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Waste Minimization for Selected Residuals in the Petroleum Refining Industry

Hazardous Waste Minimization and Management Division
Office of Solid Waste

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PREFACE

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I. Introduction

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 I.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.

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. The Agency 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 census survey of the industry.

Part of the investigation is to evaluate waste minimization opportunities for these RCs that have been implemented by the industry. Both source reduction and recycling techniques were reviewed and are described in this document. Source reduction is where the volume and/or toxicity of the residual is reduced. Recycling is where the residual is put to a useful purpose. Only those source reduction and recycling opportunities that are used, or could be applied, to the 29 RCs are reported here.

This report is organized as follows:

- Section II provides an industry overview, process description, and process flow diagrams.

- Section III presents residual descriptions for each of the 29 RCs and what source reduction options exist.
- Section IV presents the sources used, describes major findings, and evaluates the quantity and quality of waste minimization information for each source.
- Section V is the conclusion.

Table I.1. Petroleum Refining Residuals Identified in the EDF/EPA Consent Decree

Sludges\Sediments:

Clarified slurry oil sediments and filter solids from catalytic cracking (L) (CSO sludge)
Unleaded storage tank sediments (L)
Crude storage tank sediments (L)
Process sludge from sulfur complex and H_2S removal facilities (L) (sulfur complex sludge)
Sludge from HF alkylation (L)
Sludge from H_2SO_4 alkylation (L)
Desalting sludge from crude desalting (S)
Residual oil storage tank sludge (S)
Process sludge from residual upgrading (S)

Catalysts:

Catalyst from catalytic hydrotreating (L)
Catalyst from catalytic reforming (L)
Catalyst and fines from catalytic cracking (L) (FCC catalyst and FCC fines)
Catalyst from catalytic hydrorefining (L)
Catalyst from H_2SO_4 alkylation (L)
Catalyst from sulfur complex and H_2S removal facilities (L) (Claus and tail gas treating catalysts)
Catalyst from isomerization process (S)
Catalyst from catalytic hydrocracking (S)
Catalyst from polymerization (S)
Catalyst from HF alkylation (S)

Off-Spec Products:

Off-spec product and fines from thermal processes (L)
Off-spec product and fines from residual upgrading (S)
Off-spec product from sulfur complex and H_2S removal facilities (S)

Treating Clays:

Treating clay from clay filtering (S)
Treating clay from lube oil processing (S)
Treating clay from the extraction/isomerization process (S)
Treating clay from alkylation (S)

Miscellaneous Residuals:

Spent caustic from liquid treating (L)
Off-spec treating solution from sulfur complex and H_2S removal facilities (S)
Acid-soluble oil from HF alkylation (S)

L: Requires listing determination as per the EDF/EPA consent decree.
S: Requires study as per the EDF/EPA consent decree.

II. Industry Overview

A. Petroleum Refining Industry Profile

In 1992, the U.S. petroleum refining industry consisted of 185 refineries owned by 91 corporations. Refineries can be classified in terms of size and complexity of operations. Forty-four percent of the refineries process less than 50,000 barrels per day of crude, while the 20 largest companies account for 56 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.

The refining industry has undergone significant restructuring over the past 15 years. 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. Refinery utilization rates over the 1980 to 1992 period rose from 75 percent to 90 percent. 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 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. Although atmospheric and vacuum distillation, catalytic cracking, and their associated treating and reforming operations will remain the primary refinery operations, new production operations continue to be added. These include coking and desulfurization processes.

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 are causing refineries to make process modifications to their catalytic cracker units, as well as installing additional sulfur removal hydrotreaters and unit processes to manufacture additives.

B. Process Descriptions

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 II.1 depicts a hypothetical refinery that employs the major, classic unit operations used in the refinery industry. These unit operations are described briefly below.

Storage Facilities: Large storage capacities are needed for feed and products. Sediments can accumulate in these storage units. The consent decree identifies sediments (sludges) from the storage of crude oil, clarified slurry oil, and unleaded gasoline for consideration as listed wastes. Residual oil storage tank sediments were 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 prior to being released to the atmosphere. Catalyst and fines, as well as sediments from storage of 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 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 category 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, or, less frequently, fully-regenerative, continuous, or 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 extraction 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.

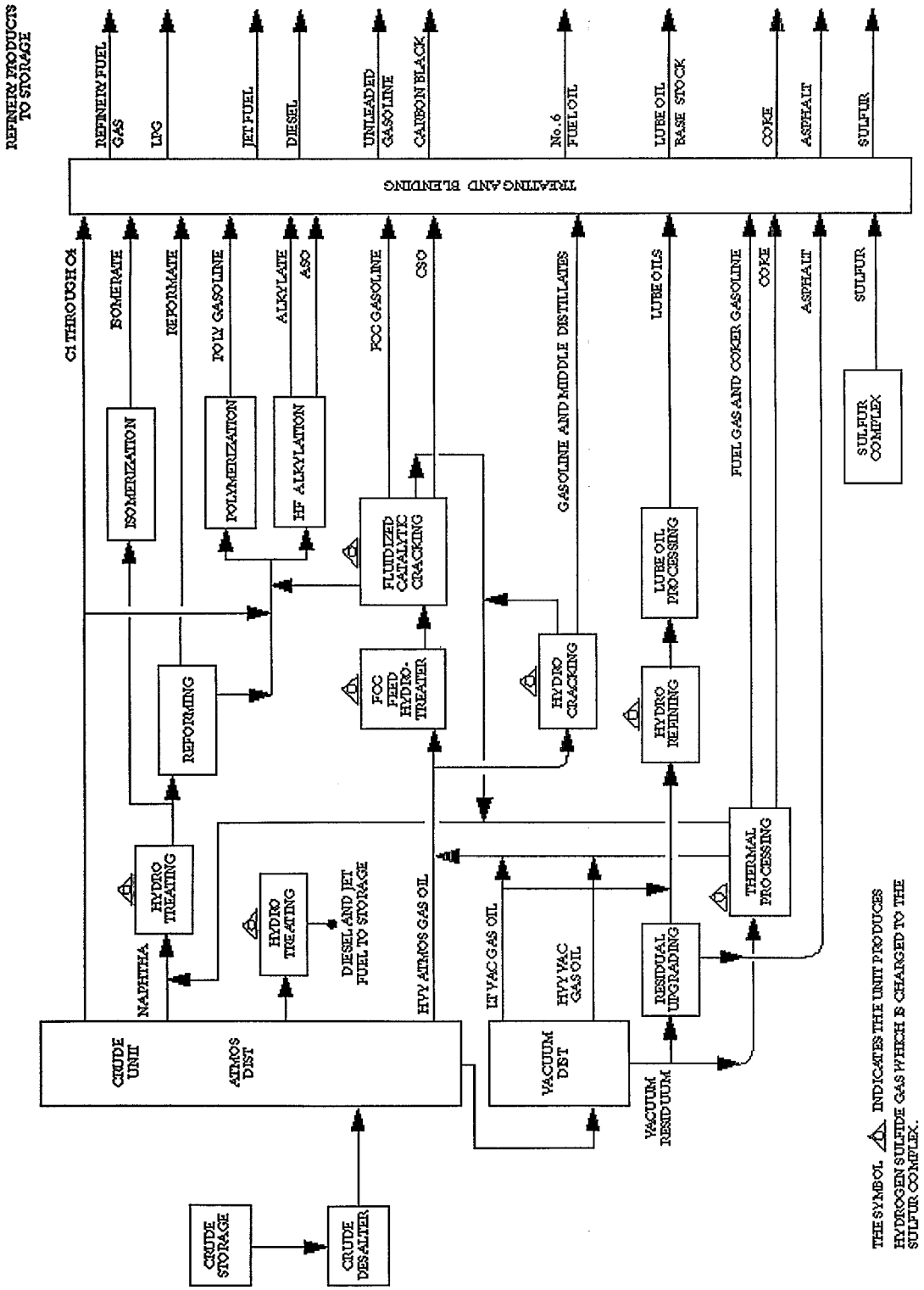
Residual Upgrading: Vacuum tower distillation bottoms and other residuum feeds can be upgraded to higher value products such as higher grade asphalt or feed to catalytic cracking processes. Residual upgrading includes processes where asphalt components are separated from gas oil components by the use 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 typically is converted to pure sulfur in a Claus plant. Off-gases from the Claus plant typically are subject to tail gas treating in a SCOT® unit 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). No residuals from this process are under investigation for either the listing determination or the study.

Figure II.1. Petroleum Refining Simplified Process Flow Diagram



III. Residual Descriptions and Source Reduction Practices for Residuals of Concern

Crude Oil Tank Sediment

Residual Description

Crude oil is stored prior to processing in an atmospheric distillation tower. It is necessary to inventory crude oil to insure a steady supply. Tank sediments are emulsions that form from solid particles, heavy oil, and water that settle to the bottom of tanks over time. Periodically the tanks are emptied and the sediments removed. Cleaning is performed to either inspect the tank, repair it, and/or remove excess quantities of sediments which build up and interfere with the tank operation.

Hazardous constituents potentially present in crude oil tank sediments are identical to those found in crude oil. They include benzene, toluene, ethylbenzene, and xylene (BTEX), sulfur (including H_2S), polynuclear aromatic hydrocarbons (PAHs), and metals.

Source Reduction Practices

Based on results from Section V of the survey, over 80 percent of facilities reporting tank cleanings since 1991 used some type of *in situ* treatment procedure prior to removing the sediments. This treatment most often consisted of washing the tank with hydrocarbon (e.g., naphtha) or water. The liquid captures organic compounds in the sediments; the liquid is typically recycled to the crude unit via the recovered oil system. Note that additional facilities may perform similar procedures outside of the tank which are not reported as *in situ* treatment.

Additional source reduction strategies which have been employed include the following:

- Use of mixers to decrease sediments generation: Many facilities use permanent mixers in their crude tanks to deliver homogenous feed to the crude unit. These mixers also serve the function of entraining particulates and heavy hydrocarbon, which would result as tank sediments, into the crude unit feed. Over 65 percent of crude tanks were report to have mixers.

- 100 percent onsite recycling of sediments in process units: Observations from site visits showed that 100 percent recycling of tank bottoms is being achieved at a small number of sites. These facilities remove sediments from the tank and use it as feedstock in another onsite unit. Factors influencing the practicality of this technique have not been investigated, but probably depend on the types of available process unit and crude type. The industry, as a whole, recycled about 44 percent of the tank sediment was reported to be recycled to the onsite coker, distillation unit, catalytic cracker, or asphalt production unit.

- Increased efficiency of washing steps: One facility has attempted to increase the amount of oil recovered from crude oil tank sediments by experimenting with different surfactants and wash procedures. Such efforts reduce the volume of sediments generated for disposal.

- Control of spills: Several facilities install some type of sheeting near tank openings to collect spills. Spilled sediment is recovered from the basin and re-incorporated with the rest of the sediment. Spill reduction decreases the quantity of contaminated soil to be disposed with the tank sediment.

The prevalence of these techniques are presented in Table III-1. This information is based on 1992 RCRA §3007 Survey data.

Table III-1. Volume Reduction Methods Used for Crude Oil Tank Sediment

Volume Reduction Method	Number of Streams[1]
Filtration, Centrifuging, Dewatering	48
Emulsion Break, Melting	6
Settling	9
Water Wash	1
TOTAL	64 (23% of total streams)

[1] The number of streams and percentage do not directly correlate to the total number of streams presented in Table IV-4 due to multiple volume reduction methods may be performed on a single stream.
Source: Section VI of RCRA §3007 Survey.

Unleaded Gasoline Tank Sediment

Residual Description

Finished gasoline is blended from many refinery streams such as alkylate, reformate, and straight run naphtha. Additives such as oxygenates are also added during blending. The finished gasoline is stored in tanks prior to sale. Periodically, the tanks are emptied, cleaned, and inspected.

The tank bottoms, sediments, or "sludge," are unlike the heavy hydrocarbon sludges that typify crude oil tank sediments. Rather, small amounts of rust and scale are removed from the tank bottom. Hazardous constituents present in gasoline will also be present in the tank bottoms; these include BTEX.

Source Reduction Practices

Most, if not all, of the refineries visited by SAIC and EPA wash the tank prior to entry and sludge removal to remove the high level of airborne hydrocarbons present in the tank atmosphere which could create both explosion and toxicity hazards (e.g., benzene) if not removed. Based on the Survey, over 85 percent of the facilities cleaning a tank since 1991 reported washing, most often with water. The liquid captures organic compounds in the tank bottoms; hydrocarbons in the liquid are typically recycled to the crude unit via the facility sewer. Many facilities do not generate a sludge from cleaning; the entire volume is treated in the refinery wastewater treatment system.

Other than washing the tank bottoms, no other pollution prevention strategies are identified. Table III-2 summarizes the prevalence of waste minimization activities from the survey.

Table III-2. Volume Reduction Methods Used for Unleaded Tank Sediment

Volume Reduction Method	Number of Streams[1]
Filtration, Centrifuging, Dewatering	7
Settling	3
Water Wash	11
TOTAL	21 (8% of total streams)

[1] The number of streams and percentage do not directly correlate to the total number of streams presented in Table IV-4 due to multiple volume reduction methods may be performed on a single stream.
Source: Section VI of RCRA §3007 Survey.

Residual Oil Tank Sediment

Residual Description

Residual oil is generally considered to be equivalent to No. 6 fuel oil and is typically produced from units such as atmospheric and vacuum distillation, hydrocracking, delayed coking, and visbreaking. Residual oil tank sediment (or sludge) consists of heavy hydrocarbons, rust and scale from process pipes and reactors, and entrapped oil that settles to the bottom of the tank.

Hazardous constituents potentially present in residual oil tank sludge are similar to those found in crude oil tank sludge. They include BTEX, sulfur (including H_2S), PAHs, and metals.

Source Reduction Practices

In many respects, the procedures for cleaning residual oil tanks are similar to those used for cleaning crude tanks. The sludge is a mixture of heavy hydrocarbons which may be partially recovered using an organic or surfactant wash, similarly to the cleaning of a crude tank.

Pollution prevention strategies which have been employed, or could be employed, include the following:

- Solids reduction in storage tank
- Use as feedstock in process units

Table III-3. Volume Reduction Methods Used for Residual Oil Tank Sediment

Volume Reduction Method	Number of Streams[1]
Filtration, Centrifuging, Dewatering	19
Distillate Wash	3
Settling	2
Thermal Emulsion Break	1
Phase Separation	1
TOTAL	26 (32% of total streams)

[1] The number of streams and percentage do not directly correlate to the total number of streams presented in Table IV-4 due to multiple volume reduction methods may be performed on a single stream.
Source: Section VI of RCRA §3007 Survey.

1. Solids Reduction in Storage Tank

Use of mixers to decrease sludge generation: Many facilities use permanent mixers in their tanks to deliver homogenous product. These mixers also serve the function of entraining particulates and heavy hydrocarbon, which would result as tank sludge. About 50 percent of the tanks were reported to have mixers.

2. Recycling

Upon cleaning a residual oil storage tank, sixteen facilities remove the sludge and recycles it to either the onsite coker, distillation unit, catalytic cracker, or asphalt production unit. Table III-3 summarizes the prevalence of waste minimization activities from the survey.

CSO Sediment and/or Filter Solids

Residual Description

The bottoms stream from a fractionator of a catalytic cracker is called slurry oil or clarified slurry oil (CSO). This material is typically sent directly to a storage tank for sale (cartridge filters are occasionally used to remove particulates, such as FCC fines, from the incoming feed). It may also be blended with other heavy refinery products. CSO sediments and/or filter solids (sludge) can be generated from the intermittent cleaning of CSO storage tanks. Periodically the tanks are emptied and the sludge removed. Cleaning is performed to either inspect the tank, repair it, and/or remove excess quantities of sludge which build up and interfere with the tank operation. According to the survey, they undergo *in situ* treatment less frequently than crude or gasoline tanks (approximately 55 percent of facilities cleaning a CSO tank since 1991 report *in situ* treatment).

Hazardous constituents potentially present in CSO tank sludge are similar to those found in crude oil tank sediments. They include BTEX, sulfur (including H_2S), PAHs, and metals. In addition, FCC catalyst will be present in the CSO. This solid will settle out in the tanks and add significantly to the sludge volume.

Source Reduction Practices

In many respects, the procedures for cleaning CSO tanks are similar to those used for cleaning crude tanks. The sludge is a mixture of heavy hydrocarbons which may be partially recovered using an organic or surfactant wash, similarly to the cleaning of a crude tank.

Pollution prevention strategies which have been employed, or could be employed, include the following:

- Solids reduction of storage tank influent
- Use as feedstock in process units

1. Solids Reduction in Storage Tank Influent

Of the 117 refineries that have catalytic crackers, approximately half use a hydroclone, slurry settler, or similar device to remove the solids (catalyst fines) in the slurry oil. These devices can remove 80+ percent of the solids, which are recycled back to the FCC. The "clarified" slurry oil is sent to tankage. Although this practice may lower sludge generation in product CSO tanks, one refinery has stated that this practice lowers the efficiency of the FCC because the recycle stream is heavier, and more difficult to crack, than the gas oil feed.

Newer FCC units have higher efficiency cyclones; at least one other refinery has modified its FCC to incorporate new cyclones. The cyclones should minimize the amount of fines that escape from the reactor with the overhead product and eventually leave the unit entrained in the decant oil.

2. Recycling

Upon cleaning a CSO storage tank, one facility removes the sludge and recycles it onsite in a coker. Table III-3 summarizes the prevalence of waste minimization activities from the survey. Recovered hydrocarbons were reported to be recycled to the catalytic cracker, coker, or asphalt production unit.

Table III-4. Volume Reduction Methods Used for CSO Sediments and/or Filter Solids

Volume Reduction Method	Number of Streams[1]
Filtration, Centrifuging, Dewatering	24
Emulsion Break	3
Distillate Wash	1
TOTAL	28 (24% of total streams)

[1] The number of streams and percentage do not directly correlate to the total number of streams presented in Table IV-4 due to multiple volume reduction methods may be performed on a single stream.
Source: Section VI of RCRA §3007 Survey.

Desalting Sludge

Residual Description

Crude oil removed from the ground is contaminated with a variety of substances, including gases, water, and various minerals (dirt). 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.

Hazardous constituents potentially present in desalting sludge are benzene and PAHs.

Source Reduction Practices

As with some tank sediments, some facilities remove their desalting sludge using a vacuum truck or similar slurrying 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). Survey data indicate that approximately 10 percent of the streams generated in 1992 underwent dewatering or a similar volume reduction procedure.

Other source reduction techniques include: use of chemical demulsifiers and electrostatic precipitation can decrease the amount of desalting sludge generated; shear mixing used to mix desalter wash water and crude; turbulence avoided by using lower pressure water to prevent emulsion formation; and alternative processes such as single-stage filtration.

Catalytic Cracking Catalyst and Fines

Residual Description

Fluid catalytic cracking is by far the most prevalent catalytic cracking process. In this process, catalyst and gas oil feed are contacted in a fluidized bed. Cracked, lower molecular weight hydrocarbon product is discharged at the top of the unit, after passing through cyclones to separate the reactor catalyst. This product is fractionated. The reactor catalyst is continuously regenerated in a parallel vessel. Flue gas from the regenerator contains some catalyst fines, which can be removed by control devices including electrostatic precipitators and wet scrubbers. To maintain activity, regenerated (equilibrium) catalyst is almost continuously removed and fresh catalyst injected into the system. FCC catalyst is deactivated by various chemical compounds, such as coke and metals. Coke is removed in the unit's regeneration cycle, but metals are not.

Source Reduction Practices

As with CSO sludge, higher efficiency cyclones will decrease the amount of catalyst entrained in the cracked product. This, in turn, will decrease the quantity of fines in the flue gas to be captured by an air pollution control device (ESP or scrubber).

Hydrotreating/Hydrorefining/Hydrocracking Catalyst

Residual Description

Hydrotreating, hydrorefining, and hydrocracking are used to remove sulfur, nitrogen, and metals and to saturate olefins and aromatics. Hydrocracking and hydrorefining, also used for mild to extreme hydrocarbon cracking. They are used to protect downstream operations (such as reforming) or to meet product specifications (such as low sulfur diesel). The catalysts are most often some combination of cobalt, nickel, and molybdenum and in rare occasions tungsten.

Hazardous constituents include the base materials (i.e., cobalt, nickel, molybdenum, and aluminum), hydrogen sulfide, and other metals or organics present in the hydrocarbon feed.

Source Reduction Practices

Catalyst loses activity as the active sites become either deactivated due to chemical reaction with feed impurities or blocked due to coke precipitation on the catalyst surface. Catalyst can be regenerated *in situ* (e.g., oxygen burn), and must periodically be replaced (in whole or in part) with fresh catalyst during reactor shutdown.

Pollution prevention strategies which have been employed, or could be employed, include the following:

- Catalyst reuse: one facility regenerates their hydrotreating catalyst offsite for onsite reuse. Catalyst is often reused in another onsite hydrotreater or hydrorefiner which requires a lower activity.

- Increasing catalyst life: silica is often present in naphtha from the coker. However, silica is a hydrotreating catalyst poison and the naphtha is often hydrotreated. One facility is experimenting with a process change to reduce the quantity of silica in this stream, and hence extend the life of the hydrotreating catalyst. Research activities are constantly working on extending catalyst's life either by developing new catalyst or through the use of contaminant inhibitors.

Table III-5. Volume Reduction Methods Used for Hydrotreating/Hydrorefining/Hydrocracking Catalyst

Volume Reduction Method	Number of Streams[1]
Screening	12
TOTAL	12 (6% of total streams)

[1] The number of streams and percentage do not directly correlate to the total number of streams presented in Table IV-4 due to multiple volume reduction methods may be performed on a single stream.
Source: Section VI of RCRA §3007 Survey.

Reforming Catalyst

Residual Description

The purpose of reforming is to rearrange and dehydrogenate the feed stream to produce high octane gasoline and petrochemical feedstocks (e.g., benzene). The dehydrogenation reaction is strongly endothermic so units have multiple fixed bed reactors with heater passes in between. The catalyst is typically platinum chloride on alumina.

The catalyst is regenerated *in situ*, reused, and only replaced when regeneration is no longer effective due to catalyst poisoning (poisons include coke, sulfur, and some metals). The frequency of regeneration is specific to unit design and can range from continuously to once per year. Regeneration procedures typically include a coke burn, reactivation using a chlorine-containing compound, and occasionally a passivation step using a sulfur containing compound.

Hazardous constituents present in the spent reforming catalyst may include feed and product hydrocarbon (e.g., benzene).

Source Reduction Practices

Source reduction strategies which have been employed, or could be employed, include optimizing the feed and operating parameters. Refineries with multiple reforming units will often adjust the feed to the particular needs of each unit. One refinery claims that by operating one such unit with optimal feeds the life of the catalyst charge is prolonged. However, it is not known if catalyst life on the one unit is prolonged at the expense of the other.

Table III-6. Volume Reduction Methods Used for Reforming Catalyst

Volume Reduction Method	Number of Streams[1]
Screening	2
TOTAL	2 (2% of total streams)

[1] The number of streams and percentage do not directly correlate to the total number of streams presented in Table IV-4 due to multiple volume reduction methods may be performed on a single stream.
Source: Section VI of RCRA §3007 Survey.

Catalyst from Isomerization

Residual Description

The purpose of isomerization is to increase the refinery's production of high octane, low aromatic gasoline. Principal applications of isomerization at refineries are naphtha isomerization, which produces a gasoline blending component, and butane isomerization, which produces isobutane feed for the alkylation unit.

The most prevalent catalyst used for both butane and naphtha isomerization is platinum or platinum chloride on alumina or zeolite. When the catalyst loses activity, it is removed from the reactor and replaced with fresh catalyst.

Hazardous constituents present in the spent isomerization catalyst may include hydrocarbons such as benzene.

Source Reduction Practices

Source reduction strategies which have been employed, or could be employed, include optimizing the feed and operating parameters. Removing catalyst contaminants from the feed, such as H_2S and water, prior to introduction into the reactor can increase catalyst life.

Due to the precious metal make-up of the catalyst, almost all of it is recycled for metals reclamation.

Treating Clay from Isomerization/Extraction

Residual Description

The purpose of isomerization is to increase the refinery's production of high octane, low aromatic gasoline. Principal applications of isomerization at refineries are naphtha isomerization, which produces a gasoline blending component, and butane isomerization, which produces isobutane feed for the alkylation unit. Not all facilities with isomerization units use "treating clay," or adsorbents. However, solid adsorbents can be used in three places in the isomerization process:

- **Hydrocarbon feed purification**. Processes using platinum chloride catalysts require a purified feed. Both spent molecular sieve (for drying) and spent metal-alumina (for sulfur removal) are generated.

- **Hydrogen feed purification**. Processes using platinum chloride catalysts require dry hydrogen gas. Spent molecular sieve is generated.

- **Paraffin separation of the feed or product**. Various types of processes use adsorbents for paraffin separation. Molecular sieve is the most common adsorbent for this application.

Extraction processes separate more valuable chemical mixtures from a mixed aromatic and paraffinic stream. At refineries, extraction processes most commonly fall into two types: (1) "heavy end" extraction, commonly used in lube oil manufacture and deasphalting operations to upgrade and further process gas oils, and (2) gasoline component extraction, commonly used to separate some of the more valuable aromatics from naphtha. Treating clay is used to remove impurities from the hydrocarbon following extraction; the most common application is the filtering of the aromatic fraction prior to benzene distillation (likely to keep impurities out of the downstream fractions), although a small number of facilities use the clay to filter the benzene product stream only. The purpose of the clay is to remove olefins, suspended solids, and trace amount of solvent by a combination of adsorption and catalytic processes.

All of these adsorbents go through adsorption/desorption cycles. Over time, the adsorbent loses its capacity or efficiency and is removed from the vessel and replaced with fresh adsorbent.

Hazardous constituents contained in the treating clay are hydrocarbons such as benzene.

Source Reduction Practices

Treating clay for isomerization and extraction are generally used as a method of prolonging the life of the catalyst or as product polishing. Because they are used as a source reduction technique for other residuals, no source reduction methods for the clays were found.

Sulfuric Acid Alkylation Sludge and Catalyst

Residual Description

In the sulfuric acid (H_2SO_4) alkylation process, olefin and isobutane are contacted over concentrated liquid sulfuric acid in a reactor to generate high-octane alkylates for gasoline blending. The product is separated and neutralized and the separated acid is returned to the start of the process.

Acid requires periodic or continuous purging and replacement to minimize impurity levels and to maintain adequate acid strength. The spent acid is stored for subsequent shipment off-site for regeneration.

There are at least two sources of sludge in this process: sludge from process waters (e.g., caustic washwater) and sludge from unit operations (e.g., tanks, reactors).

Hazardous constituents in the spent sulfuric acid is, of course, sulfuric acid. Other constituents include hydrocarbons. In the sludge, hazardous constituents include hydrocarbons. The acid is neutralized and is not a hazard.

Source Reduction Practices

Source reduction strategies which have been employed, or could be employed, include the following:

- Decreasing oil content of spent sulfuric acid
- New alkylation process
- Use of soluble neutralizing agents

1. Decreasing Oil Content of Spent Sulfuric Acid

One refinery has adopted a procedure designed to minimize the amount of hydrocarbons entrained in the spent sulfuric acid. The facility mixes alkylation fractionation section bottoms (i.e., alkylate product) with the acid discharge from the primary settler. The heavy hydrocarbons absorb light hydrocarbons and carry them to the hydrocarbon layer in the secondary settler. This procedure significantly reduces the amount of butane and lighter hydrocarbons entrained in the spent acid. Rather than becoming part of the spent sulfuric acid residual stream or vented to the

refinery flare, the light hydrocarbons become alky butane or fuel gas. This practice was designed to reduce the danger of having hydrocarbons in the vapor space of the spent sulfuric acid tanks.

2. New Alkylation Process[1]

New processes using solid catalyst and small amounts of liquid catalyst would not generate neutralization sludges the same way as present H_2SO_4 alkylation units. This is still a preliminary process under development. In addition, the large quantities of spent liquid catalyst presently produced would not be generated in the new process.

3. Decreasing Sludge Generation

Refiners have decreased sludge generation by switching from insoluble neutralizing agents (e.g., lime) to soluble agents (sodium hydroxide).

HF Alkylation Catalyst and Sludge

Residual Description

Olefin and isobutane gases are contacted over concentrated liquid hydrofluoric (HF) acid in a reactor to generate high-octane alkylate for gasoline blending. The product is separated into alkylate and lighter fractions and neutralized; the HF acid is returned to the start of the process. A portion of the acid recycle stream is continuously distilled to generate purified HF acid (as overhead) and heavy hydrocarbon/azeotrope as bottoms. The bottoms, along with neutralization waters from product treatment, are commonly discharged to an neutralization pit. Sludge, consisting of neutralization compounds and organics, commonly forms in the tank and requires periodic removal.

Hazardous constituents in the acid is the HF acid. Hazardous constituents in the sludge includes oil. The sludge is neutralized and no longer contains hydrofluoric acid.

Source Reduction Practices

Source reduction strategies for the sludge and catalyst which have been employed, or could be employed, include the following:

- Segregation of oil from sludge (sludge)
- Raw material substitution (sludge)
- New Alkylation Process (sludge and catalyst)

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1 Solid catalyst alkylation processes are currently in the pilot plant stages but the *Oil and Gas Journal* reported that they would be commercially available as early as the end of 1995.

1. Segregation of Oil

Many refineries discharge regenerator bottoms (which includes oil) is discharged to the neutralization pit. However, many other refineries do not and reuse the oil in another part of the refinery. When discharged to the pit, the oil typically becomes part of a sludge removed for disposal.

2. Raw Material Substitution

Changing the neutralization agent used in the pit can affect management options for the generated sludge. Neutralization agents commonly include sodium hydroxide, calcium hydroxide (lime), or potassium hydroxide. Its purpose is to neutralize and remove fluorides from the alkylation plant wastewaters prior to being released to the sewer.

Some refineries have switched from neutralizing with lime which generates an insoluble salts to sodium hydroxide which is soluble. However, this may cause problems at the wastewater treatment plant in meeting NPDES permit levels for fluoride.

Several facilities use neutralizing agents which precipitate the fluoride compounds and produce a marketable product (e.g., calcium fluoride). A small number of refineries do not generate a fluoride sludge at all and discharge the HF alkylation plant effluent to its wastewater treatment plant. However, this may cause problems at the wastewater treatment plant in meeting NPDES permit levels for fluoride.

3. New Alkylation Process

New processes using solid catalyst and small amounts of liquid catalyst would not generate neutralization sludges the same way as present HF alkylation units. This is still a preliminary process under development.

Additional source reduction is not possible for the catalyst because of the closed loop recycle process and the strict controls placed on this material due to the severe health hazards associated with contact and inhalation.

Acid Soluble Oil (ASO) from HF Alkylation

Residual Description

A residual of high molecular-weight reaction by-products dissolves in the HF acid catalyst and lowers its effectiveness. To maintain the catalyst activity, a slip stream of catalyst is distilled, leaving the by-product, acid soluble oil (ASO), as a residue. The ASO is charged to a decanting vessel where an aqueous phase settles out. The ASO is scrubbed with potassium hydroxide

(KOH) to remove trace amounts of HF and either recycled, sold as product (e.g., residual fuel), or burned in the unit's boiler.

Hazardous constituent possibly contained in the ASO include hydrocarbons and HF acid. Twenty-five percent of the ASO was reported to be managed as characteristically hazardous.

Source Reduction Practices

As described in previous sections, several solid-acid catalysts used for alkylation are being tested in pilot plants. The reactor systems are different from the current liquid-acid systems, but for one system the other equipment is compatible. Three types of the new solid catalyst include aluminum chloride, alumina/zirconium halide, and antimony pentafluoride (a slurry system). It is likely that ASO will not be generated in a solid catalyst system.

Treating Clay from Alkylation

Residual Description

Treating clay from alkylation predominantly includes (1) molecular sieves used for drying feed and (2) alumina used for removing fluorinated compounds from the product. Both are applications in HF alkylation; clays are not used as frequently in sulfuric acid alkylation.

After fractionation, products may be passed through a filter filled with sorbents (referred to as treating clay) to remove trace amounts of acid, caustic, or water. Sorbents typically used in this service include alumina, molecular sieve, sand, and salt.

Source Reduction Practices

As discussed in the HF alkylation catalyst section, several solid-acid catalysts used for alkylation are being tested in pilot plants. It is unclear whether these processes will generate more or less treating clays than current processes. Theoretically, these processes would not require filtering for acid and water removal.

Distillation to dry the feed to the HF acid alkylation unit has also been used. Most facilities use a molecular sieve treating clay for this step, therefore this process configuration eliminates the need for molecular sieve infrequently generating an RC.

Hazardous constituents contained in the treating clay are hydrocarbons such as volatile organic compounds.

Catalyst from Polymerization

Residual Description

Polymerization is a process utilized for the conversion of propane/propylene and/or butane/butene feeds from other operations into a low molecular weight, higher-octane, polymer product, referred to as dimate. Dimate is used as a high octane gasoline blending component of unleaded gasolines. There are primarily two polymerization processes utilized by the petroleum refining industry: phosphoric acid polymerization and the Dimersol process. Spent phosphoric acid polymerization catalyst is generated after the solid catalyst active sites have become blocked and lost their reactivity.

Dimersol catalyst is added to the reactor feed stream and exits the final reactor as part of the reactor effluent. The liquid catalyst is then removed from the reactor effluent by neutralization (contact with caustic). Spent caustic streams, containing the spent dimersol catalyst, are commonly reused on-site or sent off-site for metals reclamation or caustic recovery, and as a result are typically not solid wastes. Spent catalyst also may be generated in two other points in the process. First, during routine shutdowns spent catalyst may be generated as a component of any reactor sludge removed from the reactors. Second, certain Dimersol processes contain filters following caustic neutralization and water washing to remove entrained residual nickel from the dimate product. The filters are removed and disposed periodically.

Hazardous constituents possibly contained in the catalyst include phosphoric acid, metals, and hydrocarbons.

Source Reduction Practices

No source reduction methods were reported by industry or found in the literature search.

Off-spec Sulfur, Sulfur Sludge, Spent Amine and Sulfur Catalyst

Residual Description

Sulfur-containing compounds are removed from petroleum as hydrogen sulfide at many points in the refinery. The hydrogen sulfide is concentrated by absorption/desorption with an aqueous solution, such as amine. Sulfur is most commonly recovered as elemental sulfur in Claus units. Claus tail gas may be further treated to remove sulfur prior to being discharged to the atmosphere. This is accomplished by passing the gas through a hydrotreating bed (to reduce the sulfur dioxide to hydrogen sulfide) and absorbing the sulfur in a solution such as amine. Spent catalyst is generated from the Claus reactors and the tail gas hydrotreating reactor. Sludge is generated from the amine solutions. Like other refinery products, sulfur must meet certain

customer specifications such as color and impurity levels. The failure of the refinery to meet these requirements causes the sulfur to be "off-spec."

Source Reduction Practices for Sulfur Sludge

Source reduction strategies which have been employed for sulfur sludge, or could be employed, include the following:

- Use of alternative sulfur removal solutions: Many refineries use methyl diethanol amine (MDEA) instead of monoethanol amine (MEA) at the tail gas unit. MDEA is not as susceptible to the formation of heat stable salts and is amenable to regeneration. Using MDEA greatly reduces the amount of amine sludge and spent amine solution generated by the tail gas unit.

- Additives to reduce heat stable salt formation: At least two facilities control heat-stable salts in their MDEA amine treating system using a proprietary caustic.

- Elimination of filters: Two facilities have replaced their cloth or cartridge filters with an etched metal mechanical filter. The new filter requires less maintenance, reduces the number of filter elements disposed of, and also eliminates amine discharges to the WWTP due to filter change-outs.

Source Reduction Practices for Sulfur Catalyst

Source Reduction strategies which have been employed for sulfur catalyst, or could be employed, include process redesign. Some processes, such as the Stretford process, do not use solid catalyst. The catalyst is in a liquid state and is continuously reused. Stretford system have limited use as both sulfur recovery units and tail gas units. Note that although the solid catalyst stream is eliminated in the Stretford process, the possibility of the liquid catalyst being present in other waste or residual streams was not investigated.

Source Reduction Practices for Off-spec Sulfur

During EPA's site visit, one facility was observed to generate "off-spec" sulfur product daily. Portions of the sulfur plant are being replaced with a newer design. As a result, waste sulfur residual from equipment "low points" will no longer be generated.

Source Reduction Practices for Spent Amine

Source reduction of amine involves modifying the process. During the site visits, information was gathered that several facilities capture the amine for recycling. Two facilities replaced the cloth filter at the sulfur recovery unit with an etched metal mechanical filter. The new filter requires less maintenance, and also eliminates amine discharges to the wastewater

treatment plant due to filter change-outs. Another two facilities have installed sumps at the sulfur complex. The sumps capture amine that is drained from the filters during bag change-outs and recycle it to the amine system. Without the sumps, the amine drained from the filters is discharged to the wastewater treatment plant.

One facility described reducing amine entrainment in LPG through the installation of coalescers. Amine was kept within the system, reducing raw material requirements for make-up.

Thermal Processing Fines and Off-Spec Product

Residual Description

Delayed coking units are the most common type of thermal treatment units, and the most common type of unit to generate fines. Most refineries report that their thermal units do not generate "off-spec" product; all of their coke product is typically salable.

A thermal process heats the charge oil to a temperature at which it will crack into lighter, more valuable components. Unlike catalytic cracking processes, no catalyst is used. The cracked product is fractionated. Coke gradually builds up within the vessel and is drilled out with a water jet upon completion of the coking cycle. Coke, ranging in size from fines to large chunks, are gravity dumped to a pad. Fines may settle on the pad, or be entrained with the washwater. Some fines entrained in the water are settled. At most refineries, water is reused within the coking unit. Coke fines entrained in the water, therefore, generally do not leave the unit limits.

Hazardous constituents potentially present in coke fines is coke, metals, and heavy organic hydrocarbons.

Source Reduction Practices

Coke fines are viewed by many refineries to be part of the coke product since they are often recombined with larger coke and sold. Therefore, the following are pollution prevention strategies to keep coke fines out of waste streams:

- Recovery of coke fines in water
- Spill prevention

1. Recovery of Coke Fines in Water

Several years ago, one refinery initiated a program to keep coke fines from getting into the process water sewer. By installing filters at sewer drains and keeping the coker battery limits clean they have significantly reduced their volume of wastewater treatment (i.e., F037/F038) waste.

A water hydroclone is being built at one facility's delayed coking unit to capture coke fines that escape from their fines collector. The fines recovered by the cyclone will be incorporated into the coke and sold as product. If the fines are not captured by the cyclone, a portion of them are discharged to the WWTP where they may combine with other process wastewaters and generate hazardous waste in treatment and storage units.

2. Spill Prevention

Coke product may be spilled during loading onto railcars, product transfer, etc. Keeping the coke handling area free of dirt eliminates the contamination of spilled coke product, which can be stockpiled with the remaining coke product.

Off-specification Product and Process Sludge from Residual Upgrading

Residual Description

After vacuum distillation, there are still some valuable oils left in the vacuum-reduced crude. 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 from residual upgrading includes material generated from asphalt oxidation, solvent deasphalting, and other upgrading processes. Only one facility reported generating this residual.

Process sludge is generated from miscellaneous parts of the various residual upgrading processes. Solvent deasphalting may generate a sludge due to hydrocarbon carryover in the solvent recovery system. Similarly, the ROSE process may generate sludges due to process upsets in the solvent condensate collection system. Additional sludges may be generated during unit turnarounds and in surge drums and condensate knockout drums.

Hazardous constituents for these residuals include PAHs.

Source Reduction Practices

Source reduction techniques were reported to be process modifications and better housekeeping. This residual is generated infrequently and in very small quantities, therefore limited information was expected.

Spent Treating Clay from Lube Oil Filtering

Residual Description

Vacuum distillates are treated and refined to produce a variety of lubricants. Wax, aromatics, and asphalts are removed by unit operations such as solvent extraction and hydroprocessing; clay may also be used. The majority of treating clays (including other sorbents) generated from lube oil processing are from acid-clay treating in refining or lube oil finishing.

Source Reduction Practices

This residual is generated infrequently and in very small quantities. Treating clays use for product polishing in lube oil manufacturing is being phased out by industry. No source reduction methods were reported by industry or found in the literature search.

Spent Caustic

Residual Description

Liquid treating operations are used to remove impurities (e.g., mercaptan sulfur, organic acids) from product streams (e.g., gasoline) prior to sale. Treatment is accomplished by liquid-liquid (or gas-liquid) contacting, followed by regeneration of the caustic treating solution. The regeneration step may result in the generation of purge caustic, which is replaced by fresh make-up.

Source Reduction Practices

Refineries may reuse spent caustic for other services (i.e., cascading the caustic).

One refinery has installed a hydrotreater to reduce the sulfur content of its diesel fuel product. As a result, the caustic treating unit that was used to treat this product was eliminated from service (thus eliminating the generated waste stream).

Spent Treating Clay from Clay Filtering

Residual Description

Clay belongs to a broad class of materials designed to remove impurities via adsorption. Examples of clay include Fullers earth, natural clay, and acid treated clay. However, similar materials such as bauxite are also available and used to impart similar qualities to the product. In addition, materials such as sand, salt, molecular sieve, and activated carbon are used for removing impurities by adsorption or other physical mechanisms.

Generated at many places in the refinery, spent solid sorbents have liquid contents ranging from very low (e.g., for molecular sieves treating light hydrocarbons) to oil-saturated material (e.g., for clay used for treating kerosene). The substrate is either inorganic (such as alumina, zeolite, or clay) or organic (such as activated carbon). Most applications are fixed bed, where the material is charged to vessels and the hydrocarbon passed through the fixed bed of solid sorption media. The fixed bed can remain in service for a period of time ranging from several months to 10 years, depending on the application. At the end of service, the vessel is opened, the "spent" material removed, and the vessel recharged.

Source Reduction Practices

One facility reported that its jet fuel treating clay is regenerated once by back-washing the clay bed with jet fuel to "fluff" the clay and alleviate the pressure drop.

IV. Review of Data Sources

As discussed in more detail later in this section, waste minimization information has been compiled from the following sources for this report:

- Various sections of the 1992 RCRA §3007 Surveys (i.e., Sections V, VI, XI) for all 185 refineries operating in 1992.

- Twenty site visit reports, from refineries visited in 1993 for the listing determination and industry study.

- Relevant articles from the 1993 to 1996 issues of *Hydrocarbon Processing* and *Oil & Gas Journal*, and relevant papers presented at the Fall 1994 National Petroleum Refineries Association (NPRA) Environmental Conference.

Each of these sources provide different levels of detail for different numbers of facilities. Examples of innovative source reduction and recycling techniques are available (as discussed later in this report), but the following techniques are used on an industry-wide basis:

- *Tank Sediments (Crude, Unleaded, CSO, Residual Oil)*: Many refineries use filter presses, centrifuges, or other onsite solids separation equipment to recover hydrocarbons for recycle to the process. In-tank mixers also may be used to decrease sludge accumulation.

- *Solid Catalysts (FCC, Hydrotreating, Hydrorefining, Hydrocracking, Reforming, Isomerization, Polymerization, and Sulfur Complex)*: Where possible catalysts are regenerated, reclaimed, and/or reused on and offsite, or the process optimized to prolong catalyst use. However, ultimately catalysts must be periodically replaced with fresh catalyst. Spent catalysts are often sent offsite for metals reclamation or other reuse. In the case of reformer catalyst, commercial value is very high.

- *Sulfuric Acid Alkylation Catalyst and Spent Caustic from Liquid Treating*: Source reduction opportunities are low for these two high volume liquid streams. Standard industry practice is to send spent sulfuric acid offsite for regeneration and reuse as a feedstock or product substitute in downstream industries; many refineries also send their spent caustics offsite for reuse. Hydrotreating may be used to significantly lessen the amount of liquid treating that is needed.

- *Sludge from HF Alkylation*: This residual is generated specifically for pollution control purposes (i.e., to control fluoride levels in refinery effluent, and to mitigate airborne releases of HF Acid). As a result, the residual cannot effectively be "reduced" but many refineries are taking steps to beneficially reuse the sludge and

reduce the disposed volume. This typically requires some effort in segregating oily or low fluoride process water from relatively clean, high fluoride process water.

- *Sulfur Sludge*: Most waste minimization efforts for this residual focus on source reduction, as on- or offsite recycling is not practical. It is difficult to assess the trend in source reduction for this residual, but some techniques include switching amine systems (which reduces sludge generation) or the use of reusable solids removal equipment (which reduces the quantity of support media, such as filters, going to disposal). EPA realizes this is an expensive undertaking but has been or is currently being done by a some refineries.

- *Coke Fines*: Most refineries recombined their coke fines with their coke product for sale. Refineries generally do not report source reduction methods for fines because, as long as the fines can be recovered for incorporation into the product, they are not of concern.

- *Sulfuric Acid Alkylation Sludge*: Most refineries have switched from insoluble neutralizing agents to soluble neutralizing agents to decrease sludge accumulation.

- *Treating Clays (Clay Filtering, Alkylation, Extraction/Isomerization, and Lube Oil)*: Treating clays comprise of such a wide variety of material (clay, molecular sieve, salt) and are used for a wide variety of services (defluorination, dewatering) that waste minimization activities can vary greatly. In some cases, treating clay is used as a waste reduction process for another waste (i.e., isomerization catalyst) and, therefore, cannot be reduced.

- *ASO*: With the development of solid acid catalysts, ASO may be eliminated. Currently it is primarily recycled either as product or burned onsite for energy recovery.

- *Off-specification Product (Sulfur complex and Residual Upgrading)*: Most refineries recombined their off-spec product with their product for sale or send it for reprocessing. Refineries generally do not report source reduction methods for off-spec product because, as long as it can be recovered for incorporation into the product or recycled back into the process, they are not of concern.

- *Residual Upgrading Sludge*: Little or no waste minimization information is available for this low volume residual.

- *Desalting Sludge*: Waste minimization activities include dewatering, use of filters, and low pressure flow to reduce turbulence and emulsion generation. Use of waste minimization techniques in other parts of the refinery can increase desalting sludge production (e.g., mixers in crude tanks).

- *HF Alkylation Catalyst*: With the development of solid acid catalyst and the hazardousness of HF acid, the industry may in the future be naturally moving away from this residual.

- *Spent Amine*: Spent amine is generally generated through process losses. By increasing process efficiency, refineries could reduce raw material consumption.

Further detail on the sources used and a discussion on their usefulness is presented below.

A. RCRA §3007 Survey Section XI

Source reduction information was explicitly requested in Section XI of the survey for all residuals reported in the survey. This section included (1) the facility's past, existing, and future activities to reducing residual volume and reducing toxicity, (2) detailed discussion of residuals eliminated, and (3) discussion of regulatory barriers to source reduction. Approximately 90 of 172[2] respondents completed item (1), 18 respondents completed item (2), and 21 respondents completed item (3).

Tables IV-1 to IV-3 present source reduction information from Section XI of the survey. Most responders provided this information as non-CBI; therefore most information from this part of the survey could be presented here in detailed form. Table IV-1 summarizes ongoing facility-specific source reduction activity for the residuals. The information presented in Table IV-1 reflects only what has been reported. Insufficient information was provided (or requested) to determine what the specific source reduction practice is. In fact, for some refineries that did provide additional information, their reported practices were not source reduction at all but were rather more appropriately termed recycling. Given these limitations, this table shows that many refineries practice source reduction/recycling for crude tank sludge, FCC catalyst and fines, and spent caustic.

Table IV-2 summarizes all residuals reported to be eliminated since c. 1989 (both listing and study RCs). No trends are evident from this table due to the low number of facilities reporting on a broad range of residuals.

Table IV-3 summarizes the reported regulatory barriers to source reduction (both listing and study RCs). Many of these refineries discuss regulatory barriers that would take place if the RCs were further regulated; these concern permitting for treatment and barriers of transferring hazardous wastes between refineries for recycling or recovery.

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[2] Only 172 of the 185 refineries completed and returned RCRA §3007 Surveys, explanations to the less than 100 percent response are provided in the Petroleum Refining Listing Determination Background Document.

Section XI also requested information on toxicity reduction goals. Only two refineries reported goals for hazardous constituents; both set goals for benzene (one facility for spent caustic and another for hydrotreating/hydrorefining catalyst). Most other refineries provided goals for classes of constituents, such as "oil," or nonhazardous constituents such as water.

B. RCRA §3007 Survey Section VI

Section VI of the Survey contains management information such as on- and offsite recycling, treatment, and final disposition. All 172 refineries completed this section. Table IV-4 summarizes the relevant waste minimization information found in response to this section for the RCs. This table shows that recycling practices are widespread for the following RCs (i.e., about 80 percent of the industry practices some form of recycling):

- Crude oil tank sludge, CSO, and residual oil tank sludge are recycled onsite to the crude unit, or is pressure filtered or centrifuged.
- FCC catalyst (not fines) is most often recycled offsite to cement kilns or to other refineries.[3]
- Hydrotreating, hydrorefining, hydrocracking, reforming, isomerization, and sulfur plant tail gas catalyst are most often sent offsite for reclamation/regeneration.
- Sulfuric acid alkylation catalyst is sent offsite to sulfuric acid producers to make sulfuric acid.
- Coke fines are mixed with the coke product and sold offsite.
- Spent caustics are either recycled offsite for reuse, sold offsite for use as a raw material, or used onsite in process equipment (e.g., wastewater treatment, desalter) for its caustic qualities.
- Oil-bearing secondary materials (e.g., crude oil tank sediment, desalting sludge, etc.) are recycled to refinery process units (e.g., cokers, distillation unit, FCC unit, etc.).

Information on Section V of the survey is presented in Section III of this report. Section V of the survey contains useful information concerning *in situ* tank cleaning; this type of cleaning is conducted to recover useful hydrocarbons from the tank bottoms prior to opening the tank.

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[3] API representatives stated that spent FCC catalyst is also used as inert construction material, however, this reuse method was not reported in the §3007 survey or conveyed by the refineries during the engineering site visits.

C. Site Visits

In 1993, the Agency conducted engineering site visits to 20 refineries. Waste minimization activities applicable to the RCs were observed for every facility. Some were common, such as offsite metals reclamation, and reflected the trends noted in Table IV-4. Others were more innovative, such as the substitution of metal screens for cartridge filters in amine systems. All of these ideas are summarized in Table IV-5.

D. Journal Articles

An in-house literature search was conducted by EPA and SAIC. Source reduction activities documented in the industry trade journals *Hydrocarbon Processing* and *Oil & Gas Journal* and conference proceedings were investigated.

Over 70 articles detailing waste minimization techniques for 20 RCs were found. Additional articles detail waste minimization activities for other refinery residuals or are more general in nature. All articles are summarized in Table IV-6.

Most of the articles concerning pollution prevention for catalysts discussed new catalyst additives (such as traps to prevent poisoning) or process changes to give longer life to the catalysts. *Oil & Gas Journal* highlighted future alkylation processes in one of its issues. Other articles discuss practices observed from site visits, such as offsite metals reclamation and sludge treatment for oil recovery. It is difficult to determine whether the ideas presented in these articles are widespread or represent research by one facility.

Table IV-1. Summary of Pollution Prevention Information Available from Section XI of Surveys			
Residual of Concern	# of Sites Reporting Source Reduction Info/ # of Streams	Most Frequent Source Reduction Practices	Detailed Source Reduction Practices[1]
Listing Residuals			
Crude Tank Sludge	17/46	Equipment/ technology modification; process/ procedure modifications	crude unit shutdown; recover and reuse; using chemical treatment prior to removal
Unleaded Gasoline Tank Sludge	1/2	Equipment/ technology modification; process/ procedure modifications	---
CSO Sludge	6/18	Equipment/ technology modification	Settler removes alumina from CSO
Catalytic Cracking Catalyst and Fines	20/26	Equipment/ technology modification; process/ procedure modifications	Redesigned FCC cyclones
Hydrotreating and Hydrorefining Catalysts	8/20	Process/ procedure modifications	regeneration onsite; regeneration and reuse
Reforming Catalyst	7/9	Equipment/ technology modification; process/ procedure modifications	---
Sulfuric Acid Alkylation Catalyst	2/3	process/ procedure modifications	---
Sulfuric Acid Alkylation Sludge	0	---	---
Hydrofluoric Acid Alkylation Sludge	6/7	Equipment/ technology modification	---
Sludge from Sulfur Removal	9/18	Equipment/ technology modification; process/ procedure modifications	more time between change-out
Catalyst from Sulfur Complex	7/10	process/ procedure modifications	---
Fines and Off-spec Product from Thermal Processing	9/13	process/ procedure modifications	modify drain to recover coke fines from water
Spent Caustic	24/40	process/ procedure modifications	recycled to crude unit to neutralize acid in crude; no longer in operation; construction of oxidizer

Table IV-1. Summary of Pollution Prevention Information Available from Section XI of Surveys			
Residual of Concern	# of Sites Reporting Source Reduction Info/ # of Streams	Most Frequent Source Reduction Practices	Detailed Source Reduction Practices[1]
Study Residuals			
Isomerization Catalyst	6/6	Process/ procedure modifications	---
Off-Specification Sulfur	6/6	Process/ procedure modifications; improved housekeeping	Minimize Stretford solution carryover
Off-Specification Treating Solution from Sulfur Removal	9/16	Equipment/ technology modification	---
Hydrocracking Catalyst	4/5	Process/ procedure modifications	Offsite regeneration or offsite metals recovery
Desalter Sludge	21/32	Equipment/ technology modification; process/ procedure modifications	Unit shutdown
Acid Soluble Oil	11/14	Equipment/ technology modification	Press to recover KOH
Alkylation Treating Clay	4/4	Process/ procedure modifications; improved training	---
Treating Clay from Clay Filtering	11/14	Process/ procedure modifications; substitution of raw materials	---
Process Sludge from Residual Upgrading	2/2	Process/ procedure modifications; improved housekeeping	---

1. Some responses provided a brief description of their activity. These responses are provided here.

Table IV-2. Detailed Residual Elimination Information Available from Section XI of Surveys	
Residual of Concern	Discussion of RC Eliminated[1]
Crude Tank Sludge	Permanent shutdown of crude units eliminated desalter waste, distillation tower waste, crude tank sludge. The two refineries likely substituted unfinished products from other refineries for crude oil as their raw material. Tank mixers are used to reduce tank sludge accumulation.
Unleaded Gasoline Tank Sludge	Tank mixers are used to reduce tank sludge accumulation.
Catalytic Cracking Catalyst and Fines	Caked FCC catalyst (generated at turnaround) were eliminated due to equipment and process changes.
Hydrotreating and Hydrorefining Catalysts	Hydroprocessing catalysts are now nonhazardous due to a new sweep procedure, reducing facility's requirement to ship as hazardous waste.
Reforming Catalyst	Reforming catalysts are now nonhazardous due to a new sweep procedure, reducing facility's requirement to ship as hazardous waste.
HF Acid Alkylation Sludge	Spent caustic from the HF alkylation system were previously sent offsite for deepwell injection. A treater now generates solid calcium fluoride and an aqueous phase that is sent to wastewater treatment.
Sludge from Sulfur Removal	Amine reclaimer bottoms are no longer produced due to equipment and process changes. Amine treating clay replaced with regenerative carbon. Corrosion inhibitors are used to prevent sludge accumulation on the amine filters.
Fines and Off-spec Product from Thermal Processing	Coke fines and coke are sold instead of landfilled.
Spent Caustic	Two refineries installed distillate hydrodesulfurization units and took caustic units out of service, eliminating spent caustic residuals. "Sulfinol, from gas liquid unit," was eliminated due to equipment/ process modification Spent Merox caustic is no longer produced.
Amine solution	Amine treating solution is regenerated within the process by contract amine cleaning technology. Cleaning process generates clean amine and heat stable salts, which are managed in the wastewater treatment system. Equipment modification (NOS)

Table IV-2. Detailed Residual Elimination Information Available from Section XI of Surveys	
Residual of Concern	Discussion of RC Eliminated[1]
Desalter sludge	Permanent shutdown of crude units eliminated desalter waste, distillation tower waste, crude tank sludge Desalter no longer in operation
ASO	Equipment modification (NOS) Recycled through the slop oil system.
Isomerization residuals	Discontinued use of the isomerization process.
Merox unit sand filter	Improved draining and washing/steaming the filter before removing the sand. Removes oil and caustic contaminants allowing material to be recycled into roadway antiskid.
General Responses	Catalysts are recycled instead of landfilled. None eliminated, but some reduced. Opportunities are limited because of contaminants in crude oil requiring removal, required use of catalysts in process equipment, filters to keep product on-spec, use of caustic and wash water to remove impurities. However, there are options for waste minimization through recycling.

1. The responses of each facility are presented here, edited only slightly for clarity.

Table IV-3. Detailed Regulatory Barriers Reported from Section XI of Surveys	
Residual of Concern	Discussion of Regulatory Barrier[1]
Crude Tank Sludge	Many tanks (crude and product) may require accelerated cleanout to comply with upcoming OPA-90 regulations Regulatory barriers are associated with permitting: transportable treatment permit for sludge treatment.
Unleaded Gasoline Tank Sludge	Many tanks (crude and product) may require accelerated cleanout to comply with upcoming OPA-90 regulations Oxygenated fuels program required accelerated tank cleaning schedule to store MTBE-blended fuel. If MTBE program is discontinued, tanks may again require cleaning prior to changing product service
CSO Sludge	Many tanks (crude and product) may require accelerated cleanout to comply with upcoming OPA-90 regulations
Catalytic Cracking Catalyst and Fines	Catalysts could be used as micronutrients in fertilizer. This represents a large beneficial reuse/cost reduction opportunity. However, current regulation 40 CFR 261.2(e)(2)(i) excludes use to make a fertilizer. FCC fines result from inefficient air pollution control equipment and cannot be eliminated.
Hydrotreating and Hydrorefining Catalysts	Reformulated gasoline and low sulfur/aromatic diesel rules will result in more spent hydrotreating catalyst Regulatory barriers are associated with permitting: hazardous waste permitting for catalyst regeneration facilities result in a lack of such facilities and more landfilling of residuals which could be sent to such facilities. Extending catalyst life results in permit modification since a higher metals content would result. Catalysts could be used as micronutrients in fertilizer. However, current regulation 40 CFR 261.2(e)(2)(i) excludes use to make a fertilizer. This represents a large beneficial reuse/cost reduction opportunity.
HF Acid Alkylation Sludge	Fluoride limits on NPDES permit affects potential to reduce alky sludge Alky scrubber solution result from air pollution permits and cannot be eliminated.
Sulfur Complex Catalyst	Catalysts could be used as micronutrients in fertilizer. This represents a large beneficial reuse/cost reduction opportunity. However, current regulation 40 CFR 261.2(e)(2)(i) excludes use to make a fertilizer.
Spent Caustic	Any regulation of caustics will be a blow to refinery's attempt to reuse and recycle.
ASO	BIF regulations are so involved that ASO combustion, which was under consideration at one time, was canceled.

Table IV-3. Detailed Regulatory Barriers Reported from Section XI of Surveys	
Residual of Concern	Discussion of Regulatory Barrier[1]
General Comments: Permitting	90 day storage prevents onsite treatment for this Alaska refinery. Movement of secondary residuals and recyclables among different facilities owned by same corporation requires special permission from various federal agencies. CBI comments from two refineries in California and Pennsylvania discuss permitting hurdles with waste treatment units.
General Responses: Cokers	Significant reduction of hazardous waste could occur if facilities could legally transfer RCRA wastes from a facility to another, for injection to coker, without becoming a TSD. If RCs are listed, the facilities decision to recycle the residuals in a proposed coker would depend on whether the coker requires a RCRA permit.
General Responses: Recycling	Recyclable materials could be exempted from regulation when recycled at another facility. Could continue to regulate certain methods of recycling (e.g., use on land) and exempt others. Options to reuse and recycle hazardous waste are hampered by these regulations. If RCs are listed, recycling and reuse could be encouraged by allowing low flash point liquids to be reused for fuel and high/low pH materials for their characteristic properties. NJ regulation that spent material being recycled or reused are not exempt from solid waste regulations. Reuse and recycling, particularly those conducted offsite, can be very difficult for hazardous wastes. Residuals are properly managed at present.
General Responses: Other	No barriers presently exist. If RCs are listed, source reduction efforts may be hampered if they involve further onsite processing (treatment). Sufficient regulatory controls are in place for storage, treatment, and processing of these RCs. The rapidly expanding universe of hazardous waste created by new regulations keeps us busy looking for approved disposal methods for the new wastes and does not allow time to look for source reduction methods for existing wastes. Many listed regulated wastes could be removed from the hazardous waste envelope if the delisting process could be streamlined and risk based criteria could be applied on a case-by-case basis. Facility is measured by reductions in hazardous waste more than nonhazardous waste. If wastes are listed, landfill exclusions reduce ability to be disposed of by cheaper methods. Congress, EPA, and much of industry have developed a mindset of command-and-control, end-of-pipe treatment approaches based on 20 years of experience. EPA should provide incentives to develop source reduction strategies and increase flexibility to implement process changes without undo permitting burdens. More statutory flexibility must be provided in regulations by setting "targets" without prescribing how the target should be met. More cost-effective programs can be designed by allowing companies to consider site-specific factors and focus on results.

1. The responses of each facility are presented here, edited only slightly for clarity. Note that only some of these responses are relevant to listing RCs; other responses are relevant to study RCs or are general in nature.

Table IV-4. Recycling of RCs Reported in Section VI of Survey

RC		Total 1992 Quantity, MT[1]	Total # of Streams (1992)[1]	Percent, Quantity Recycled/ Reused in 1992			Percent, # of Streams Recycled/ Reused in 1992			Predominant Recycle/Reuse Methods
				Onsite	Offsite	Total	Onsite	Offsite	Total	
Crude Oil Tank Sludge		22,017	127	44	4	48	23	7	30	Onsite recovery in crude unit
CSO Sludge		24,010	46	2	8	10	9	7	16	Onsite recovery
Unleaded Gasoline Tank Sludge		3,583	141	3	5	8	9	1	10	Onsite recovery in coker
Residual Oil Tank Sludge		9,107	43	3	11	14	23	5	28	Onsite recovery
Desalting Sludge		4,841	117	1	40	41	5	17	22	Offsite use as fuel
Catalytic Cracking Catalyst and Fines	Catalyst	124,061	181	3	71	74	6	62	68	Reuse at another refinery; offsite cement kiln
	Fines	67,816	108	<1	17	17	1	20	21	Offsite cement kiln
Hydrotreating Catalyst		5,640	201	4	76	80	4	65	69	Offsite catalyst regeneration/ metals reclamation
Hydrorefining Catalyst		18,634	72	0	83	83	0	89	89	Offsite catalyst regeneration/ metals reclamation
Hydrocracking Catalyst		18,029	77	1	85	86	1	79	80	Offsite catalyst regeneration/ metals reclamation; reuse at another refinery
Reforming Catalyst		3,613	115	2	96	98	7	86	93	Offsite catalyst regeneration/ metals reclamation
Isomerization Catalyst		337	20	0	87	87	0	85	85	Offsite catalyst regeneration/ metals reclamation
Treating Clay from Isomerization or Extraction		2,471	65	0	3	3	0	14	14	Offsite catalyst regeneration/ metals reclamation
Polymerization Catalyst		4,119	39	18	13	31	3	18	21	Offsite use as fertilizer
Sulfuric Acid Alkylation Catalyst		1,760,071	59	19	81	>99	19	66	85	Offsite acid recovery
Sulfuric Acid Alkylation Sludge		608	16	0	13	13	0	13	13	Offsite acid recovery

Table IV-4. Recycling of RCs Reported in Section VI of Survey

RC		Total 1992 Quantity, MT[1]	Total # of Streams (1992)[1]	Percent, Quantity Recycled/ Reused in 1992			Percent, # of Streams Recycled/ Reused in 1992			Predominant Recycle/Reuse Methods
				Onsite	Offsite	Total	Onsite	Offsite	Total	
Acid Soluble Oil		33,493	73	21	13	34	21	10	31	Onsite recovery; offsite use as fuel
HF Catalyst		152	3	0	0	0	0	0	0	-----
HF Alkylation Sludge		11,288	30	12	0	12	3	0	3	Onsite recovery in coker
Treating Clay from Alkylation		2,895	86	0	50	50	0	22	22	Offsite metals reclamation
Sludge from Sulfur Removal		8,520	301	<1	4	4	2	8	10	Offsite carbon reclamation
Catalyst from Sulfur Complex	Claus	3,819	95	<1	22	22	1	21	22	Offsite cement kiln
	Tail Gas	361	23	0	52	52	0	56	56	Offsite metals reclamation
Off-Spec Sulfur		9,647	90	<1	5	5	6	9	15	Sell with product
Off-spec Treating Solution from Sulfur Removal		23,881	96	5	33	38	10	8	18	Offsite regeneration/ metals reclamation
Fines and Off-spec Product from Thermal Processing		194,262	110	5	87	92	3	43	46	Sell with coke product
Off-spec Product from Residual Upgrading		800	1	100	0	100	100	0	100	Recycle to process
Sludge from Residual Upgrading		242	32	7	2	9	3	16	19	Sell with product
Treating Clay from Lube Oil		733	19	48	34	82	63	5	68	Onsite regeneration
Treating Clay from Clay Filtering		8,990	231	<1	7	7	1	12	13	Offsite regeneration/ metals reclamation
Spent Caustic		917,656	712	19	50	69	15	31	46	Offsite reclamation/reuse; onsite use in WWTP for pH control

[1] Includes streams with unknown or unreported quantities.

Data source: 1992 RCRA §3007 Survey data.

Table IV-5. Summary of Waste Minimization Information Available from Engineering Site Visits		
Residual of Concern	# of Facilities Reporting Waste Minimization	Source Reduction Techniques
Crude Tank Sludge	12	Sell for reprocessing; onsite recycling in another unit; recycle to crude tanks; onsite treatment to recover oil; spill prevention precautions decrease quantity of contaminated soil during turnaround.
Unleaded Gasoline Tank Sludge	1	Recycle to other gasoline tanks.
CSO Sludge	12	In-line solid settlers; new cyclones decrease fines in reactor product; hydroclones recycle fines in slurry oil to FCC; spill prevention precautions decrease quantity of contaminated soil during turnaround; recycle to other CSO tank or coker.
Residual Oil Tank Sludge	12	Techniques similar to those used for crude oil tank sludge and CSO sludge can be used.
Catalytic Cracking Catalyst and Fines	11	E-cat sent offsite to another unit; sell catalyst and fines outside of refining industry; e-cat reused onsite in another unit.
Hydrotreating and Hydrorefining Catalysts	10	Offsite metals reclamation; offsite regeneration ad reintroduction to reactor; onsite treatment to reduce dust generation; separation of support material for onsite reuse ; upstream process changes to eliminate catalyst poisons.
Reforming Catalyst	7	Offsite metals reclamation; increasing time between turnaround by optimizing feeds; separation of support material for onsite reuse
Sulfuric Acid Alkylation Catalyst	5	Onsite regeneration; offsite regeneration; process change to decrease oil content of spent acid.
Sulfuric Acid Alkylation Sludge	1	Reduced the number of times acid level was tested in the reactor.
Hydrofluoric Acid Alkylation Sludge	4	Reuse/sale of neutralized fluoride salt; non-generation of solid fluoride salt.
Sludge from Sulfur Removal	5	Replacing filter elements with metal screens; using MDEA rather than MEA decreases the generation and removal of heat stable salts; control of heat stable salts using caustic.
Catalyst from Sulfur Complex	2	Offsite metals recovery (both Claus and SCOT).
Fines and Off-spec Product from Thermal Processing	4	Internal recycle of coker water; improved operation keeps coke fines out of sewers; filter aid in treating other waste; sell with product coke.

Table IV-5. Summary of Waste Minimization Information Available from Engineering Site Visits		
Residual of Concern	# of Facilities Reporting Waste Minimization	Source Reduction Techniques
Spent Caustic	11	Neutralization and recovery of H_2S prior to discharge to WWTP; substitution for fresh caustic in WWTP; sold to Merichem; process changes to reduce spent caustic generation.
Alkylation Treating Clay	1	Distillation is used to dry the alkylation feed, eliminating the need for molecular sieve (which would require the infrequent generation of a solid residual).
Off-Spec Treating Solution for H_2S Removal	4	Replacement of cloth filter with an etched metal mechanical filter reduces amine loss to the wastewater treatment plant during maintenance; capture and recycle of amine during cloth filter bag replacement via sump; recycle of all amine-containing water in the sulfur unit via sump.
Off-spec Sulfur	1	Waste sulfur residual from equipment "low points," presently generated daily, will be eliminated with the installation of a newly-designed system.
Clay	1	Jet fuel treating clay is regenerated once by back-washing the clay bed with jet fuel to "fluff" the clay and alleviate the pressure drop.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
Crude Oil, CSO, Unleaded, and Residual Oil Tank Sludges		
Tank bottoms (applicable to different sludges)	"Waste Minimization in the Petroleum Industry: A Compendium of Practices," API, November, 1991.	Sludge formation can be minimized by mixing contents of tank.
	"Tank-Cleaning Method Removes, Processes F037 Waste," *Oil & Gas Journal*, October 9, 1995.	Case study of ex-situ sludge dewatering/deoiling. Tank sludge is pumped to a centrifuge using a cutter stock. The sludge volume reduction was over 90 percent. The tank stored wastewater and sludge.
	"Re-refiner Fluidizes Tank Residue Using Portable Mixer," *Oil & Gas Journal*, September 5, 1994.	A portable mixer was used to cut lighter oil into the partially gelled residue.
	Emery, G.E., "Tank-Bottoms Reclamation Unit Upgraded to Meet Stricter Rules," *Oil & Gas Journal*, April 12, 1993.	Recycling through equipment modification.
Crude Oil Tank Sediments	"Refinery Seeks Way to Use Oil Storage Tank Residue," *Hydrocarbon Processing*, April 1993.	Energy recovery.
	Davis, G.B., Goss, M.L., Schoemann, P., and Tyler, S.S., "Crude Oil Tank-Cleaning Process Recovers Oil, Reduces Hazardous Waste," *Oil & Gas Journal*, December 13, 1993.	Raw material recovery.
	Rhodes, A., "New Process Effectively Recovers Oil from Refinery Waste Streams," *Oil & Gas Journal*, August 15, 1994.	Technology modification.
	"Bulk Heating Cleans Paraffinic Bottoms from Crude Tanks," *Oil & Gas Journal*, February 20, 1995.	Diluent plus heat was successfully used to clean six Canadian tanks. The generated solvent/sludge was sold, and sludge remaining in the tank was removed by conventional methods.
Tank emissions	"New Equation Estimates Emissions from Tank Turnovers," *Oil & Gas Journal*, September 25, 1995.	Discusses techniques that affect VOC loss from tanks and how to estimate VOC loss.
	"TAPS Storage Tank Bottoms Fitted With Improved Cathodic Protection," *Oil & Gas Journal*, October 23, 1995.	Case study of new cathodic protection for Alaska crude tanks. Cathodic protection is an established method of preventing tank corrosion and, therefore, releases.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
Desalting Sludge		
Desalting Sludge	"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.
	"Filtration Method Efficiently Desalts Crude in Commercial Test," *Oil & Gas Journal*, May 17, 1993.	Alternative process, single-stage filtration, reduces sludge generation.
	D.T. Cindric, B. Klein, A.R. Gentry and H.M. Gomaa. "Reduce Crude Unit Pollution With These Technologies," *Hydrocarbon Processing*, August, 1993.	Includes topic of more effective separation of phases in desalter.
	Rhodes, A., "New Process Effectively Recovers Oil from Refinery Waste Streams," *Oil & Gas Journal*, August 15, 1994.	Technology modification.
Fluid Catalytic Cracking (FCC) Catalyst and Fines		
FCC Operations	"NPRA Q&A Conclusion: Refiners Exchange Experiences on FCC Problems, Coking Operation," *Oil & Gas Journal*, May 2, 1994.	Preventative maintenance.
FCC Catalyst and Fines	Leemann, J.E., "Waste Minimization in the Petroleum Industry," *JAPCA*, June 1988.	Recycling.
	Waste Minimization in the Petroleum Industry: A Compendium of Practices. American Petroleum Institute. November 1991.	Recycling.
	"Generation and Management of Residual Materials," API. August 1993.	Recycling.
	"Question & Answer Session on Waste Issues," *NPRA Environmental Conference Proceedings*, September 18-20, 1994.	Recycling.
FCC fines	"Stepwise Method Determines Source of FCC Catalyst Losses," *Oil & Gas Journal*, August 28, 1995.	Troubleshooting techniques identifies catalyst leaks for future equipment maintenance.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
FCC Catalyst	Sarrazin, P., Cameron, C.J., Barthel, Y., and Morrison, M.E., "Processes Prevent Detrimental Effects from As and Hg in Feedstocks," *Oil & Gas Journal*, January 25, 1993.	Equipment modification.
	Wong, R.F., "Increasing FCC Regenerator Catalyst Level," *Hydrocarbon Processing*, November 1993.	Process modification.
	Dougan, T.J., Alkemade, U., Lakhanpal, B., and Boock, L.T., "New Vanadium Trap Proven in Commercial Trials," *Oil & Gas Journal*, September 26, 1994.	Equipment modification.
	"Refiners Discuss Fluid Catalytic Cracking At Technology Meeting," *Oil & Gas Journal*, April 24, 1995.	Increasing the oxygen content of regenerator air may quicken the catalyst deactivation rate.
Hydrotreating, Hydrorefining, Hydrocracking Catalyst		
Hydroprocessing 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.
	Berrebi, G., Dufresne, P., and Jacquier, Y., "Recycling of Spent Hydroprocessing Catalysts: EURECAT Technology," *Environmental Progress*, May 1993.	Metals reclamation.
	Gorra, F., Scribano, G., Christensen, P., Anderson, K.V., and Corsaro, O.G, "New Catalyst, Improve Presulfiding Result in 4+ Year Hydrotreater Run," *Oil & Gas Journal*, August 23, 1993.	Material substitution to extend catalyst life.
	"Generation and Management of Residual Materials," API, August 1993.	Recycling.
	"Petroleum-derived Additive Reduces Coke on Hydrotreating Catalyst," *Oil & Gas Journal*, December 27, 1993.	Process modification extends life of catalyst.
	Monticello, D.J., "Biocatalytic Desulfurization," *Hydrocarbon Processing*, 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," *Oil & Gas Journal*, March 28, 1994.	Methods in improving catalyst life and performance: regeneration and top-bed skimming.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
Hydroprocessing Catalyst (Cont.)	"Industry Briefs," *Oil & Gas Journal*, January 2, 1995.	Patent received for commercialization of petroleum biocatalytic desulfurization process.
	"Coke, Sulfur Recovery from U.S. Refineries Continues to Increase," *Oil & Gas Journal*, January 2, 1995.	Commercialization of petroleum biocatalytic desulfurization process, trends affecting sulfur production and removal (and associated waste generation).
	"Bug Process Studied for Low Sulfur Diesel," *Oil & Gas Journal*, April 3, 1995.	A pilot plant for a biocatalytic desulfurization process may be constructed in France and commercialized in 1996 or 1997.
	"HP Innovations," *Hydrocarbon Processing*, November 1995.	Biocatalytic desulfurization. Similar to *Oil & Gas Journal*, April 3, 1995, page 39.
	"Hydrotreating Operations Discussed At Refining Meeting," *Oil & Gas Journal*, June 12, 1995.	"Scale baskets" placed at the front of reactors may or may not keep debris out of the catalyst bed and extend the time between turnarounds.
	"Catalyst Handling, Disposal Become More Important in Environmental Era," *Oil & Gas Journal*, March 18, 1996.	Catalyst loading, unloading, and offsite reclamation are described. Operations to improve catalyst handling while loading and unloading are described.
Hydrocracking Catalyst and Operations	"New Hydrocracking Catalysts Increase Throughput, Run Length," *Oil & Gas Journal*, June 26, 1995.	Discusses operational changes to product slate. No waste generation aspects.
	"Catalyst Separation Method Reduces Platformer Turnaround Costs," *Oil & Gas Journal*, September 18, 1995.	Technology separates highly-deactivated catalyst from reusable catalyst, allowing less catalyst to be shipped offsite. Technique has been applied to reforming and hydrocracking catalyst.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
Hydrorefining Catalyst	"Japanese Refiner Solves Problem in Resid Desulfurization Unit," *Oil & Gas Journal*, November 13, 1995.	By adjusting operating conditions, catalyst type, and catalyst loading, one refinery increased the time between catalyst replacement by 6 months.
	"Simple Changes Reduce Catalyst Deactivation, Pressure Drop Buildup," *Oil & Gas Journal*, November 20, 1995.	Same case study as Nov. 13 article, with similar topics.
Reforming Catalyst		
Reforming Catalyst	J. Liers, J. Mensinger, A. Mosch, W. Reschefilowski, "Reforming Using Erionite Catalysts," *Hydrocarbon Processing*, August, 1993.	The platinum catalyst together with erionite increases isomerization.
	"NPRA Q&A 1: Refiners Focus on FCC, Hydroprocessing, and Alkylation Catalyst," *Oil & Gas Journal*, March 28, 1994.	Regeneration.
	"Olefins Can Limit Desulfurization of Reformer Feedstock," *Oil & Gas Journal*, July 3, 1995.	Choosing a hydrotreating catalyst that hydrogenates olfins will improve sulfur removal, thus prevent deactivation of reforming catalyst.
	"Catalyst Separation Method Reduces Platformer Turnaround Costs," *Oil & Gas Journal*, September 18, 1995.	Technology separates highly-deactivated catalyst from reusable catalyst, allowing less catalyst to be shipped offsite. Technique has been applied to reforming and hydrocracking catalyst.
Alkylation Unit (HF Acid Releases)		
HF Alkylation	"Alkylation Safety Major Topic at Oil & Gas Journal Seminar," *Oil & Gas Journal*, January 16, 1995.	Discusses controls at HF acid alkylation to mitigate acid leaks.
	"Survey Reveals Nature of Corrosion in HF Alky Units," *Oil & Gas Journal*, March 6, 1995.	Lists materials, maintenance practices, problems found during survey of half of world's HF alkylation units.
	"Alkylate - A Key Gasoline Component," *Hydrocarbon Processing*, August 1995.	Additives to HF acid alkylation are being developed to lessen risk during spill.
	"New HF Detector Accepted for Use by Refining Consortium," *Oil & Gas Journal*, February 19, 1996.	An improved method of detecting HF acid leaks has been tested at one refinery and will be installed at others.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
HF and Sulfuric Acid Catalyst		
Alkylation catalysts	"NPRA Q&A 1: Refiners Focus on FCC, Hydroprocessing, and Alkylation Catalyst." *Oil & Gas Journal.* March 28, 1994.	Solid acid catalyst substitution.
	Rhodes, A.K. "Searches for New Alkylation Catalysts, Processes Forge Ahead." *Oil & Gas Journal.* August 22, 1994.	Equipment modification. Process modification.
	"U.S. Refiners Must Increase Alkylation Capacity to Meet Demand" *Oil & Gas Journal.* August 22, 1994.	Solid catalyst substitution.
	Rhodes, A.K. "New Process Schemes, Retrofits, Fine Tune Alkylation Capabilities." *Oil & Gas Journal.* August 22, 1994.	Process substitution. Process modification.
	"Pilot-plant results in on fixed-bed alkylation process." *Oil & Gas Journal.* April 1, 1996.	Solid catalyst for alkylation out of the test stage and in the process of being put on the market.
	"HP Innovations," *Hydrocarbon Processing*, February 1996.	Solid catalyst for gasoline alkylation has been developed and will be tested. It would compete with systems using liquid sulfuric or hydrofluoric acid catalysts.
Acid Soluble Oil		
ASO	"Portuguese Refiner Starts Up New Gasoline Complex," *Oil & Gas Journal*, March 13, 1995.	Feed change to alkylation unit (by installing a unit to reduce the butadiene content of feed) is expected to decrease ASO generation.
Treating Clay from Alkylation		
Alkylation treating clay	"Conoco Refinery Markets Fluorinated Alumina," *Oil & Gas Journal*, February 1, 1993.	Used clay is sold to an aluminum plant.
HF Alkylation Sludge		
HF Sludge	*Waste Minimization in the Petroleum Industry: A Compendium of Practices.* American Petroleum Institute. November 1991.	

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
Off-spec Product and Fines from Thermal Processes		
Coke fines	"NPRA Q&A Conclusion: Refiners Exchange Experiences on FCC Problems, Coking Operation." *Oil & Gas Journal.* May 2, 1994.	Process modification. Process control.
	"Choosing a Coke Recovery System," *Hydrocarbon Processing*, September 1995.	Details coke and coke fine collection devices.
Spent Treating Solution and Other Sulfur Plant Wastes		
Spent amine	*Waste Minimization in the Petroleum Industry: A Compendium of Practices.* American Petroleum Institute. November 1991.	Recycling.
	"Generation and Management of Residual Materials," API, August 1993.	Recycling.
	Stewart, E.J. and Lanning, R.A., "Reduce Amine Plant Solvent Losses, Part 1," *Hydrocarbon Processing*, May, 1994.	Process modification.
	Stewart, E.J. and Lanning, R.A., "Reduce Amine Plant Solvent Losses, Part 2," *Hydrocarbon Processing*, June, 1994.	Process modification.
	"Clean Amine Solvents Economically and On-line," *Hydrocarbon Processing*, August 1995.	Heat stable salts were removed from one refinery's amine system while on-line. Alternatives included disposing system's contents.
	"HP Innovations," *Hydrocarbon Processing*, December 1995.	Amine entrainment in LPG was reduced following installation of coalescers. Amine was kept within the system, reducing raw material requirements for make-up.
Sulfur plant	"Liquid Catalyst Efficiently Removes H_2S From Liquid Sulfur," *Oil & Gas Journal*, July 17, 1989.	Lower catalyst quantities needed to remove H_2S in the sulfur degassing process.
Spent Caustic from Liquid Treating		
Spent Caustic	*Waste Minimization in the Petroleum Industry: A Compendium of Practices.* American Petroleum Institute. November 1991.	Recycling.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
Treating Clay from Clay Filtering		
Spent clay	*Waste Minimization in the Petroleum Industry: A Compendium of Practices.* American Petroleum Institute. November 1991.	
Non-RC Solid Wastes from Refining		
Various wastes and pollution prevention planning	Hethcoat, H.G. "Minimize Refinery Waste." *Hydrocarbon Processing.* June 1990.	P2 planning. Processes highlighted: crude tank sludge, coke fines, spent amine, and FCC catalyst.
Various wastes	*Waste Minimization in the Petroleum Industry: A Compendium of Practices.* American Petroleum Institute. November 1991.	Discusses recycling, source reduction for many process and wastewater treatment wastes from refining.
	"Generation and Management of Residual Materials." API. August 1993.	Recycling and source reduction methods.
	"Environmental Processes '93: Challenge in the '90's," *Hydrocarbon Processing*, August, 1993.	A variety of technologies described, such as bioslurry treatment of oily wastes, oily-waste recovery, and evaporation/solvent extraction.
	"Waste Recycling Project Receives Go-Ahead," *Hydrocarbon Processing*, August 1995.	A facility will be constructed to convert chlorinated wastes and other wastes into carbon raw material via a molten bath.
Sludges	Kuriakose, A.P., Manjooran, S. Jochu Baby, "Utilization of Refinery Sludge for Lighter Oils and Industrial Bitumen," *Energy & Fuels*, 8(3), May-June, 1994.	Utilizing waste sludge.
	"New Process Effectively Recovers Oil From Refinery Waste Streams," *Oil & Gas Journal*, August 15, 1994.	Enhanced separation of oil, water and solids.
Wastewater treatment sludge	"HP Informer," *Hydrocarbon Processing*, October 1995.	Onsite thermal desorption unit recovers oil and decreases volume of disposed waste.
Sludge processing	"Industry Briefs," *Oil & Gas Journal*, December 25, 1995.	Oil from hazardous waste will be recovered in an unspecified recycling system at three refineries; the solids will be burned in cement kilns.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
Hydrogen Production	"Alternative Technologies to Steam-Methane Reforming" *Hydrocarbon Processing*, November 1995.	Discusses trade-offs including emissions for alternative hydrogen-generating technology.
Related Environmental Topics		
Pollution Prevention Planning	"Amoco-U.S. EPA Pollution Prevention Project, Yorktown, Virginia, Project Summary." January 1992 (Revised June 1992).	Pollution Prevention Planning
	Radecki, P.P., Hertz, D.W., and Vinton, C. "Build Pollution Prevention Into System Design." *Hydrocarbon Processing*. August 1994.	P2 planning.
	"Question & Answer Session on Waste Issues." *NPRA Environmental Conference Proceedings*. September 18-20, 1994.	Pollution Prevention Planning
	Richardson, K.E. "Refinery Waste Minimization." *NPRA Environmental Conference Proceedings*. September 18-20, 1994.	Pollution Prevention Planning
Audits	"Companies Wary of Use of Environmental Audits," *Oil & Gas Journal*, April 17, 1995.	Survey of many industries shows companies fear enforcement risks from self-initiated audits.
Wastewater treatment	"Croatian Refiner Meets Waste Water Treatment Standards, Reduces Fines," *Oil & Gas Journal*, November 27, 1995.	Installation of end-of-pipe control decreases hydrocarbons in effluent, but notes problems to recycling the water in the plant. Oil is recovered.
	"HP Impact," *Hydrocarbon Processing*, December 1995.	Liquid-liquid extraction may be used in the future for wastewater treatment.
Air emissions from wastewater treatment	"How to Renovate a 50-year-old Wastewater Treating Plant," *Hydrocarbon Processing*, February 1996.	Documents retrofitting required to comply with benzene NESHAPs requirements.
Multimedia emissions	"U.S. Refinery Emissions at Issue," *Oil & Gas Journal*, December 11, 1995.	EDF reported TRI releases and other factors affecting chemical reporting for refineries.
Emissions at Foreign refineries	"HP Impact," *Hydrocarbon Processing*, February 1996.	Report summarizes disposal patterns at European refineries.

Table IV-6. Bibliography to Waste Minimization Documents		
Waste	Reference	Subject
Used oil	"Oil Recycling Moves Upscale," *Oil & Gas Journal*, March 13, 1995.	U.K. company reprocesses and recycles used oil for fuel.
	"Re-refining Process Expands Worldwide," *Hydrocarbon Processing*, August 1995.	A new refinery is operating, which processes used oil, heavy refining bottoms, and other low value feedstocks.
Oil spills	"U.S. Spill Cleanup Capability Shows Marked Improvement," *Oil & Gas Journal*, January 1, 1996.	Reports on equipment availability and guidelines for spill cleanup.

V. Conclusions

As stated by several refineries in Table IV-2 of this report, source reduction has limitations within refineries due to the nature of the raw material, crude oil. When reporting source reduction activities, most refineries are actually reporting waste minimization because the bulk of their activities are recycling activities, such as oil recovery and offsite sales. However, given this limitation, some refineries are conducting or experimenting with innovative source reduction or waste minimization activities that are not widely used.

This report is limited by the data contained in the RCRA §3007 Survey responses. The differences in interpretation between source reduction and recycling among each of the refineries are reflected in their responses. While the survey responses are helpful in identifying which RCs have greater source reduction activities than others, the responses lack detail as to what these practices are. In addition, some facilities may not be able to report accurate residual quantities in Section VI, especially for those residuals that are not shipped offsite and instead recycled onsite. In these cases, facilities used engineering judgement of often report that estimates cannot be made. This inaccuracies will serve to possibly skew the volumes presented in this report, but would generally not change the number of facilities affected.