 Catalyst and fines from catalytic cracking (FCC catalyst and FCC fines)
 Catalyst from catalytic hydrorefining
 Catalyst from H₂SO₄ alkylation
 Catalyst from sulfur complex and H₂S removal facilities (Claus and tail gas treating catalysts)
 Off-spec product and fines from thermal processes (Off-spec coke and fines)
 Spent caustic from liquid treating

Study Residuals

Desalting sludge from crude desalting
 Residual oil storage tank sludge
 Process sludge from residual upgrading
 Catalyst from extraction/isomerization processes*
 Catalyst from catalytic hydrocracking
 Catalyst from polymerization
 Catalyst from HF alkylation
 Off-spec product and fines from residual upgrading
 Off-spec product from sulfur complex and H₂S removal facilities (Off-spec sulfur)
 Off-spec treating solution from sulfur complex and H₂S removal facilities (Spent amine and spent Stretford solution)
 Acid-soluble oil from HF alkylation (ASO)
 Treating clay from clay filtering
 Treating clay from lube oil processing
 Treating clay from the extraction/isomerization process
 Treating clay from alkylation

*As described in Section 3.5 Extraction, catalyst used for extraction does not exist. The Agency believes it has been classified as a residual of concern inappropriately based on erroneous old data. Therefore, only catalyst from isomerization will be discussed in this study.

1.2 OTHER EPA REGULATORY PROGRAMS IMPACTING THE PETROLEUM REFINING INDUSTRY

Each of EPA's major program offices has long-standing regulatory controls tailored to the petroleum refining industry. Some of the more significant programs with some relevance to OSW's listing determinations and industry study include:

- The Clean Air Act's Benzene National Emissions Standards for Hazardous Air Pollutants (NESHAPS), designed to control benzene releases from process and waste management units.

- The Clean Air Act's National Ambient Air Quality Standards (NAAQS), which prescribe limits for sulfur oxides (SO_x), carbon monoxide (CO), particulates, nitrogen oxides (NO_x), volatile organic compounds (VOCs), and ozone.
- The Clean Air Act's NESHAPs for Petroleum Refineries (40 CFR Part 63, Subpart CC, see 60 *FR* 43244, August 18, 1995), designed to control hazardous air pollutants (HAPs).
- The Clean Water Act sets specific technology-based limits and water quality-based standards for discharges to surface waters and publically-owned treatment works (POTWs) including standards designed specifically for discharges from the petroleum refining industry.
- The Toxicity Characteristic, particularly for benzene, in combination with the F037/F038 sludge listings, has had a significant impact on the industry's wastewater treatment operations, forcing closure of many impoundments and redesign of tank-based treatment systems.
- The Land Disposal Restrictions (LDR) Program, including the ongoing Phase III and IV development work.

1.3 INDUSTRY STUDY FINDINGS

This document describes EPA's approach to conducting the industry study required by the EDF/EPA consent decree. The consent decree requires that EPA “fully characterize” the study residuals and how they are managed. “The report shall include a discussion of the concentration of toxic constituents in each waste, the volume of each waste generated, and the management practices for each waste (including plausible mismanagement practices).”

The statutory definition of “hazardous waste” is waste that may cause harm or pose a hazard to human health or the environment “when improperly treated, stored, transported, or disposed of, or otherwise managed.”

To implement this section of the statute, EPA considers available information on current management practices, and also exercises judgment as to plausible ways the waste could be managed in addition to those practices actually reported. EPA then judges which management practices have the potential to pose the greatest risk to human health or the environment and those practices would be assessed in a risk assessment.

As EPA explained in the preamble to the dyes and pigments proposed listing [59 *FR* 66072], EPA generally assumes that placement in an unlined landfill is a reasonably plausible management scenario for solids that potentially poses significant risks and thus would be “mismanagement” that should be examined by further risk assessment. For liquid wastes, unlined surface impoundments are such a presumptive mismanagement scenario. In past risk assessment work, EPA has found that these two scenarios are generally the scenarios most likely to pose a risk to ground water and thus would be mismanagement scenarios for a hazardous waste. In some cases, EPA has also found it appropriate to examine waste piles for solids prone

to transport by wind or erosion and to look at an aerated tank for volatile hazardous constituents in waste waters.

EPA also considers other scenarios, such as land application without Federal regulatory controls, as possible mismanagement scenarios and, where there is evidence that such practices occur for a particular waste stream, would consider whether further evaluation is appropriate. If EPA determines that a presumptive mismanagement scenario, such as disposal in an unlined surface impoundment, does not occur and would not reasonably be expected to occur, EPA may consider it implausible and instead use a more likely scenario as the plausible mismanagement scenario for subsequent analysis.

In the recent proposal to list petroleum residuals, EPA found the following waste management practices to pose the greatest risk and be the basis for judging whether these wastes posed a potential risk to human health or the environment when mismanaged:

- Unlined landfills
- Unlined surface impoundments
- Land application units not subject to Federal regulations

With respect to the residuals in this study, EPA found that the following management practices and their associated residuals (see Table 1.2) were reported and thus would be mismanagement scenarios EPA would further evaluate to ascertain if there were a potential risk:

- **Unlined landfills**
 - Residual oil storage tank sludge
 - Process sludge from residual upgrading
 - Catalyst from catalytic hydrocracking
 - Catalyst from polymerization
 - Off-spec product from sulfur complex and H₂S removal facilities (off-spec sulfur)
 - Off-spec treating solution from sulfur complex and H₂S removal facilities (spent amine and spent Stretford solution)

Table 1.2. Overview of 15 Study Residuals of Concern as Managed in 1992

Management Practice	Residuals of Concern: Study Residuals																
	ASO	Isom Catalyst	HF Catalyst	Polymer Catalyst	Desalting Sludge	Hydro-Cracking Catalyst	Off-spec Prod. Resid Upgrading	Off-spec Sulfur Product	Sludge Resid Upgrad	Resid Oil Tank Sludge	Off-spec Treating Solution	Treating Clay Alkylation	Treating Clay Filter	Treat Clay Isom/ Extract	Treating Clay from Lube Oil	TOTALS	Percent of Total
	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	MT	
DISPOSAL																	
Disposal offsite Subtitle D landfill				1,429	29	1,593		5,043	138	6,458	200	634	3,641	937	37	20,138	16.8%
Disposal offsite Subtitle C landfill		44		65	221	992		3,576	0	622	39	24	1,735	516	79	7,913	6.6%
Disposal onsite Subtitle C landfill				349				289	62	4		67	52	58	5	886	0.7%
Disposal onsite Subtitle D landfill				256	102			226	7	30	711	626	1,032	496		3,485	2.9%
Disposal onsite or offsite underground injection					2						673					675	0.6%
Storage or disposal onsite surface impoundment	0									132	1					133	0.1%
Other disposal onsite/roadbed mixing									0			4	16	138		158	0.1%
Use as cover in onsite landfill										7						7	0.0%
Use as cap for onsite landfarm, fill material, or vent													20			20	0.0%
TOTAL DISPOSED	0	44	0	2,099	354	2,584	0	9,133	207	7,254	1,624	1,355	6,497	2,145	120	33,417	27.9%
DISCHARGED																	
Discharge to onsite wastewater treatment facility	1,258				128				3	47	205	0	7			1,648	1.4%
Discharge to POTW					647				1		0					648	0.5%
Discharge to surface water under NPDES	3,600		152		1,266						6,849		507			12,374	10.3%
Discharge to offsite POTW											1,566					1,566	1.3%
TOTAL DISCHARGED	3,600	0	152	0	1,913	0	0	0	1	0	8,415	0	507	0	0	14,588	12.2%
RECOVERED, RECYCLED, REUSED, REGENERATED																	
Metals Reclamation																	
Transfer metal catalyst for reclamation or regeneration		293				13,185					5,127	91	89	33		18,819	15.7%
Recycle to Processes																	
Recovery onsite via distillation, coker, or cat cracker	50							0	16	310						376	0.3%
Onsite reuse													20			20	0.0%
Other recycling, reclamation or reuse/sulfur recov. unit								2			13					15	0.0%
Recovery onsite in catalytic cracker	3,641									0	1,150					4,791	4.0%
Recovery onsite in coker	1,019			749	52					0			20			1,840	1.5%
Other recovery onsite/alkyl	1,300															1,300	1.1%
Other recovery onsite/hydroprocessing	510															510	0.4%
Other recovery onsite/reuse in extraction process							800									800	0.7%
Miscellaneous On-site Recycling																	
Reuse onsite as replacement catalyst for another unit						159										159	0.1%
Other recovery onsite	370														354	724	0.6%
Other recycling, reclamation or reuse/offsite reuse												30	38			68	0.1%
Other recycling, reclamation or reuse/cement plant												771	161	28	249	1,210	1.0%
TOTAL RECYCLED	6,890	293	0	749	52	13,345	800	2	16	310	6,290	892	329	62	603	30,633	25.6%
STORAGE																	
Storage in pile				0								30	128	20		178	0.1%
TOTAL STORED (interim)	0	0	0	0	0	0	0	0	0	0	0	30	128	20	0	178	0.1%

Table 1.2. Overview of 15 Study Residuals of Concern as Managed in 1992 (continued)

Management Practice	Residuals of Concern: Study Residuals																
	ASO	Isom Catalyst	HF Catalyst	Polymer Catalyst	Desalting Sludge	Hydro-Cracking Catalyst	Off-spec Prod. Resid Upgrading	Off-spec Sulfur Product	Sludge Resid Upgrad	Resid Oil Tank Sludge	Off-spec Treating Solution	Treating Clay Alkylation	Treating Clay Filter	Treat Clay Isom/ Extract	Treating Clay from Lube Oil	TOTALS	Percent of Total
	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	mt	MT	
TRANSFER																	
Transfer of acid or caustic for recycle, reuse, reclamation											2,475						
Transfer for use as ingredient in products placed on land				543				15		35			176			768	0.6%
Transfer to N.O.S. offsite entity and final management								0	0					14		14	0.0%
Transfer to another petroleum refinery						2,100				927						3,027	2.5%
Transfer for direct use as a fuel or to make a fuel	741				1,938								95			2,773	2.3%
Transfer with coke product or other refinery product	3,731							7	5				5			3,747	3.1%
Transfer to other offsite entity/carbon regeneration													54			54	0.0%
Transfer to other offsite entity/amine reclaimer											166					166	0.1%
Transfer to other offsite entity/alumina manufacturer												405				405	0.3%
Transfer to other offsite entity/smelter												155				155	0.1%
Transfer to other offsite entity/used as a raw material feed								488								488	0.4%
TOTAL TRANSFERRED	4,472	0	0	543	1,938	2,100	0	509	5	962	2,641	560	329	14	0	14,073	11.8%
TREATMENT																	
Evaporation*													8			8	0
Bioremediation*													21			21	0
Neutralization	11,388	0		0							0					11,388	9.5%
Offsite incineration, stabilization, or reuse	0			0	56			1	9				42			108	0.1%
Onsite boiler	2,610										9					2,619	2.2%
Onsite industrial furnace	3,274															3,274	2.7%
Onsite land treatment				728	346					530		59	923	231	10	2,827	2.4%
Offsite land treatment					53			1		4			198			256	0.2%
TOTAL TREATED (interim)	17,272	0	0	728	455	0	0	2	9	534	9	59	1,193	231	10	20,502	17.1%
GRAND TOTAL	33,493	337	152	4,119	4,841	18,029	800	9,647	242	9,107	23,881	2,895	8,990	2,471	733	119,738	
	28.0%	0.3%	0.1%	3.4%	4.0%	15.1%	0.7%	8.1%	0.2%	7.6%	19.9%	2.4%	7.5%	2.1%	0.6%		

* To avoid double counting, these intermediate steps were not included in the total.

- Treating clay from clay filtering
- Treating clay from lube oil processing
- Treating clay from the extraction/isomerization process
- Treating clay from alkylation
- **Unlined surface impoundments**
 - Residual oil storage tank sludge
 - Off-spec treating solution from sulfur complex and H₂S removal facilities (spent amine and spent Stretford solution)
- **Land application not subject to Federal regulations**
 - Residual oil storage tank sludge
 - Catalyst from polymerization
 - Off-spec product from sulfur complex and H₂S removal facilities (off-spec sulfur)
 - Treating clay from clay filtering
 - Treating clay from lube oil processing
 - Treating clay from the extraction/isomerization process
 - Treating clay from alkylation

In addition, EPA found that the management practice of mixing of treating clays with roadbed materials for onsite use was reported and would merit evaluation as a potential mismanagement scenario.

Section 2.0 provides an overview of the petroleum refining industry and EPA's approach to this study. The fifteen study residuals identified in the consent decree accounted for approximately 120,000 metric tons in 1992, compared to over 3.1 million metric tons of listing residuals generated in 1992. Table 1.2 provides a description of the 15 study residuals by management practice and volume generated. The Agency believes that the management practices reported consist of virtually all of the plausible management practices to which the residuals may be subjected. Section 3.0 describes the refinery processes associated with generating the consent decree residuals of concern and detailed characterization of each of the study residuals as required by the consent decree.

2.0 INDUSTRY DESCRIPTION

2.1 PETROLEUM REFINING INDUSTRY PROFILE

In 1992¹, the U.S. petroleum refining industry consisted of 185 refineries (of which 171 were fully active during the year) owned by 91 corporations. Atmospheric crude oil distillation capacity totaled 15,120,630 barrels per calendar day (bpcd) (DOE, 1993). As of January 1, 1996, U.S. capacity totaled 15,341,000 bpcd, showing little change in the Nation's refining capacity since the Agency's baseline year. Figure 2.1 illustrates the distribution of refineries across the country. Refineries can be classified in terms of size and complexity of operations. Forty-four percent of the refineries operating in 1992 processed less than 50,000 barrels per day of crude, while the 20 largest companies account for 77 percent of the nation's total refining capacity.

The simplest refineries use distillation to separate gasoline or lube oil fractions from crude, leaving the further refining of their residuum to other refineries or for use in asphalt. Approximately 18 percent of the U.S.'s refineries are these simple topping, asphalt, or lube oil refineries. More sophisticated refineries will have thermal and/or catalytic cracking capabilities, allowing them to extract a greater fraction of gasoline blending stocks from their crude. The largest refineries are often integrated with chemical plants, and utilize the full range of catalytic cracking, hydroprocessing, alkylation and thermal processes to optimize their crude utilization. Section 3.1 describes the major unit operations typically found in refining operations.

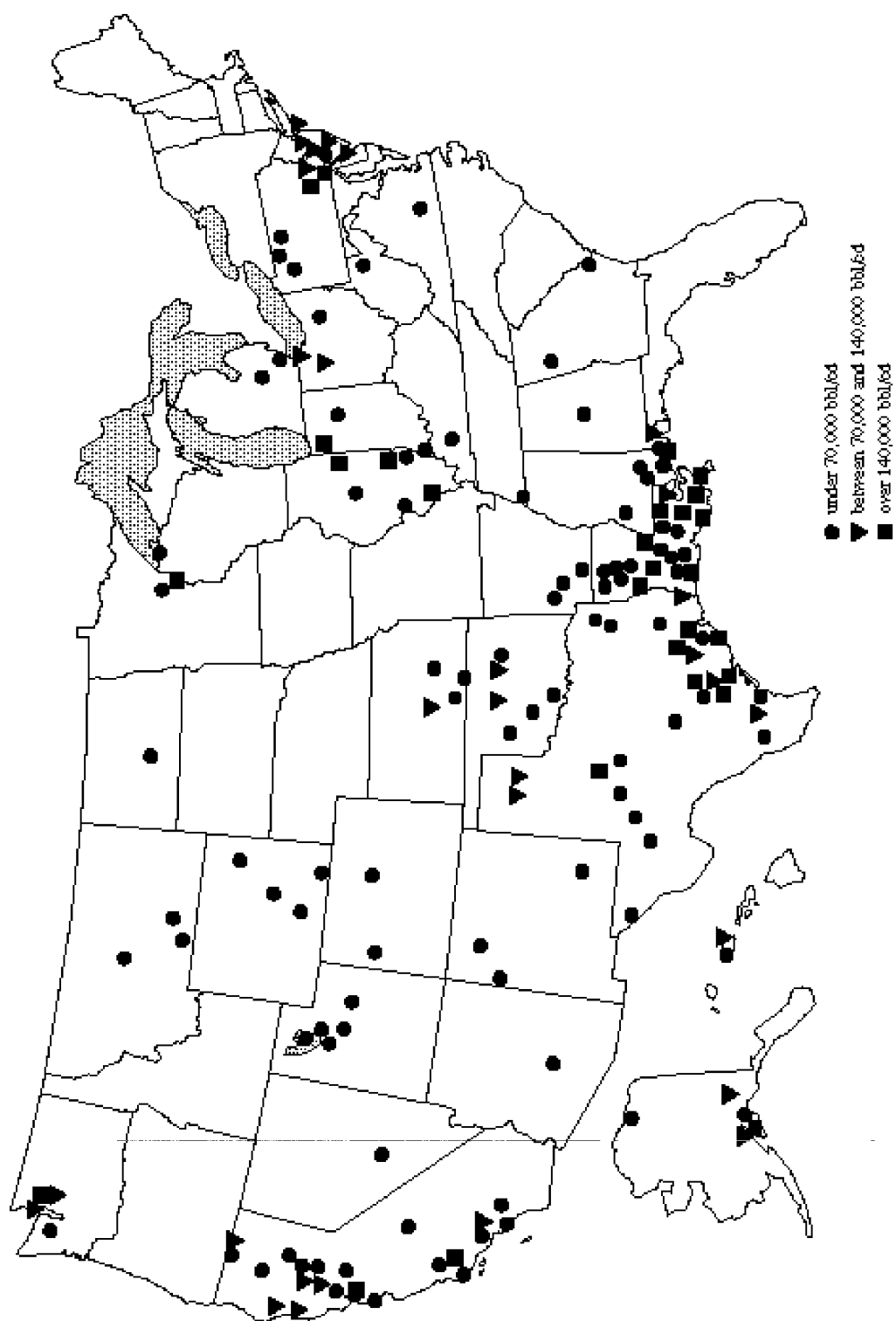
The refining industry has undergone significant restructuring over the past 15 years. Much of this restructuring has been in response to the price allocation programs of the 1970s and industry deregulation in the 1980s. While the total national refining capacity dropped 17 percent since 1980 to 15 million barrels per day, the number of refineries dropped 45 percent from 311 in 1980 to approximately 171 active in 1992 (and 169 as of 1/1/96). Refinery utilization rates over the 1980 to 1992 period rose from 75 percent to 90 percent. (API, 1993). Very few new refineries have been constructed in the past decade; the industry instead tends to focus on expansions of existing plants.

The facilities closed tended to be smaller, inefficient refineries. Larger existing facilities with capacities over 100,000 bbl/day have increased production to off-set the facility closings.

The data presented above indicates that the petroleum refining industry has been going through a consolidation, which has resulted in a large decrease in the number of refineries in the United States, but only a slight decrease in production. It is expected that this trend will

¹The Agency conducted its industry-wide survey in 1993-1994, characterizing residual generation in 1992. Thus, 1992 was considered the Agency's baseline year. The Agency has no reason to conclude that 1992 was not representative of industry management practices. EPA's risk assessment modeling used as input the 1992 data for the RCs as a "snap shot" of the industry's management practices. However, information for years other than 1992 is provided in the pertinent sections of the study.

Figure 2.1. Geographical Distribution of U.S. Refineries



continue, with refineries continuing to close, but expansions occurring at others, keeping the total refinery capacity in line with demand for refinery products.

In addition to restructuring, the industry is adding and changing production operations. Many of these process changes are being implemented as a result of two factors: (1) today's crudes tend to be heavier and contain higher levels of sulfur and metals, requiring process modifications, and (2) a series of important pollution control regulations have been implemented, including new gasoline reformulation rules designed to reduce the amount of volatile components in gasoline, and new regulations requiring low-sulfur diesel fuels. These heavier crudes and new rules have caused refineries to make process modifications to their gasoline production units such as catalytic cracker units, installing additional sulfur removal hydrotreaters, and constructing unit processes to manufacture additives such as oxygenates.

Many of the process modifications in response to the reformulated gasoline and low sulfur diesel fuels have been implemented since 1992. The **Oil and Gas Journal** (December, 1993, 1994, and 1995) reports the following major processing capacity changes from year end 1992 to year end 1995:

- 5.5 percent capacity increase in thermal operations (forecast to further increase by new construction scheduled to be completed in 1996)
- 8.7 percent capacity increase in hydrocracking operations
- 9.8 percent capacity increase in combined hydrorefining and hydrotreating operations (there was a 16 percent increase in hydrotreating capacity offset by a 12 percent decrease in hydrorefining capacity).
- 13.8 percent increase in aromatic and isomerization unit capacity.
- 5.6 percent increase in alkylation capacity
- 11.3 percent increase in lube production capacity
- 7.7 percent decrease in asphalt production
- Small capacity increases for crude distillation, reforming, and catalytic cracking (increases of 0.9, 0.7, and 1.6 percent, respectively).

2.2 INDUSTRY STUDY

OSW's current listing determination and industry study for the petroleum refining industry has been underway since 1992 and can be characterized in terms of two major avenues for information collection: field work and survey evaluation. As part of the Agency's field work, site selection, engineering site visits, familiarization sampling, and record sampling were conducted. The survey effort included the development, distribution, and assessment of an extensive industry-wide RCRA §3007 survey. Each of these elements is described further below, reflecting the relative order in which these activities were conducted.

2.2.1 Site Selection

EPA's field work activities were focussed on a limited number of refineries, allowing the Agency to establish strong lines of communication with the selected facilities, and maximizing efficiency of information collection. After considering logistical and budgetary constraints, the Agency determined that it would limit its field work to 20 refineries.

The Agency defined a site selection procedure that was used in selecting the 20 site visits from the population of 185 domestic refineries in the continental U.S.. The objectives of the selection procedure were:

- to ensure that the characterization data obtained from residuals at the 20 selected facilities could be used to make valid, meaningful statements about those residuals industry-wide.
- to give the Agency first-hand exposure to both large and small refineries.
- to be fair to all domestic refineries.

The Agency chose to select facilities randomly rather than purposefully. Although a randomly selected group of refineries did not offer as many sampling opportunities as a hand-picked group (e.g., focusing on those larger refineries that generate most of the RCs), the Agency favored random selection because it did not require subjective input, and also because it lends itself to statistical analysis, which is useful in making general statements about the population of residuals.

The Agency broke the industry into two strata based on atmospheric distillation capacity and made random selections from each stratum independently. The high-capacity stratum (those with a crude capacity of 100,000 bpcd or greater) contains the top 30 percent of refineries, which together account for 70 percent of the refining industry's capacity. The stratification enables the Agency to weigh the selection toward the larger facilities on the basis that they produce larger volumes of residuals, and that they offer a larger number of residual streams per site visit. The Agency chose to select 12 of the 20 site visits, 60 percent, from the high-capacity stratum. The smaller facilities had a lower chance of being selected, but not as low as they would have if the likelihood of selection was based strictly on size. The selected facilities are presented in Table 2.1².

²Upon initial contact with several of the randomly selected refineries, it was determined that they were inappropriate candidates for site visits because they had stopped operation and were not generating any residuals of interest to the Agency. Replacement facilities were then selected randomly from the same stratum.

The list of refineries slated for field investigations was expanded in June, 1994 to allow the Agency to fill out certain categories of samples that proved to be difficult to find in the field. The final list presented in Table 2.1 represents those refineries at which site visits actually occurred.

Table 2.1. Engineering Site Visit Facilities

Refinery	Location	Initial Site Visit Date
Amoco Oil	Texas City, Texas	March 29, 1993
Arco	Ferndale, Washington	June 9, 1993
Ashland	Canton, Ohio	May 24, 1993
Ashland	Catlettsburg, Kentucky	March 22, 1993
BP Oil	Belle Chasse, Louisiana	May 3, 1993
BP Oil	Toledo, Ohio	May 26, 1993
Chevron (purchased by Clark) ¹	Port Arthur, Texas	August 31, 1994
Chevron ¹	Salt Lake City, Utah	February 21, 1995
Conoco ¹	Commerce City, Colorado	To be determined
Exxon	Billings, Montana	June 9, 1993
Koch	St. Paul, Minnesota	May 19, 1993
Little America	Evansville, Wyoming	June 8, 1993
Marathon	Garyville, Louisiana	April 22, 1993
Murphy	Superior, Wisconsin	May 17, 1993
Pennzoil	Shreveport, Louisiana	May 5, 1993
Phibro Energy ¹	Houston, Texas	April 20, 1995
Rock Island (purchased by Marathon)	Indianapolis, Indiana	April 26, 1993
Shell	Deer Park, Texas	March 31, 1993
Shell	Norco, Louisiana	April 20, 1993
Shell	Wood River, Illinois	May 28, 1993
Star Enterprise ¹	Convent, Louisiana	August 30, 1994
Star Enterprise ¹	Port Arthur, Texas	September 21, 1994
Sun	Philadelphia, Pennsylvania	May 12, 1993
Texaco	Anacortes, Washington	June 10, 1993
Total	Ardmore, Oklahoma	June 23, 1993
Young	Douglasville, Georgia	June 21, 1993

¹Refinery selected to augment record sample availability.

2.2.2 Engineering Site Visits

The field activities were initiated with a series of engineering site visits to the selected facilities. The purpose of these trips was to:

- Develop a firm understanding of the processes associated with the RCs
- Understand how, when, why, and where each residual is generated and managed
- Establish a schedule of sampling opportunities
- Establish a dialogue with the refinery personnel to ensure optimal sampling and collection of representative samples.

An engineering site visit report was developed for each of the trips; these are available in the CBI and non-CBI dockets, as appropriate. For the later site visits conducted in 1994 and 1995, the engineering site visit reports were combined with the analytical data reports prepared for each facility. The site visit reports included the following elements:

- Purpose of the site visit
- Refinery summary, including general information gathered during the site visit, as well as data gleaned from telephone conversations and reviews of EPA files, the refinery's process flow diagram, and expected residual availability
- A discussion of the processes used at the refinery generating the residuals of concern
- Source reduction and recycling techniques employed by the refinery
- A description of onsite residual management facilities
- A chronology of the site visit.

2.2.3 RCRA §3007 Questionnaire

EPA developed an extensive questionnaire under the authority of §3007 of RCRA for distribution to the petroleum refining industry. A blank copy of the survey instrument is provided in the RCRA docket. The questionnaire was organized into the following areas:

- I. Corporate and facility information
- II. Crude oil and product information
- III. Facility process flow diagram
- IV. Process units: general information
- V. Process units: flow diagrams and process descriptions
- VI. Residual generation and management
- VII. Residual and contaminated soil and debris characterization
- VIII. Residual management units: unit-specific characterization
- IX. Unit-specific media characterization

- X. General facility characterization (focusing on exposure pathway characterization)
- XII. Source reduction efforts
- XIII. Certification.

The survey was distributed in August 1993 to all refineries identified as active in 1992 in the DOE Petroleum Supply Annual. Of the 185 surveys distributed, completed responses were obtained for 172 refineries. Thirteen refineries notified EPA that they had stopped operations at some point in or after 1992 and thus were unable to complete the survey due to no staffing or inaccessible or unavailable data.

The survey responses were reviewed by SAIC chemical engineers for completeness and then entered into a relational data base known as the 1992 Petroleum Refining Data Base (PRDB). The entries were subjected to a series of automated quality assurance programs to identify inappropriate entries and missing data links. An exhaustive engineering review of each facility's response was then conducted, resulting in follow-up letters to most of the industry seeking clarifications, corrections, and additional data where needed. The responses to the followup letters were entered into the data base. A wide variety of additional quality assurance checks were run on the data to ensure that the residuals of concern were characterized as completely and accurately as possible. Follow-up telephone interviews were conducted as necessary to address remaining data issues. After extensive review, the Agency believes that the data are reliable and represent the industry's current residual generation and management practices.

Table 2.2 describes the survey results for each of the study residuals of concern, sorted by total volume generated in metric tons (MT).

2.2.4 Familiarization Sampling

The early phases of the analytical phase of this listing determination consisted of the development of a Quality Assurance Project Plan (QAPjP) for sampling and analysis, followed by the collection and analysis of six "familiarization" samples (five listing residuals and one study residual). The purpose of collecting these samples was to assess the effectiveness of the methods identified in the QAPjP for the analysis of the actual residuals of concern. Due to the high hydrocarbon content of many of the RCs, there was concern at the outset of the project that analytical interferences would prevent the contracted laboratory from achieving adequate quantitation limits; familiarization analysis allowed the laboratories to experiment with the analytical methods and waste matrices and optimize operating procedures.

In addition, the first version of the QAPjP identified a list of target analytes that was derived from previous Agency efforts to characterize refinery residuals. These included the Delisting Program's list of analytes of concern for refinery residuals, the "Skinner List", an evaluation of compounds detected in the sampling and analysis program for listing refinery residuals in the 1980s, and the judgment of EPA and SAIC chemists who evaluated the process chemistry of the residuals of concern. During familiarization sample analysis, particular attention was paid to the tentatively identified compounds to determine whether they should be added to the target analyte list.

Table 2.2. Study Residuals Volume Statistics

Study Residual Description	# of Reported Residuals	Total Volume (MT)
Acid Soluble Oil	80	33,493
Hydrocracking Catalyst	83	18,029
Off-specification Product from Sulfur Complex and H ₂ S Removal	93	9,647
Residual Oil Tank Sludge	62	9,107
Treating Clay from Clay Filtering	244	8,990
Desalting Sludge	141	4,841
Off-specification Treating Solution from Sulfur Complex and H ₂ S Removal (spent amine and spent Stretford solution)	76	23,881
Catalyst from Polymerization (phosphoric acid and Dimersol)	42	4,119
Treating Clay from Alkylation	88	2,895
Treating Clay from Isomerization/Extraction	43	2,472
Off-specification Product from Residual Upgrading	3	800
Treating Clay from Lube Oil	19	733
Catalyst from Isomerization	21	337
Sludge from Residual Upgrading	34	242
Catalyst from HF Alkylation	3	152
Total	1,061	119,738

Samples of five listing residuals were collected for familiarization analysis: crude oil tank sediments, hydrotreating catalyst, sulfur complex sludge, H₂SO₄ alkylation catalyst, and spent caustic. One study residual, acid soluble oil, was analyzed under this program. The results of the familiarization effort essentially confirmed the techniques identified in the QAPjP and indicated that the laboratories generally would be able to achieve adequate quantitation of the target analytes. The familiarization and final QAPjPs are provided in the docket to the November 20, 1995 proposed rulemaking.

2.2.5 Record Sampling

Upon completion of the familiarization sampling and analysis effort, the Agency initiated record sampling and analysis of the listing and study residuals. Given budgetary constraints, the Agency set a goal of collecting 4-6 samples of each of the listing residuals, and 2-4 samples of the study residuals for a total of 134 samples³. Table 2.3 shows the 103 samples that were actually collected. The numbers in the darkened boxes refer to Table 2.4 which lists each of the sample numbers, sample dates, facility names, and other information describing the residual samples.

³The Agency determined that one listing residual, catalyst from sulfuric acid alkylation, would not be sampled due to the existing regulatory exemption for sulfuric acid destined for reclamation, and that one study residual, catalyst from HF alkylation, could not be sampled due to its extremely rare generation.

Table 2.3. Residuals Collected for Record Analysis

Listing Residuals	Record Samples						Familiarization Samples
	1	2	3	4	5	6	1
Crude oil tank sludge	33	67	73	53	89	91	F5
Unleaded gasoline tank sludge	34	42	65				
CSO sludge	14	49	72	88			
FCC catalyst and fines	1	12	13	26	27	28	
Catalyst from hydrotreating	6	44	55	83	94	69	F2
Catalyst from hydrorefining	21	36	85				
Catalyst from reforming	3	22	37	56	79	75	
Sulfuric acid alkylation sludge	46						
HF alkylation sludge	19	47	51	74	96		
Sulfur complex sludge	10	25	29	80	70		F3
Catalyst from sulfur complex	9	15	23	24	52	54	
Off-spec product & fines/thermal process	30	45	59	63	81	84	
Spent caustic	16	17	32	62	64	95	F1

Study Residuals	1	2	3	4
Residual oil tank sludge	41	92		
Desalting sludge	5	50	90	102
Hydrocracking catalyst	4	43	87	
Catalyst from isomerization	39	48	71	97
Treating clay from isomerization/extraction	68	98		
Catalyst from polymerization	35	66A	66B	
Treating clay, alkylation (HF and H ₂ SO ₄)	20	76	86	99
ASO	18	38	77	93
Off-spec sulfur product	2	8	40	100
Spent treating solution (amine)	61	58	82	78
Process sludge from residual upgrading	11			
Off-spec product, residual upgrading				
Treating clay from lube oil	60			
Treating clay from clay filtering	7	31	57	101

F4

Notes: Sulfuric Acid Alkylation catalyst is not presented in this figure. One familiarization sample of sulfuric acid catalyst was captured and analyzed. HF catalyst is constant boiling mixture (CBM) and is not shown in this figure.

The sampling team maintained monthly phone contact with the targeted refineries to maintain an optimized sampling schedule. Despite careful coordination with the refineries and best efforts to identify and collect all available samples, there were several categories of study residuals for which the targeted minimum number of samples could not be collected:

- Two samples of residual oil tank sludge were collected. This residual is available only for a brief period during tank turnarounds, which may occur only every 10 years. In several cases, refineries mixed their residual oil and clarified slurry oil (CSO) in the same tank.

Table 2.4. Descriptions of Samples Collected for Record Analysis

Count	Residual Name	Sample Number	Sample Date	Notes	Refinery
1	FCC catalyst and fines	R2-FC-01	30-Sep-93	ESP Fines.	Shell, Wood River, Illinois
2	Off-spec sulfur	R2-SP-01	30-Sep-93	Taken from low spots on the unit.	Shell, Wood River, Illinois
3	Catalyst from reforming	R2-CR-01	01-Oct-93	Platinum catalyst.	Shell, Wood River, Illinois
4	Catalyst from hydrocracking	R2-CC-02	04-Oct-93	2nd stage, Ni/W.	Shell, Wood River, Illinois
5	Desalting sludge	R1-DS-01	26-Oct-93	Removed from vessel.	Marathon, Indianapolis
6	Catalyst from hydrotreating	R1-TC-01	26-Oct-93	Naphtha reformer pretreat, CoMo.	Marathon, Indianapolis
7	Treating clay	R1-CF-01	27-Oct-93	Kerosene.	Marathon, Indianapolis
8	Off-spec sulfur	R1-SP-01	27-Oct-93	From product tank.	Marathon, Indianapolis
9	Catalyst from sulfur complex	R1-SC-01	27-Oct-93	Al ₂ O ₃ .	Marathon, Indianapolis
10	Sulfur complex sludge	R1-ME-01	27-Oct-93	MEA reclaimers bottoms.	Marathon, Indianapolis
11	Process sludge from residual upgrading	R1-RU-01	27-Oct-93	ROSE butane surge tank sludge.	Marathon, Indianapolis
12	FCC catalyst and fines	R4-FC-01	16-Nov-93	Equilibrium cat. from hopper.	Little America, Evansville, Wy
13	FCC catalyst and fines	R4-FC-02	16-Nov-93	ESP fines. truck trailer comp.	Little America, Evansville, Wy
14	CSO sludge	R4-SO-01	16-Nov-93	Tank sludge from pad.	Little America, Evansville, Wy
15	Catalyst from sulfur complex	R4-SC-01	16-Nov-93	Claus unit alumina, super sack comp.	Little America, Evansville, Wy
16	Spent caustic	R3-LT-01	18-Nov-93	Tank samp. Cresylic, concentrated.	Exxon, Billings, Montana
17	Spent caustic	R3-LT-02	18-Nov-93	Tank samp. Sulfidic, concentrated.	Exxon, Billings, Montana
18	ASO	R3-AS-01	18-Nov-93	Non-neutralized, separator drum sample	Exxon, Billings, Montana
19	HF alkylation sludge	R3-HS-01	18-Nov-93	Not dewatered. Dredge from pit.	Exxon, Billings, Montana
20	Treating clay from alkylation	R3-CA-01	18-Nov-93	HF. Propane treater. Drum composite.	Exxon, Billings, Montana
21	Catalyst from hydrotreating	R5-TC-01	07-Feb-94	Heavy Gas Oil, CoMo	Marathon, Garyville, LA
22	Catalyst from reforming	R5-CR-01	07-Feb-94	CCR fines, Pt	Marathon, Garyville, LA
23	Catalyst from sulfur complex	R5-SC-01	07-Feb-94	Claus	Marathon, Garyville, LA
24	Catalyst from sulfur complex	R5-SC-02	07-Feb-94	Tail gas, CoMo	Marathon, Garyville, LA
25	Sulfur complex sludge	R5-ME-02,03	07-Feb-94	Refinery MDEA filter cartridge	Marathon, Garyville, LA
26	FCC catalyst and fines	R5-FC-02	07-Feb-94	Wet Scrubber Fines	Marathon, Garyville, LA
27	FCC catalyst and fines	R6-FC-01	09-Feb-94	Equil. from unit	Shell, Norco, LA
28	FCC catalyst and fines	R6-FC-02	09-Feb-94	Wet scrubber fines	Shell, Norco, LA
29	Sulfur complex sludge	R6-ME-01	09-Feb-94	Refinery DEA filter cartridge	Shell, Norco, LA
30	Off-spec product & fines from thermal process	R6-TP-01	09-Feb-94	Coke fines.	Shell, Norco, LA
31	Treating clay	R6-CF-01	09-Feb-94	Kerosene	Shell, Norco, LA
32	Spent caustic	R6-LT-01	09-Feb-94	Naph. Comb. Gas oil & Kero	Shell, Norco, LA
33	Crude oil tank sludge	R6B-CS-01	15-Mar-94	Mix of centrifuge and uncentrifuged	Shell, Norco, LA
34	Unleaded gasoline tank sludge	R6B-US-01	31-Mar-94	Water washed solids, collected by refinery	Shell, Norco, LA
35	Catalyst from polymerization	R6B-PC-01	15-Mar-94	Dimersol. filter	Shell, Norco, LA
36	Catalyst from hydrotreating	R7B-RC-01	14-Mar-94	Diesel hydrotreater	BP, Belle Chase, LA
37	Catalyst from reforming	R7B-CR-01	14-Mar-94	Platinum	BP, Belle Chase, LA
38	ASO	R5B-AS-01	16-Mar-94	Acid regen settler bottoms. not neutralized	Marathon, Garyville, LA

Table 2.4. Descriptions of Samples Collected for Record Analysis (continued)

Count	Residual Name	Sample Number	Sample Date	Notes	Refinery
39	Catalyst from isomerization	R5B-1C-01	16-Mar-94	Butamer, platinum	Marathon, Garyville, LA
40	Off-spec sulfur	R7B-SP-01	14-Mar-94	From cleaned out tank	BP, Belle Chase, LA
41	Residual oil tank sludge	R8A-RS-01	30-Apr-94	CSO and Resid.	Amoco, Texas City
42	Unleaded gasoline tank sludge	R8A-US-01	14-Apr-94	Collected by refinery	Amoco, Texas City
43	Catalyst from hydrocracking	R8A-CC-01	30-Mar-94	Hydroproc., 1st stage cracker, CoMo	Amoco, Texas City
44	Catalyst from hydrotreating	R8A-TC-01	30-Mar-94	NiMo, landfilled	Amoco, Texas City
45	Off-spec product & fines from thermal processes	R8A-TP-01	30-Mar-94	Fines, F&K processed	Amoco, Texas City
46	H2SO4 alkylation sludge	R8B-SS-01	30-Apr-94	From Frog pond, not dewatered	Amoco, Texas City
47	HF alkylation sludge	R8B-HS-01	30-Apr-94	Not dewatered, dredged	Amoco, Texas City
48	Catalyst from isomerization	R8B-IC-01	30-Apr-94	Butamer, Pt	Amoco, Texas City
49	CSO sludge	R9-SO-01,02	17-May-94	Filters (and blank)	Murphy, Superior, WI
50	Desalting sludge	R9-DS-01	17-May-94		Murphy, Superior, WI
51	HF alkylation sludge	R9-HS-01	17-May-94		Murphy, Superior, WI
52	Catalyst from sulfur complex	R7B-SC-01	14-Mar-94	SCOT catalyst	BP, Belle Chase, LA
53	Crude oil tank sludge	R10-CS-01	26-Aug-94		Ashland, Catletsburg, KY
54	Catalyst from sulfur complex	R11-SC-01	10-May-94	SCOT, CoMo	ARCO, Ferndale, WA
55	Catalyst from hydrotreating	R11-TC-01	10-May-94	NiMo, naphtha treater	ARCO, Ferndale, WA
56	Catalyst from reforming	R11-CR-01	10-May-94	Pt/Rh	ARCO, Ferndale, WA
57	Treating clay	R11-CF-01	10-May-94	Reformer sulfur trap	ARCO, Ferndale, WA
58	Spent amine	R11-SA-01	10-May-94	DEA	ARCO, Ferndale, WA
59	Off-spec product & fines from thermal processes	R11-TP-01	10-May-94	Coke fines	ARCO, Ferndale, WA
60	Treating clay from lube oil	R13-CL-01	30-Apr-94	Clay dust	Shell, Deer Park, TX
61	Spent amine	R13-SA-01	30-Apr-94	DEA	Shell, Deer Park, TX
62	Spent caustic	R13-LT-01	30-Apr-94	Sulfidic	Shell, Deer Park, TX
63	Off-spec product & fines from thermal processes	R12-TP-01	12-May-94	Coke fines, from trap	Texaco, Anacortes, WA
64	Spent caustic	R12-LT-01	12-May-94	Cresylic	Texaco, Anacortes, WA
65	Unleaded gasoline tank sludge	R16-US-01	03-Aug-94		Koch
66	Catalyst from polymerization	R16-PC-01,02	03-Aug-94	2 catalysts from Dimersol and H2PO4	Koch
67	Crude oil tank sludge	R8C-CS-01	01-Jul-94	collected by refinery from tank bottom	Amoco, Texas City
68	Treating clay from extraction	R8D-CI-01	15-Nov-96	collected by refinery	Amoco, Texas City
69	Catalyst from hydrotreating	R18-TC-01	20-Oct-94	naphtha	Ashland, Canton, OH
70	Sulfur complex sludge	R18-ME-01	14-Oct-94	MEA sludge, collected by refinery	Ashland, Canton, OH
71	Catalyst from isomerization	R18-IC-01	20-Oct-94	Penex	Ashland, Canton, OH
72	CSO sludge	R1B-CS-01	26-Aug-94	mixed CSO/resid	Marathon, Indianapolis
73	Crude oil tank sludge	R4B-CS-01	26-Aug-94	Filter cake sludge	Little America
74	HF alkylation sludge	R15-HS-01	02-Aug-94	Dredged from pit	Total, Ardmore, OK
75	Catalyst from reforming	R15-CR-01	02-Aug-94	CCR fines	Total, Ardmore
76	Treating clay from alkylation	R15-CA-01	02-Aug-94	Butane	Total, Ardmore

Table 2.4. Descriptions of Samples Collected for Record Analysis (continued)

Count	Residual Name	Sample Number	Sample Date	Notes	Refinery
77	ASO	R15-AS-01	02-Aug-94	Neut., skimmed from pit	Total, Ardmore, OK
78	Spent amine	R15-SA-01	02-Aug-94	MDEA	Total, Ardmore, OK
79	Catalyst from reforming	R14-CR-01	07-Jun-94	Cyclic Pt reformer	BP, Toledo, OH
80	Sulfur complex sludge	R14-ME-01	07-Jun-94	DEA diatomaceous earth	BP, Toledo, OH
81	Off-spec product & fines from thermal processes	R14-TP-01	07-Jun-94	Delayed coking fines	BP, Toledo, OH
82	Spent amine	R14-SA-01	07-Jun-94	DEA from sump	BP, Toledo, OH
83	Catalyst from hydrotreating	R3B-TC-01	12-Jul-94	Naptha treater	Exxon, Billings, MT
84	Off-spec product & fines from thermal processes	R3B-TP-01	12-Jul-94	Fluid coker chunky coke	Exxon, Billings, MT
85	Catalyst from hydrotreating	R21-RC-01	31-Aug-94		Chevron, Port Arthur, TX
86	Treating clay from alkylation	R21-CA-01	31-Aug-94		Chevron, Port Arthur, TX
87	Catalyst from hydrocracking	R20-CC-01	30-Aug-94	H-Oil unit, moving bed	Star, Convent, LA
88	CSO sludge	R20-SO-01	30-Aug-94		Star, Convent, LA
89	Crude oil tank sludge	R19-CS-01	12-Oct-96		Pennzoil, Shreveport, LA
90	Desalting sludge	R11B-DS-01	01-Sep-94	collected by refinery	ARCO, Ferndale, WA
91	Crude oil tank sludge	R22-CS-01	21-Sep-94		Star, Port Arthur, TX
92	Residual oil tank sludge	R22-RS-01	21-Sep-94		Star, Port Arthur, TX
93	ASO	R7C-AS-01	12-Oct-96		BP, Belle Chase, LA
94	Catalyst from hydrotreating	R22-TC-01	21-Sep-94		Star, Port Arthur, TX
95	Spent caustic	R22B-LT-01	11-Oct-96	caustic from H2SO4 alky, sulfidic	Star, Port Arthur, TX
96	HF alkylation sludge	R7C-HS-01	12-Oct-96	Filter press	BP, Belle Chase, LA
97	Catalyst from isomerization	R23B-CI-01	19-Apr-95	Pt catalyst	Chevron, Salt Lake City
98	Treating clay from isomerization	R23B-IC-01	19-Apr-95	Mole sieve, butamer feed treater	Chevron, Salt Lake City
99	Treating clay from alkylation	R23-CA-01	19-Jan-95	propane treater	Chevron, Salt Lake City
100	Off-spec sulfur	R23-SP-01	19-Jan-95		Chevron, Salt Lake City
101	Treating clay from clay filtering	R23-CF-01	19-Jan-95	diesel washed	Chevron, Salt Lake City
102	Desalting sludge	R24-DS-01	20-Apr-95	Sludge from Lakos separator	Phibro, Houston, TX
Familiarization Samples					
F1	Spent Caustic	A-SC-01	08-May-93	Commingled.	Marathon, Garyville
F2	Catalyst from hydrotreating	A-HC-01	10-May-93	Cobalt molybdenum.	Marathon, Garyville
F3	Sulfur complex sludge	C-SS-01	23-Jun-93	MEA Reclaimer sludge.	Amoco, Texas City
F4	ASO	C-AS-01	23-Jun-93	Neutralized.	Amoco, Texas City
F5	Crude oil tank sludge	B-TS-01	15-May-93	Filter cake.	Sun, Philadelphia
F6	Sulfuric Acid Catalyst	B-SA-01	15-May-93	Spent from third unit.	Sun, Philadelphia

- Two samples of treating clay from isomerization/extraction were collected. This residual is available only for a brief period during unit turnarounds, which may occur only every 3-5 years. This residual was not readily available from the set of facilities selected for sampling.
- One sample of treating clay from lube oil processes was collected. Due to the specialty of the processes, a limited number of refineries produce lube oils and not all of these facilities use clay filtering. This residual is not readily available, and was extremely difficult to find from the facilities randomly selected for sampling.
- One sample of residual upgrading sludge was collected. This residual is not readily available from the set of facilities selected for sampling.
- No samples of off-specification product from residual upgrading were collected. As is discussed further in Section 3.7.2, the Agency believes that this residual was inappropriately classified as a residual due to the evaluation of inaccurate old data. This residual was reported as being generated by only one facility in the 1992 §3007 Survey.

Each of the samples collected was analyzed for the total and Toxicity Characteristics Leaching Procedure (TCLP) concentrations of the target analytes identified in the QAPjP. In addition, certain residuals were tested for different characteristics based on the Agency's understanding of the residuals developed during the engineering site visits. Each sample was also analyzed for the ten most abundant nontarget volatile and the 20 most abundant nontarget semi-volatile organics in each sample. These tentatively identified compounds (TICs) were not subjected to QA/QC evaluation (e.g., MS/MSD analyses) and thus were considered tentative.

2.2.6 Split Samples Analyzed by API

The American Petroleum Institute (API) accompanied the EPA contractor (SAIC) on virtually all sampling trips and collected split samples of many of the record samples. API's analytical results for a number of the samples were made available to EPA for comparison purposes. In general, the Agency found that the API and EPA split sample analyses had very good agreement. Appendix B of the Listing Background Document, available in the RCRA docket for the 11/20/95 proposal, presents the Agency's comparison of the split sample results.

2.2.7 Synthesis

The results of the Agency's four year investigation have been synthesized in this report and in the Listing Background document for the November 20, 1995 proposed rulemaking. Additional supporting documents are available in the docket for that rulemaking.

3.0 PROCESS AND WASTE DESCRIPTIONS

3.1 REFINERY PROCESS OVERVIEW

Refineries in the United States vary in size and complexity and are generally geared to a particular crude slate and, to a certain degree, reflect the demand for specific products in the general vicinity of the refinery. Figure 3.1 depicts a process flow diagram for a hypothetical refinery that employs the major, classic unit operations used in the refinery industry. These unit operations are described briefly below, and in more detail in the remainder of this section. Each subsection is devoted to a major unit operation that generates one or more of the study residuals of concern and provides information related to the process, a description of the residual and how and why it is generated, management practices used by the industry for each residual, the results of the Agency's characterization of each residual, and summary information regarding source reduction opportunities and achievements.

Storage Facilities: Large storage capacities are needed for refinery feed and products. Sediments from corrosion and impurities accumulate in these storage tanks. The consent decree identifies sludges from the storage of crude oil, clarified slurry oil, and unleaded gasoline for consideration as listed wastes. Residual oil storage tank sludge was identified as a study residual.

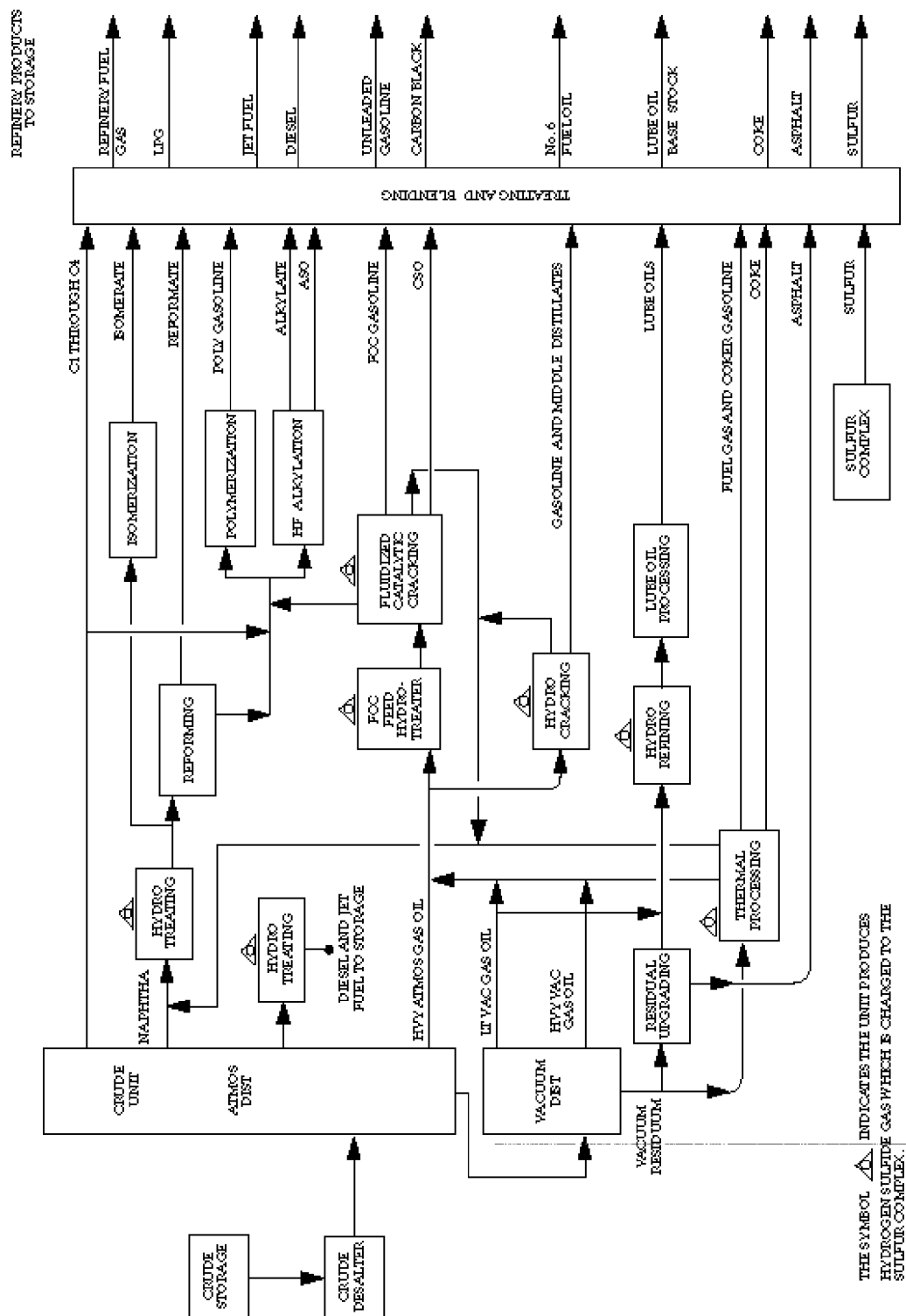
Crude Desalting: Clay, salt, and other suspended solids must be removed from the crude prior to distillation to prevent corrosion and deposits. These materials are removed by water washing and electrostatic separation. Desalting sludge is a study residual.

Distillation: After being desalted, the crude is subjected to atmospheric distillation, separating the crude by boiling point into light ends, naphtha, middle distillate (light and heavy gas oil), and a bottoms fraction. The bottoms fraction is frequently subjected to further distillation under vacuum to increase gas oil yield. No residuals from distillation are under investigation.

Catalytic Cracking: Catalytic cracking converts heavy distillate to compounds with lower boiling points (e.g., naphthas), which are fractionated. Cracking is typically conducted in a fluidized bed reactor with a regenerator to continuously reactivate the catalyst. Cracking catalysts are typically zeolites. The flue gas from the regenerator typically passes through dry or wet fines removal equipment and carbon monoxide oxidation prior to being released to the atmosphere. Catalyst and fines, as well as sediments from storage of and solids removal from clarified slurry oil (the bottoms fraction from catalytic cracking), are listing residuals of concern.

Hydroprocessing: Hydroprocessing includes (1) **hydrotreating and hydrorefining (or hydrodesulfurization)**, which improve the quality of various products (e.g., by removing sulfur, nitrogen, oxygen, metals, and waxes and by converting olefins to saturated compounds); and (2) **hydrocracking**, which cracks heavy materials, creating lower-boiling, more valuable products. Hydrotreating is typically less severe than hydrorefining and is applied to lighter cuts. Hydrocracking is a more severe operation than hydrorefining, using higher temperature and longer contact time, resulting in significant reduction in feed molecular size. Hydroprocessing catalysts

Figure 3.1. Simplified Refinery Process Flow Diagram



are typically some combination of nickel, molybdenum, and cobalt. Typical applications of hydroprocessing include treating distillate to produce low-sulfur diesel fuel, treating naphtha reformer feed to remove catalyst poisons, and treating catalytic cracking unit feed to reduce catalyst deactivation. Hydrotreating and hydrorefining catalysts are listing residuals, while hydrocracking catalyst is a study residual.

Thermal Processes: Thermal cracking uses the application of heat to reduce high-boiling compounds to lower-boiling products. **Delayed (batch) or fluid (continuous) coking** is essentially high-severity thermal cracking and is used on very heavy residuum (e.g., vacuum bottoms) to obtain lower-boiling cracked products. (Residuum feeds are not amenable to catalytic processes because of fouling and deactivation.) Products are olefinic and include gas, naphtha, gas oils, and coke. **Visbreaking** is also thermal cracking; its purpose is to decrease the viscosity of heavy fuel oil so that it can be atomized and burned at lower temperatures than would otherwise be necessary. **Other processes** conducting thermal cracking also would be designated as thermal processes. Off-spec product and fines is a listing residual from these processes.

Catalytic Reforming: Straight run naphtha is upgraded via reforming to improve octane for use as motor gasoline. Reforming reactions consist of (1) dehydrogenation of cycloparaffins to form aromatics and (2) cyclization and dehydrogenation of straight chain aliphatics to form aromatics. Feeds are hydrotreated to prevent catalyst poisoning. Operations may be semiregenerative (cyclic), fully-regenerative, or continuous (moving bed) catalyst systems. Precious metal catalysts are used in this process. Spent reforming catalyst is a listing residual.

Polymerization: Polymerization units convert olefins (e.g., propylene) into higher octane polymers. Two principal types of polymerization units include fixed-bed reactors, which typically use solid-supported phosphoric acid as the catalyst, and Dimersol® units, which typically use liquid organometallic compounds as the catalyst. Spent polymerization catalyst is a study residual.

Alkylation: Olefins of 3 to 5 carbon atoms (e.g., from catalytic cracking and coking) react with isobutane (e.g., from catalytic cracking) to give high octane products. Sulfuric (H_2SO_4) or hydrofluoric (HF) acid act as catalysts. Spent sulfuric acid, sulfuric acid alkylation sludges, and HF sludges are listing residuals, while spent HF acid, acid soluble oil and treating clays are study residuals.

Isomerization: Isomerization converts straight chain paraffins in gasoline stocks into higher octane isomers. Isomer and normal paraffins are separated; normal paraffins are then catalytically isomerized. Precious metal catalysts are used in this process. Spent catalysts and treating clays are study residuals from this process.

Extraction: Extraction is a separation process using differences in solubility to separate, or extract, a specific group of compounds. A common application of extraction is the separation of benzene from reformate. Treating clay is a study residual from this process.

Lube Oil Processing: Vacuum distillates are treated and refined to produce a variety of lubricants. Wax, aromatics, and asphalts are removed by unit operations such as solvent extrac-

tion and hydroprocessing; clay may also be used. Various additives are used to meet product specifications for thermal stability, oxidation resistances, viscosity, pour point, etc. Treating clay is a study residual from this process.

Residual Upgrading: Vacuum tower distillation bottoms and other residuum feeds can be upgraded to higher value products such as higher grade asphalt or feed to catalytic cracking processes. Residual upgrading includes processes where asphalt components are separated from gas oil components by the use of a solvent. It also includes processes where the asphalt value of the residuum is upgraded (e.g., by oxidation) prior to sale. Off-spec product and fines, as well as process sludges, are study residuals from this category.

Blending and Treating: Various petroleum components and additives are blended to different product (e.g., gasoline) specifications. Clay and caustic may be used to remove sulfur, improve color, and improve other product qualities. Spent caustic is a listing residual, while treating clay is a study residual.

Sulfur Recovery: Some types of crude typically contain high levels of sulfur, which must be removed at various points of the refining process. Sulfur compounds are converted to H_2S and are removed by amine scrubbing. The H_2S often is converted to pure sulfur in a Claus plant. Off-gases from the Claus plant typically are subject to tail gas treating in a unit such as a SCOT® treater for additional sulfur recovery. Process sludges and spent catalysts are listing residuals; off-spec product and off-spec treating solutions are study residuals.

Light Ends (Vapor) Recovery: Valuable light ends from various processes are recovered and separated. Fractionation can produce light olefins and isobutane for alkylation, n-butane for gasoline, and propane for liquid petroleum gas (LPG). Caustic may be used to remove sulfur compounds. Spent caustic is a listing residual of concern.

3.2 CRUDE OIL DESALTING

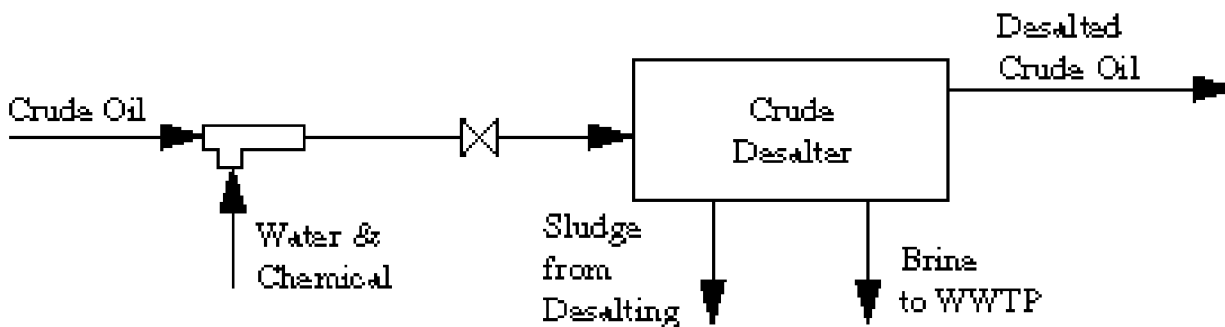
Crude oil removed from the ground is contaminated with a variety of substances, including gases, water, and various minerals (dirt). Cleanup of the crude oil is achieved in two ways. First, field separation, located near the site of the oil wells, provides for gravity separation of the three phases: gases, water (with entrained dirt), and crude oil. The second cleanup operation is crude oil desalting conducted at the refinery. Crude oil desalting is a water-washing operation prior to atmospheric distillation which achieves additional crude oil cleanup. Water washing removes much of the water-soluble minerals and suspended solids from the crude. If these contaminants were not removed, they would cause a variety of operating problems throughout the refinery including the blockage of equipment, the corrosion of equipment, and the deactivation of catalysts.

3.2.1 Process Description

To operate efficiently and effectively the crude oil desalter must achieve an intimate mixing of the water wash and crude, and then separate the phases so that water will not enter downstream unit operations. The crude oil entering a desalting unit is typically heated to 100 - 300°F to achieve reduced viscosity for better mixing. In addition, the desalter operates at pressures of at least 40 lb/in² gauge to reduce vaporization. Intimate mixing is achieved through a throttling valve or emulsifier orifice and the oil-water emulsion is then introduced into a gravity settler. The settler utilizes a high-voltage electrostatic field to agglomerate water droplets for easier separation. Following separation, the water phase is discharged from the unit, carrying salt, minerals, dirt, and other water-soluble materials with it.

Desalting efficiency can be increased by the addition of multiple stages, and in some cases acids, caustic, or other chemicals may be added to promote additional treatment. A simplified process flow diagram for crude oil desalting is shown in Figure 3.2.1.

Figure 3.2.1. Desalting Process Flow Diagram



3.2.2 Desalting Sludge

3.2.2.1 Description

Desalting sludge is continuously separated from the crude oil and settles to the bottom of the desalter with the water wash. The majority of the sludge is removed from the desalter with the water wash and is discharged to the facility's wastewater treatment plant. The sludge then becomes part of the wastewater treatment sludges. On a regular basis (e.g., weekly), water jets at the bottom of the desalter are activated, stirring up sludge that has built up on the bottom of the unit and flushing it to wastewater treatment. This process is known as “mud washing” and allows the units to continue to operate without shutting down for manual sludge removal.

Desalting sludge is removed from the unit during unit turnarounds, often associated with turnarounds of the distillation column. These turnarounds are infrequent (e.g., every several years). Some refineries operate enough desalters in parallel to allow for turnarounds while the distillation columns continue to operate.

At turnaround, the sludge can be removed in several different ways. Based on the results of the questionnaire, approximately half of the total number of desalting sludge waste streams are removed from the desalter using a vacuum truck, permanent or portable piping, or other similar means where the sludge is removed in a slurry state. Another 25 percent of the sludges are removed manually by maintenance workers while the removal method for the remaining 25 percent of the sludges was not clear. The questionnaire data further indicated that half of the desalting sludge streams are further piped or stored in tanker trucks following removal, while the remaining half are stored in drums or a dumpster.

As with some tank sludges, some facilities remove their desalting sludge using a vacuum truck or similar slurring device, then centrifuge the material and store the solids in a drum or dumpster. Such procedures would explain the apparent discrepancy between the number of streams removed as solid and the number of streams stored in containers (presumably also as solid). Questionnaire data indicate that approximately 10 percent of the streams generated in 1992 underwent dewatering or a similar volume reduction procedure.

3.2.2.2 Generation and Management

Eighty facilities reported generating a total quantity of 4,841 MT of desalting sludge in 1992, according to the 1992 RCRA §3007 Survey. Desalting sludge includes material generated from turnaround operations; materials continuously flushed to wastewater treatment are generally omitted. The survey contained a residual identification code for “desalter sludge”. All residuals assigned this code, and any misidentified residual determined to be desalter sludge generated from a process assigned process code for “desalting” were considered “desalter sludge” residuals. This corresponds to residual code 02-A in Section VII.2 of the survey and process code 01-A, 01-B, 01-C, and 01-D in Section IV-1.C. Quality assurance was conducted to ensure that all desalting sludge residuals were correctly identified and coded.

Based on the results of the survey, 148 facilities use desalting units and are thus likely to generate desalting sludge. Due to the infrequent generation of this residual, not all of these 148 facilities generated desalting sludge in 1992. In addition, some facilities do not generate desalting sludge at all because they do not conduct unit turnarounds, or do not find any settled sludge when conducting maintenance. However, there was no reason to expect that 1992 would not be a typical year with regard to desalting sludge generation and management. Table 3.2.1 provides a description of the quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

Table 3.2.1. Generation Statistics for Desalting Sludge, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Discharge to onsite wastewater treatment facility	25	9	2,041.62	81.66
Disposal in onsite or offsite underground injection	1	0	2.00	2.00
Disposal in offsite Subtitle D landfill	14	1	28.80	2.06
Disposal in offsite Subtitle C landfill	15	5	221.40	14.76
Disposal in onsite Subtitle D landfill	2	0	102.00	51.00
Offsite incineration	8	1	56.00	7.00
Offsite land treatment	4	0	53.20	13.30
Onsite land treatment	8	0	345.76	43.22
Recovery onsite in a coker	3	3	52.40	17.47
Transfer for direct use as a fuel or to make a fuel	17	1	1,937.60	113.98
TOTAL	97	20	4,840.78	49.90

Note that 42 percent of desalting sludge volumes are discharged to onsite wastewater treatment. During engineering site and sampling visits, it was observed that refineries would simply flush the sludge to wastewater treatment during desalter turnarounds in a manner similar to mud washing.

Over half of the desalting sludge residuals (48) were reported to be managed as characteristically hazardous (most commonly D018), accounting for 40 percent of the sludge volume.⁴ Twenty seven of these streams were managed with F or K listed wastes, reflecting their frequent management in wastewater treatment systems.

⁴These percentages do not match up directly with any one of the management scenarios because the number of streams and the volume are a combination of several management scenarios (i.e., managed in WWTP, Subtitle C landfill, transfer as a fuel, etc.).

3.2.2.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.2.1. The Agency gathered information suggesting other management practices had been used in other years including: “disposal in onsite Subtitle C landfill” (86 MT), “disposal in onsite surface impoundment” (1 MT), and “recovery onsite via distillation” (0.5 MT). These non-1992 practices are generally comparable to practices reported in 1992 (i.e., off-site Subtitle C landfilling and recovery in a coker). The very small volume reported to have been disposed in a surface impoundment reflects the management of this residual with the refinery’s wastewater in a zero discharge wastewater treatment facility with a final evaporation pond; this management practice is comparable to the 1992 reported practice of “disposal in onsite wastewater treatment facility”. EPA also compared management practices reported for desalting sludge to those reported for crude oil tank sediment because of expected similarities in composition and management. Similar land disposal practices were reported for both residuals.

3.2.2.4 Characterization

Two sources of residual characterization data were developed during the industry study:

- Table 3.2.2 summarizes the physical properties of desalting sludge as reported in Section VII.A of the RCRA §3007 survey.
- Four record samples of desalting sludge were collected and analyzed by EPA. These sludges represent the various types of desalting operations and sludge generation methods typically used by the industry and are summarized in Table 3.2.3. The samples represent sludges generated during turnaround operations (the most common way desalting sludge is generated), and also represents sludges both with and without undergoing interim deoiling or dewatering steps.

Table 3.2.4 provides a summary of the characterization data collected under this sampling effort. The record samples are believed to be representative of desalting sludge as typically generated by the industry. All four record samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. Two of three samples analyzed for TCLP Benzene exhibited the toxicity characteristic for benzene (i.e., the level of benzene in these samples' TCLP extracts exceeded the corresponding regulatory level). Only constituents detected in at least one sample are shown in Table 3.2.4.

3.2.2.5 Source Reduction

The electrostatic desalter removes most of the solids, salts and water present in the crude oil. Minimizing the introduction or recycling of solids to the crude unit will assist the reduction of desalting sludge, since solids attract oil and produce emulsions.

The amount of desalting sludge formed is a function of the efficiency of the desalter but more fundamentally is a characteristic of the crude oil. Methods of managing desalting sludge center on increasing the efficiency of the desalter and de-emulsifiers which increase the capability of separating the oil, water and solid phases.

Reference	Waste Minimization/Management Methods
"New Process Effectively Recovers Oil From Refinery Waste Streams." <i>Oil & Gas Journal</i> . August 15, 1994.	Enhanced separation of oil, water and solids.
"Filtration Method Efficiently Desalts Crude in Commercial Test." <i>Oil & Gas Journal</i> . May 17, 1993.	Alternative process: single-stage filtration.
D.T. Cindric, B. Klein, A.R. Gentry and H.M. Goma. "Reduce Crude Unit Pollution With These Technologies." <i>Hydrocarbon Processing</i> . August, 1993.	Includes topic of more effective separation of phases in desalter.
"Waste Minimization in the Petroleum Industry: A Compendium of Practices." API. November, 1991.	Practices described: 1. Shear mixing used to mix desalter wash water and crude. 2. Turbulence avoided by using lower pressure water to prevent emulsion formation.

Table 3.2.2. Desalter Sludge: Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	50th %	90th %
pH	118	144	6.10	7.00	8.40
Reactive CN, ppm	60	202	0.15	1.00	250.00
Reactive S, ppm	67	195	0.80	82.00	500.00
Flash Point, °C	73	189	43.89	60.00	94.44
Oil and Grease, vol%	103	159	5.00	16.00	70.00
Total Organic Carbon, vol%	47	215	1.00	15.00	35.00
Vapor Pressure, mm Hg	14	248	0.00	10.50	150.00
Vapor Pressure Temperature, °C	9	253	20.00	30.00	40.00
Viscosity, lb/ft-sec	3	259	0.00	0.00	1500.00
Viscosity Temperature, °C	5	257	0.00	30.00	50.00
Specific Gravity	69	193	0.90	1.10	1.70
BTU Content, BTU/lb	56	206	270.00	3,590.00	10,000.00
Aqueous Liquid, %	157	105	0.00	30.00	78.00
Organic Liquid, %	151	111	0.00	15.00	50.00
Solid, %	170	92	9.00	45.00	100.00
Other, %	111	151	0.00	0.00	30.00
Particle >60 mm, %	10	252	0.00	0.00	50.00
Particle 1-60 mm, %	9	253	0.00	90.00	100.00
Particle 100 µm-1 mm, %	12	250	0.00	10.00	100.00
Particle 10-100 µm, %	9	253	0.00	0.00	100.00
Particle <10 µm, %	8	254	0.00	0.00	0.00
Median Particle Diameter, microns	7	255	0.00	200.00	2,000.00

¹Facilities were not required to do additional testing, therefore information provided was based on previously collected data or engineering judgment.

Table 3.2.3. Desalting Sludge Record Sampling Locations

Sample No.	Facility	Description
R1-DS-01	Marathon, Indianapolis, IN	From electrostatic precipitator turnaround. Sludge/slurry removed directly from unit
R9-DS-01	Murphy, Superior, WI	Turnaround sludge/slurry taken from drums
R11-DS-01	ARCO, Ferndale, WA	Dewatered sludge from turnaround taken from bins
R24-DS-01	Phibro, Houston, TX	Continuously generated "solids" from brine separator; sample mostly aqueous

Table 3.2.4. Desalting Sludge Characterization

Volatile Organics - Method 8260A µg/kg					(µg/L)			
	CAS No.	R1-DS-01	R9-DS-01	R11B-DS-01	R24-DS-01	Average Conc	Maximum Conc	Comments
Acetone	67641	200,000	< 625	< 1,250	160	67,292	200,000	
Benzene	71432	230,000	22,000	28,000	36	93,333	230,000	
n-Butylbenzene	104518	< 62,500	42,000	31,000	< 5	36,500	42,000	1
sec-Butylbenzene	135988	< 62,500	24,000	19,000	< 5	21,500	24,000	1
Ethylbenzene	100414	180,000	150,000	48,000	J 7	126,000	180,000	
Isopropylbenzene	98828	< 62,500	36,000	27,000	< 5	31,500	36,000	1
p-Isopropyltoluene	99876	< 62,500	25,000	18,000	< 5	21,500	25,000	1
Methylene chloride	75092	J 49,000	< 625	< 1,250	< 5	16,958	49,000	
Methyl ethyl ketone	78933	< 62,500	< 625	< 1,250	41	NA	NA	
n-Propylbenzene	103651	< 62,500	74,000	44,000	< 5	60,167	74,000	
Toluene	108883	660,000	220,000	61,000	77	313,667	660,000	
1,2,4-Trimethylbenzene	95636	350,000	230,000	68,000	35	216,000	350,000	
1,3,5-Trimethylbenzene	108678	140,000	85,000	34,000	12	86,333	140,000	
o-Xylene	95476	290,000	190,000	54,000	38	178,000	290,000	
m,p-Xylenes	108383 / 106423	950,000	380,000	67,000	70	465,667	950,000	
Naphthalene	91203	< 62,500	55,000	54,000	32	54,500	55,000	1
TCLP Volatile Organics - Methods 1311 and 8260A µg/L								
	CAS No.	R1-DS-01	R9-DS-01	R11B-DS-01	R24-DS-01	Average Conc	Maximum Conc	Comments
Acetone	67641	770	< 50	B 260	NA	360	770	
Benzene	71432	5,200	1,700	280	NA	2,393	5,200	
Ethylbenzene	100414	550	340	120	NA	337	550	
Toluene	108883	5,200	2,000	760	NA	2,653	5,200	
1,2,4-Trimethylbenzene	95636	< 250	190	J 69	NA	130	190	1
1,3,5-Trimethylbenzene	108678	< 250	J 54	J 22	NA	38	54	1
Methylene chloride	75092	1,000	1,200	J 23	NA	741	1,200	
o-Xylene	95476	1,100	540	200	NA	613	1,100	
m,p-Xylene	108383 / 106423	2,400	1,100	490	NA	1,330	2,400	
Naphthalene	91203	< 250	< 50	JB 52	NA	51	52	1
Semivolatile Organics - Method 8270B µg/kg					(µg/L)			
	CAS No.	R1-DS-01	R9-DS-01	R11B-DS-01	R24-DS-01	Average Conc	Maximum Conc	Comments
Benzo(a)pyrene	50328	J 4,300	J 5,600	< 10,000	< 5	4,950	5,600	1
Carbazole	86748	< 13,200	< 20,625	< 20,000	43	NA	NA	
Chrysene	218019	< 6,600	< 10,313	J 13,000	< 5	9,971	13,000	
Dibenzofuran	132649	< 6,600	12,000	J 16,000	< 5	11,533	16,000	
2,4-Dimethylphenol	105679	< 6,600	< 10,313	< 10,000	190	NA	NA	
Fluorene	86737	J 6,000	24,000	26,000	< 5	18,667	26,000	

Table 3.2.4. Desalting Sludge Characterization (continued)

Semivolatile Organics - Method 8270B µg/kg (continued)						(µg/L)				
	CAS No.	R1-DS-01		R9-DS-01		R11B-DS-01	R24-DS-01	Average Conc	Maximum Conc	Comments
Phenanthrene	85018	J	12,000		61,000	68,000	26	47,000	68,000	
Phenol	108952	<	6,600	<	10,313	< 10,000	900	NA	NA	
Pyrene	129000	<	6,600	J	10,000	< 10,000	< 5	8,867	10,000	
1-Methylnaphthalene	90120		48,000		220,000	180,000	81	149,333	220,000	
2-Methylnaphthalene	91576		66,000		330,000	240,000	130	212,000	330,000	
2-Methylchrysene	3351324	<	13,200	J	13,000	< 20,000	< 10	13,000	13,000	1
2-Methylphenol	95487	<	6,600	<	10,313	< 10,000	340	NA	NA	
3/4-Methylphenol	NA	<	6,600	<	10,313	< 10,000	530	NA	NA	
Naphthalene	91203		33,000		110,000	130,000	110	91,000	130,000	
TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L										
	CAS No.	R1-DS-01		R9-DS-01		R11B-DS-01	R24-DS-01	Average Conc	Maximum Conc	Comments
Benzo(a)pyrene	50328	JB	16	<	50	< 50	NA	16	16	1
Bis(2-ethylhexyl)phthalate	117817	<	50	B	500	< 50	NA	200	500	
Di-n-butyl phthalate	84742	<	50	<	50	J 20	NA	20	20	1
2,4-Dimethylphenol	105679	J	26	<	50	J 73	NA	50	73	
1-Methylnaphthalene	90120	J	32	J	50	J 71	NA	51	71	
2-Methylnaphthalene	91576	J	34	J	60	J 92	NA	62	92	
2-Methylphenol	95487	J	48	J	25	J 43	NA	39	48	
3/4-Methylphenol	NA	J	68	J	40	J 49	NA	52	68	
Naphthalene	91203	J	86	J	61	120	NA	89	120	
Phenol	108952		200	<	50	J 54	NA	101	200	
Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg						(mg/L)				
	CAS No.	R1-DS-01		R9-DS-01		R11B-DS-01	R24-DS-01	Average Conc	Maximum Conc	Comments
Aluminum	7429905		2,600		3,700	7,500	11.0	4,600	7,500	
Antimony	7440360		16.0		14.0	< 6.00	0.28	12.0	16.0	
Arsenic	7440382		16.0		34.0	16.0	0.05	22.0	34.0	
Barium	7440393		2,200		1,700	1,400	1.80	1,767	2,200	
Beryllium	7440417	<	0.50	<	0.50	1.40	< 0.0025	0.80	1.40	
Cadmium	7440439		2.90		1.80	3.40	< 0.0025	2.70	3.40	
Calcium	7440702		16,000		5,300	3,300	230	8,200	16,000	
Chromium	7440473		110		76.0	150	0.17	112	150	
Cobalt	7440484		27.0		16.0	13.0	< 0.025	18.7	27.0	
Copper	7440508		680		340	430	1.20	483	680	
Iron	7439896		71,000		55,000	77,000	200	67,667	77,000	

Table 3.2.4. Desalting Sludge Characterization (continued)

Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg (continued)					(mg/L)			
	CAS No.	R1-DS-01	R9-DS-01	R11B-DS-01	R24-DS-01	Average Conc	Maximum Conc	Comments
Lead	7439921	1,100	390	160	0.36	550	1,100	
Magnesium	7439954	2,200	3,200	3,300	68.0	2,900	3,300	
Manganese	7439965	310	250	450	1.60	337	450	
Mercury	7439976	41.0	4.40	39.0	0.0085	28.1	41.0	
Molybdenum	7439987	17.0	19.0	16.0	< 0.034	17.3	19.0	
Nickel	7440020	76.0	100	110	0.48	95.3	110	
Potassium	7440097	< 500	< 500	< 500	41.0	NA	NA	
Selenium	7782492	140	22.0	75.0	< 0.0025	79.0	140	
Sodium	7440235	< 500	< 500	< 500	830	NA	NA	
Thallium	7440280	< 1.00	7.00	< 1.00	< 0.005	3.00	7.00	
Vanadium	7440622	36.0	37.0	120	0.12	64.3	120	
Zinc	7440666	1,300	1,900	5,400	2.20	2,867	5,400	
TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L								
	CAS No.	R1-DS-01	R9-DS-01	R11B-DS-01	R24-DS-01	Average Conc	Maximum Conc	Comments
Aluminum	7429905	7.60	< 1.00	< 1.00	NA	3.20	7.60	
Barium	7440393	2.60	< 1.00	3.50	NA	2.37	3.50	
Calcium	7440702	580	150.00	54.0	NA	261	580	
Chromium	7440473	0.87	< 0.05	0.12	NA	0.35	0.87	
Iron	7439896	210	24.00	190	NA	141	210	
Magnesium	7439954	71.0	< 25.0	< 25.0	NA	40.3	71.0	
Manganese	7439965	6.00	1.60	4.60	NA	4.07	6.00	
Nickel	7440020	< 0.20	< 0.20	0.52	NA	0.31	0.52	
Zinc	7440666	2.00	2.90	57.00	NA	20.6	57.0	

Comments:

- 1 Detection limits greater than the highest detected concentration are excluded from the calculations.

Notes:

- B Analyte also detected in the associated method blank.
 J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
 NA Not Applicable.

3.3 HYDROCRACKING

Petroleum refining hydroprocessing techniques include hydrocracking, hydrotreating, and hydrorefining. Hydrorefining and hydrotreating processes and their respective catalyst residuals are described in the Listing Background Document for the November 20, 1995 proposed rule. Hydrocracking processes are similar to hydrotreating and hydrorefining processes in that they remove organic sulfur and nitrogen from the process feeds, but differ in that they also serve to break heavier fraction feeds into lighter fractions. As refinery crudes have become heavier, hydrocracking, a more recent process development compared to long-established conversion processes such as thermal cracking, has become more widely used. The current trend to heavier feeds and lighter high-quality feeds causes hydrocracking to offer advantages to future refining operations.

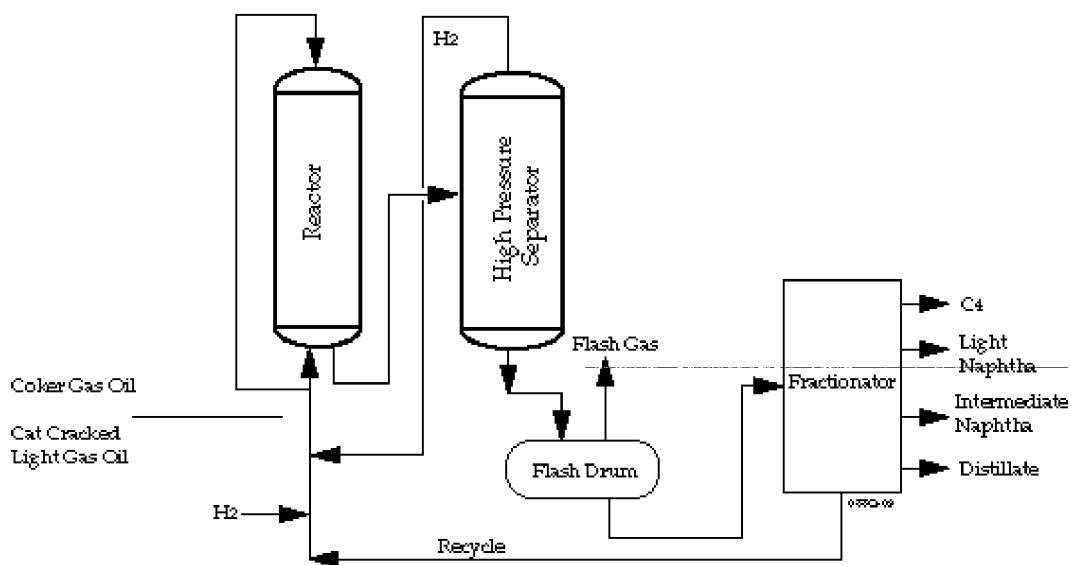
In addition, hydrocracking is a versatile process, and under mild conditions can be utilized for hydrotreating (typically fractions that need to be saturated to give good burning quality) and under more severe conditions can be utilized as a cracker (typically feeds that are too heavy or too contaminant-laden for catalytic cracking). As a result of this flexibility, hydrocracking processes can appear in refinery operations in a number of different places.

3.3.1 Process Description

The process flow for hydrocracking is similar to that for hydrotreating: the feed is mixed with a hydrogen-rich gas, pumped to operating pressure and heated, and fed to one or more catalytic reactors in series. Hydrocracking units are typically designed with two stages: the first uses a hydrotreating catalyst to remove nitrogen and heavy aromatics, while the second stage conducts cracking. The catalysts for each stage are held in separate vessels. Organic sulfur and nitrogen are converted to H_2S and NH_3 , and some unsaturated olefins or aromatics are saturated or cracked to form lighter compounds. In addition, heavy metal contaminants are adsorbed onto the catalyst. Following the reactor, the effluent is separated via stabilization and fractionation steps into its various fractions. There are two major differences between hydrocracking and hydrotreating: 1) operating pressures are much higher, in the range from 2,000 - 3,000 lb/in² gauge, and 2) hydrogen consumption is much higher, in the range from (1,200 - 1,600 SCF/barrel of feed), dependent on the feed. The feed is generally a heavy gas oil or heavier stream.

Catalysts employed in hydrocracking reactors have multiple functions. First, the catalyst has a metallic component (cobalt, nickel, tungsten, vanadium, molybdenum, platinum, palladium, or a combination of these metals) responsible for the catalysis of the hydrogenation and desulfurization/denitrification reactions. In addition, these metals are supported on a highly acidic support (silica-alumina, acid-treated clays, acid-metal phosphates, or alumina) responsible for the cracking reactions. A simplified process flow diagram is shown in Figure 3.3.1.

Figure 3.3.1. Hydrocracking Process Flow Diagram



3.3.2 Spent Hydrocracking Catalyst

3.3.2.1 Description

Metal deposition acts to deactivate, or poison, the hydrocracking catalyst. In addition, carbon from the cracking reactions deactivates the catalyst. The catalyst's life is dependent on the severity of cracking and metal deposition and is changed out every 6 months to 8 years. The catalyst closest to the entrance (top) of the reactor becomes deactivated first, and for this reason is sometimes replaced more frequently than the entire reactor contents (a "topping" operation). When catalyst activity is unacceptable, the reactor is taken out of service and typically undergoes a hydrogen sweep to burn residual hydrocarbon, then a nitrogen sweep to cool the reactor and remove occupational hazards such as hydrogen sulfide and benzene. Such procedures were reported by most facilities. The following additional procedures were reported to be employed by fewer facilities, typically only one or two:

- Oxidation (to burn residual hydrocarbon)
- Cat nap technology or diesel wash (to lower vapor pressure of hazardous volatiles)
- Wet dump, water wash, or soda ash wash (to neutralize sulfides and remove volatiles)
- Steam stripping (to remove volatiles)
- Evacuation (a technique possibly similar to nitrogen sweep)
- Some facilities report using no pretreatment methods prior to catalyst removal.

In some processes, a moving bed of catalyst is used instead of a fixed bed. In this process, catalyst is continuously and slowly moved countercurrent to the hydrocarbon flow. Spent catalyst is generated almost continuously and fresh catalyst added as needed for makeup. This configuration differs significantly from the fixed bed design with respect to spent catalyst generation frequency.

Unlike hydrotreating and hydrorefining catalysts (discussed in *Listing Background Document*), both precious metal and nonprecious metal catalysts are used in hydrocracking processes. Based on a total of 46 facilities reporting spent hydrocracking catalyst generation, 34 (74%) reported using nickel/molybdenum, 11 (24%) reported using nickel/tungsten, and 11 (24%) reported using palladium. An additional 16 facilities (35%) reported using other metals in their catalyst such as cobalt, copper, magnesium, monometallic nickel, phosphorus, tin, and zinc. As stated in Section 3.3.1, many hydrocracking units are constructed as a hydrorefining stage followed by a cracking stage. In reporting catalysis use, refineries may not have differentiated between hydrorefining and cracking functions in their response. In this section, data for both pretreatment (hydrorefining function) and hydrocracking catalysts are presented.

Approximately 2,500 MT of the hydrocracking catalyst generated in 1992 was identified as displaying hazardous characteristics.⁵ This is approximately 15 percent of the total volume managed. The most commonly displayed hazardous waste codes were D001 (ignitable), D003 (reactive), D004 (TC arsenic) and D018 (TC benzene).

3.3.2.2 Generation and Management

During reactor change-outs, spent hydrocracking catalysts are removed from the reactors using a variety of techniques including gravity dumping and water drilling. Upon removal from the catalyst bed, the catalyst may be screened to remove fines or catalyst support media. The catalyst is typically stored in covered bins pending shipment off site for disposal or recovery.

Twenty-eight facilities reported generating a total quantity of 18,000 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be “spent hydrocracking catalyst” if they were assigned a residual identification code of “spent solid catalyst” or “spent catalyst fines” and were generated from a process identified as a hydrocracking unit. These correspond to residual code 03-A in Section VII.2 of the questionnaire and process code 05 in Section IV-1.C of the questionnaire. Quality assurance was conducted by ensuring that all hydrocracking catalysts previously identified in the questionnaire (i.e., in Section V.B) were assigned in Section VII.2.

⁵These percentages do not match up directly with any one of the management scenarios because the number of streams and the volume are a combination of several management scenarios (i.e., Subtitle C landfill, transfer for metals reclamation, etc.).

Based on the results of the questionnaire, 47 facilities use hydrocracking units and are thus likely to generate spent hydrocracking catalyst. Due to the infrequent generation of this residual, not all of these 47 facilities generated spent catalyst in 1992. However, there was no reason to expect that 1992 would not be a typical year with regard to hydrocracking catalyst generation and management. Table 3.3.1 provides a description of the quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

Table 3.3.1. Generation Statistics for Hydrocracking Catalyst, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Disposal in offsite Subtitle D landfill	7	0	1,592.70	227.53
Disposal in offsite Subtitle C landfill	8	0	991.50	123.94
Reuse onsite as replacement catalyst for another unit	1	0	159.40	159.40
Transfer metal catalyst for reclamation or regeneration	45	2	13,185.56	293.01
Transfer to another petroleum refinery	14	0	2,100.00	150.00
TOTAL	75	2	18,029.16	295.56

3.3.2.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.3.1. The Agency gathered information suggesting other management practices had been used in other years including: “disposal in onsite Subtitle D landfill” (8 MT) and “other recycling, reclamation, or reuse: cement plant” (320 MT). These non-1992 practices are comparable to 1992 practices (i.e., off-site Subtitle D landfilling) or to typical practices for alumina-based catalysts (e.g., cement plants).

The Agency has no other data to suggest other management practices are used for hydrocracking catalysts due to the physical characteristics and chemical composition of the waste. EPA compared the management practice reported for hydrocracking catalysts to those reported for hydrotreating and hydrorefining catalysts based on expected similarities. Similar land disposal practices were reported for all three residuals.

3.3.2.4 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.3.2 summarizes the physical properties of the spent catalyst as reported in Section VII.A of the §3007 survey.
- Three record samples of spent hydrocracking catalyst were collected and analyzed by EPA and are summarized in Table 3.3.3. The record samples represent the most frequently used catalysts (i.e., nickel/tungsten and nickel/molybdenum, together used

by well over half of the refineries with hydrocracking processes. In addition, heavy gas oil or similar distillate/residual feed is the most common application of hydrocracking reactors, according to the questionnaire. Therefore, the record samples are expected to represent most of the spent catalyst generated in the industry.

However, another frequently used catalyst (palladium) is not represented, and catalysts employing feeds other than heavy gas oil (e.g., lube oil) may not have the same characteristics when spent.

Table 3.3.4 provides a summary of the characterization data collected under this sampling effort. All three record samples were analyzed for total and TCLP levels of volatiles, semivolatiles, metals and ignitability. One of three samples exhibited the ignitability characteristic. Only constituents detected in at least one sample are shown in Table 3.3.4.

Table 3.3.2. Hydrocracking Catalyst Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	50th %	90th %
pH	39	102	5.00	6.80	9.14
Reactive CN, ppm	21	120	0.30	3.20	10.00
Reactive S, ppm	38	103	1.00	12.50	9,500.00
Flash Point, °C	36	105	60.00	157.50	200.00
Oil and Grease, vol%	17	124	0.00	0.36	9.00
Total Organic Carbon, vol%	14	127	0.00	0.63	8.00
Specific Gravity	54	87	0.80	1.74	3.15
Specific Gravity Temperature, °C	10	131	17.80	20.00	25.00
BTU Content, BTU/lb	4	137	0.00	0.00	7,485.00
Aqueous Liquid, %	64	77	0.00	0.00	0.00
Organic Liquid, %	63	78	0.00	0.00	0.00
Solid, %	101	40	100.00	100.00	100.00
Other, %	62	79	0.00	0.00	0.00
Particle >60 mm, %	28	113	0.00	0.00	0.00
Particle 1-60 mm, %	42	99	95.00	99.00	100.00
Particle 100 µm-1 mm, %	31	110	0.00	1.00	5.00
Particle 10-100 µm, %	27	114	0.00	0.00	0.00
Particle <10 µm, %	27	114	0.00	0.00	0.00
Median Particle Diameter, microns	13	128	0.00	1,600.00	2,000.00

¹Facilities were not required to do additional testing, therefore information provided was based on previously collected data or engineering judgement.

Table 3.3.3. Spent Hydrocracking Catalyst Record Sampling Locations

Sample No.	Facility	Description
R2-CC-01	Shell, Wood River, IL	Nickel/tungsten catalyst, fixed bed, heavy gas oil feed
R8A-CC-01	Amoco, Texas City, TX	Nickel/molybdenum catalyst, moving bed, heavy gas oil feed
R20-CC-01	Star, Convent, LA	Mixed nickel/tungsten and nickel/molybdenum catalyst, moving bed, heavy gas oil feed

3.3.2.5 Source Reduction

There is little that can be done to reduce the quantity of these generated catalyst since, by design, they must be periodically replaced with fresh catalyst. As a result, the greatest opportunity for waste minimization arises from sending these materials offsite for metals regeneration, reclamation, or other reuse.

Refinery hydrocracking catalysts generally consist of cobalt and molybdenum or nickel and molybdenum on an alumina support. Typically, the catalysts are regenerated after use. However, industry is interested in finding more specific, long-lasting catalysts. Extensive research is performed in producing new catalysts. Information on hydrotreating and hydrorefining catalysts are also presented below because some of this information may be relevant to hydrocracking catalysts.

Reference	Waste Minimization/Management Methods
Monticello, D.J. "Biocatalytic Desulfurization." <i>Hydrocarbon Processing</i> . February, 1994.	An alternative to metal catalysts is the development of microorganisms that can catalyze the reaction.
"NPRA Q&A 1: Refiners Focus on FCC, Hydroprocessing, and Alkylation Catalyst." <i>Oil & Gas Journal</i> . March 28, 1994.	Methods in improving catalyst life and performance.
Gorra, F., Scribano, G., Christensen, P., Anderson, K.V., and Corsaro, O.G. "New Catalyst, Improve Presulfiding Result in 4+ Year Hydrotreater Run." <i>Oil & Gas Journal</i> . August 23, 1993.	Material substitution to extend catalyst life.
"Petroleum-derived Additive Reduces Coke on Hydrotreating Catalyst." <i>Oil & Gas Journal</i> . December 27, 1993.	Process modification extends life of catalyst.
"Waste Minimization in the Petroleum Industry: A Compendium of Practices." API. November, 1991.	Practices listed: 1. Metals reclamation, 2. Recycling to cement, 3. Recycling to fertilizer plants.

Table 3.3.4. Spent Hydrocracking Catalyst Characterization

Volatile Organics - Method 8260A µg/kg							
	CAS No.	R2-CC-02	R8A-CC-01	R20-CC-01	Average Conc	Maximum Conc	Comments
Acetone	67641	5,300	< 6,250	< 1,250	3,275	5,300	1
Acrolein	107028	2,500	< 6,250	< 1,250	1,875	2,500	1
Benzene	71432	370,000	15,000	< 1,250	128,750	370,000	
n-Butylbenzene	104518	10,000	40,000	12,000	20,667	40,000	
sec-Butylbenzene	135988	< 1,250	18,000	13,000	10,750	18,000	
Ethylbenzene	100414	35,000	95,000	< 1,250	43,750	95,000	
Isopropylbenzene	98828	< 1,250	34,000	3,700	17,625	34,000	
p-Isopropyltoluene	99876	< 1,250	28,000	8,500	12,583	28,000	
Naphthalene	91203	< 1,250	64,000	7,600	24,283	64,000	
n-Propylbenzene	103651	5,000	49,000	< 1,250	27,000	49,000	
Toluene	108883	300,000	120,000	< 1,250	140,417	300,000	
1,2,4-Trimethylbenzene	95636	25,000	170,000	21,000	72,000	170,000	
1,3,5-Trimethylbenzene	108678	8,000	48,000	4,200	20,067	48,000	
o-Xylene	95476	23,000	120,000	3,400	48,800	120,000	
m,p-Xylenes	108383 / 106423	60,000	250,000	7,100	105,700	250,000	
TCLP Volatile Organics - Methods 1311 and 8260A µg/L							
	CAS No.	R2-CC-02	R8A-CC-01	R20-CC-01	Average Conc	Maximum Conc	Comments
Benzene	71432	10,000	230	< 50	3,427	10,000	
Ethylbenzene	100414	470	180	< 50	233	470	
Methylene chloride	75092	< 50	250	< 50	117	250	
Toluene	108883	6,600	640	< 50	2,430	6,600	
1,2,4-Trimethylbenzene	95636	J 94	120	J 44	86	120	
1,3,5-Trimethylbenzene	108678	< 50	< 50	J 61	54	61	
o-Xylene	95476	290	270	< 50	203	290	
m,p-Xylene	108383 / 106423	750	410	< 50	403	750	
Semivolatile Organics - Method 8270B µg/kg							
	CAS No.	R2-CC-02	R8A-CC-01	R20-CC-01	Average Conc	Maximum Conc	Comments
Acenaphthene	83329	< 165	20,000	32,000	17,388	32,000	
Benz(a)anthracene	56553	< 165	J 6,900	< 10,313	3,533	6,900	1
Benzo(a)fluoranthene (total)	NA	< 165	J 5,000	31,000	12,055	31,000	
Benzo(g,h,i)perylene	191242	< 165	28,000	42,000	23,388	42,000	
Benzo(a)pyrene	50328	< 165	J 3,100	29,000	10,755	29,000	
Carbazole	86748	< 330	74,000	J 24,000	32,777	74,000	
4-Chlorophenyl phenyl ether	7005723	< 165	< 4,125	83,000	29,097	83,000	
Chrysene	218019	< 165	17,000	68,000	28,388	68,000	
Dibenzofuran	132649	1,200	9,700	J 13,000	7,967	13,000	
7,12-Dimethylbenz(a)anthracene	57976	< 165	< 4,125	45,000	16,430	45,000	

Table 3.3.4. Spent Hydrocracking Catalyst Characterization (continued)

Semivolatile Organics - Method 8270B µg/kg (continued)							
	CAS No.	R2-CC-02	R8A-CC-01	R20-CC-01	Average Conc	Maximum Conc	Comments
Fluoranthene	206440	< 165	20,000	25,000	15,055	25,000	
Fluorene	86737	2,800	40,000	82,000	41,600	82,000	
Indeno(1,2,3-cd)pyrene	193395	< 165	J 4,600	< 10,313	2,383	4,600	1
3-Methylcholanthrene	56495	< 165	< 4,125	23,000	9,097	23,000	
2-Methylchrysene	3351324	< 330	J 13,000	64,000	25,777	64,000	
1-Methylnaphthalene	90120	< 330	56,000	230,000	95,443	230,000	
2-Methylnaphthalene	91576	< 165	110,000	390,000	166,722	390,000	
2-Methylphenol	95487	< 165	< 4,125	J 7,000	3,763	7,000	
Naphthalene	91203	< 165	43,000	45,000	29,388	45,000	
Phenanthrene	85018	1,200	180,000	160,000	113,733	180,000	
Pyrene	129000	1,600	430,000	680,000	370,533	680,000	
TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L							
	CAS No.	R2-CC-02	R8A-CC-01	R20-CC-01	Average Conc	Maximum Conc	Comments
Carbazole	86748	< 100	J 78	< 100	78	78	1
2,4-Dimethylphenol	105679	< 50	J 23	J 44	34	44	1
1-Methylnaphthalene	90120	< 100	J 24	J 41	33	41	1
2-Methylnaphthalene	91576	< 50	J 46	J 59	52	59	
2-Methylphenol	95487	J 66	J 70	J 25	54	70	
3/4-Methylphenol (total)	NA	J 76	J 49	J 17	47	76	
Naphthalene	91203	< 50	J 44	J 26	35	44	1
Phenol	108952	J 53	< 50	J 63	55	63	
Phenanthrene	85018	< 50	J 23	< 50	23	23	1
Pyrene	129000	< 50	J 42	< 50	42	42	1
Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg							
	CAS No.	R2-CC-02	R8A-CC-01	R20-CC-01	Average Conc	Maximum Conc	Comments
Aluminum	7429905	120,000	53,000	110,000	94,333	120,000	
Antimony	7440360	< 6.0	220	< 6.0	77.3	220	
Arsenic	7440382	12.0	29.0	< 5.0	15.3	29.0	
Beryllium	7440417	< 0.5	160	18.0	59.5	160	
Chromium	7440473	130	68.0	< 1.0	66.3	130	
Cobalt	7440484	24.0	440	< 5.0	156	440	
Copper	7440508	55.0	35.0	< 2.5	30.8	55.0	
Iron	7439896	52,000	2,200	570	18,257	52,000	
Lead	7439921	< 0.3	15.0	1.6	5.6	15.0	
Manganese	7439965	390	16.0	< 1.5	136	390	
Molybdenum	7439987	< 6.5	5,400	17,000	7,469	17,000	
Nickel	7440020	19,000	28,000	27,000	24,667	28,000	

Table 3.3.4. Spent Hydrocracking Catalyst Characterization (continued)

Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg (continued)							
	CAS No.	R2-CC-02	R8A-CC-01	R20-CC-01	Average Conc	Maximum Conc	Comments
Selenium	7782492	< 0.5	4.0	< 0.5	1.7	4.0	
Sodium	7440235	1,200	2,000	< 500	1,233	2,000	
Vanadium	7440622	37.0	140,000	49,000	63,012	140,000	
Zinc	7440666	82.0	110	< 2.0	64.7	110	
TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L							
	CAS No.	R2-CC-02	R8A-CC-01	R20-CC-01	Average Conc	Maximum Conc	Comments
Aluminum	7429905	26.0	< 1.00	< 1.00	9.33	26.00	
Chromium	7440473	0.35	< 0.05	< 0.05	0.15	0.35	
Iron	7439896	130	< 0.50	< 0.50	43.7	130	
Manganese	7439965	10.0	< 0.08	< 0.08	3.38	10.0	
Nickel	7440020	110	3.60	0.43	38.0	110	
Vanadium	7440622	< 0.25	4.70	< 0.25	1.73	4.70	
Zinc	7440666	0.58	< 0.10	< 0.10	0.26	0.58	
Miscellaneous Characterization							
		R2-CC-02	R8A-CC-01	R20-CC-01			
Ignitability (oF)		138	145	NA			

42 Comments:

- 1 Detection limits greater than the highest detected concentration are excluded from the calculations.

Notes:

- B Analyte also detected in the associated method blank.
 J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
 ND Not Detected.
 ND Not Applicable.

