

**STUDY OF SELECTED
PETROLEUM REFINING RESIDUALS

INDUSTRY STUDY**

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Solid Waste
Hazardous Waste Identification Division
401 M Street, SW
Washington, DC 20460

3.8 RESIDUAL UPGRADING

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 and fines, as well as process sludges, are study residuals from this category.

3.8.1 Process Descriptions

A total of 47 refineries reported using residual upgrading units. Four types of residual upgrading processes were reported in the 1992 RCRA §3007 Petroleum Refining Survey:

- Solvent Deasphalting
- Asphalt Oxidation
- Supercritical Extraction
- Asphalt Emulsion

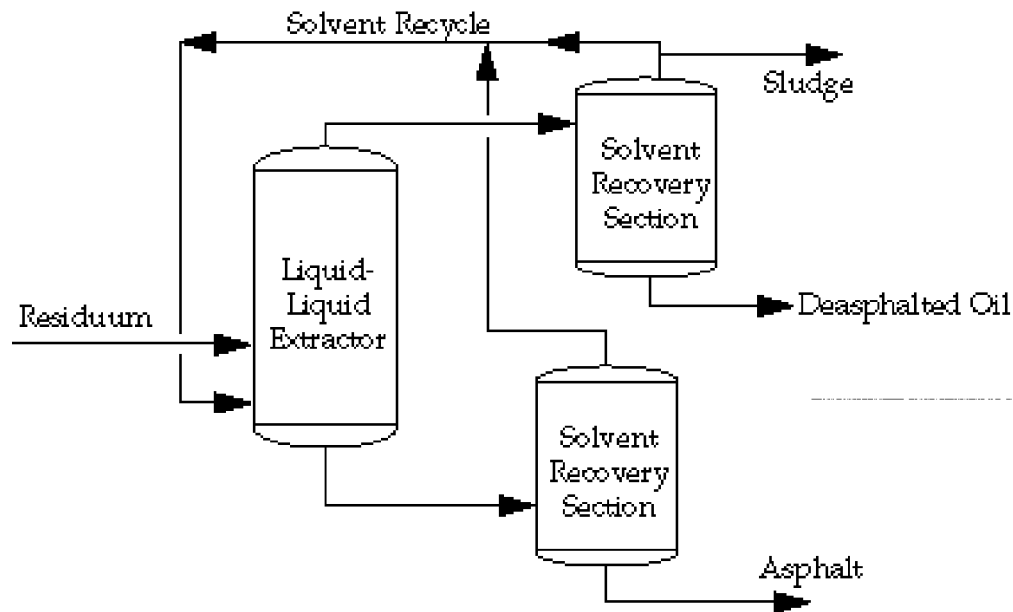
Asphalt uses are typically divided into use as road oils, cutback asphalts, asphalt emulsions, and solid asphalts. These asphalt products are used in paving roads, roofing, paints, varnishes, insulating, rust-protective compositions, battery boxes, and compounding materials that go into rubber products, brake linings, and fuel briquettes (REF).

3.8.1.1 Solvent Deasphalting

Residuum from vacuum distillation is separated into asphalt components and gas oil components by solvent deasphalting. Figure 3.8.1 provides a simplified process flow diagram. The hydrocarbon solvent is compressed and contacted with the residuum feed. The extract contains the paraffinic fractions (deasphalted oil or DAO), and the raffinate contains the asphaltic components. The extract and raffinate streams are sent to separate solvent recovery systems to reclaim the solvent. The DAO may be further refined or processed, used as catalytic cracking feed, sent to lube oil processing/blending, or sold as finished product. The following types of solvents are typically used for the following residual upgrading processes:

- Propane is the best choice for lube oil production due to its ability to extract only paraffinic hydrocarbons and to reject most of the carbon residue. (McKetta)
- A mixture of propane and butane is valuable for preparing feedstocks for catalytic cracking processes due to its ability to remove metal-bearing components. (McKetta)
- Pentane deasphalting, plus hydrodesulfurization, can produce more feed for catalytic cracking or low sulfur fuel oil. (McKetta)

Figure 3.8.1. Solvent Deasphalting Process Flow Diagram



- One facility reported using propane and phenol solvents for deasphalting residuum. The DAO is sent to lube oil processing and the asphalt fraction is sent to delayed coking or fuel oil blending.

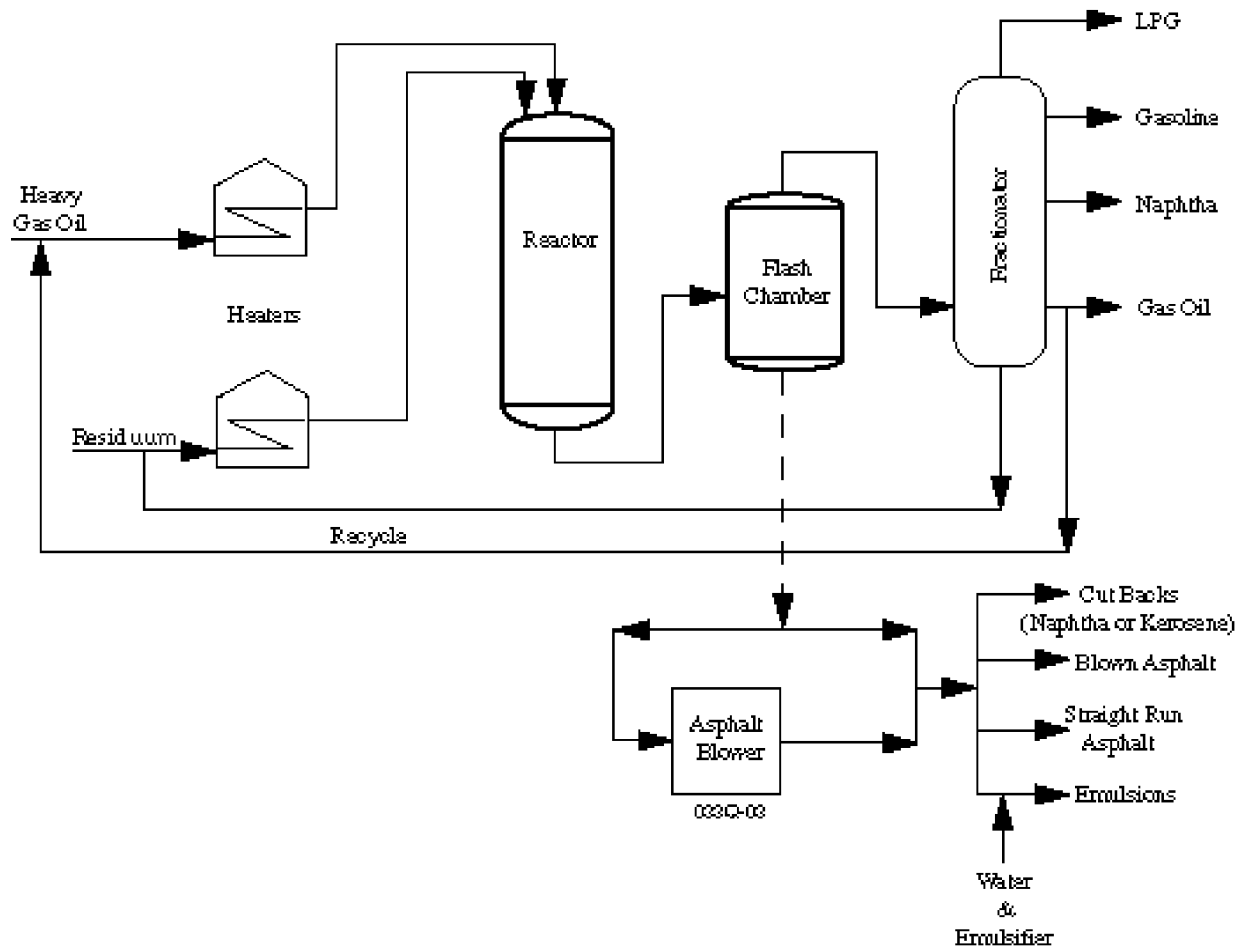
During process upsets, heavy hydrocarbons may become entrained in the solvent recovery systems, and off-specification product may be generated. The entrained hydrocarbons are periodically removed from the unit as a process sludge and typically disposed in an industrial landfill. The off-specification product are returned to the process for re-processing.

3.8.1.2 Asphalt Oxidation (Asphalt Blowing)

Residuum from the vacuum tower or from solvent deasphalting is upgraded by oxidation with air. Figure 3.8.2 provides a simplified process flow diagram. Air is blown through the asphalt that is heated to about 500°F, starting an exothermic reaction. The temperature is controlled by regulating the amount of air and by circulating oil or water through cooling coils within the oxidizer. The oxygen in the air reacts with hydrogen in the residuum to form water, and the reaction also couples smaller molecules of asphalt into larger molecules to create a heavier product. These reactions changes the characteristics of the asphalt to a product with the desired properties.

During this process, coke will form on the oxidizer walls and the air sparger. The coke is removed periodically (1 to 2 years) and sent to the coke pad for sale, mixed with asphalt for use as road material, stored, or disposed. The off-gases from the process are scrubbed to remove hydrocarbons prior to burning in an thermal unit such as an incinerator or furnace.

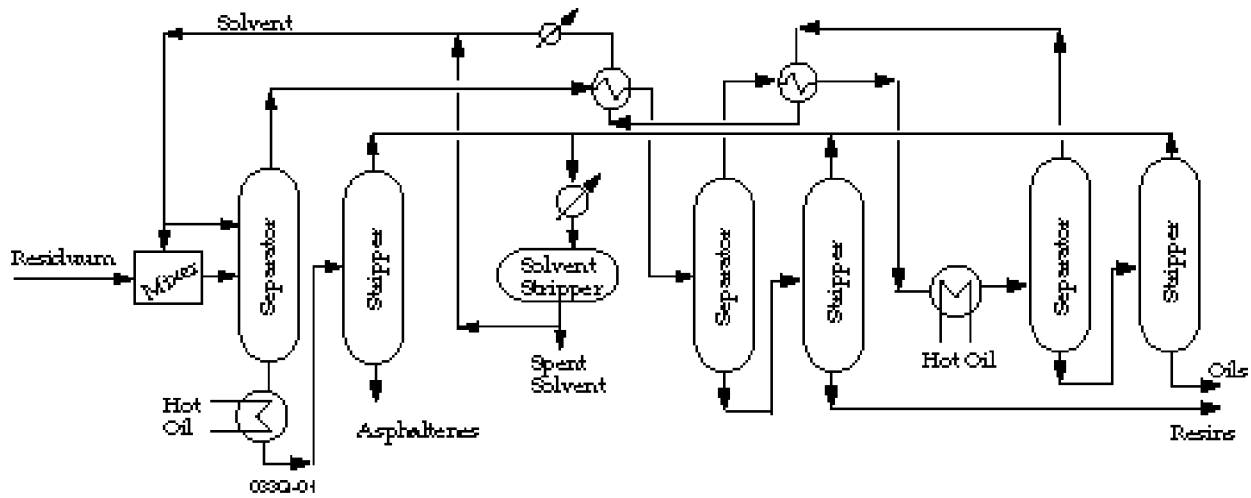
Figure 3.8.2. Asphalt Oxidation Process Flow Diagram



Supercritical Extraction

The Residuum Oil Supercritical Extraction (ROSE) process is not, in a strict sense, a supercritical fluid extraction process. The primary extraction step is not carried out at supercritical conditions, but at liquid conditions that take advantage of the variable solvent power of a near-critical liquid. A simplified process flow diagram is provided in Figure 3.8.3. The first stage of the ROSE process consists of mixing residuum with compressed liquid butane or pentane and precipitating the undesired asphaltene fraction. Butane is used for its higher solvent power for heavy hydrocarbons. If an intermediate resin fraction is desired, another separator and stripper system would be used directly after the asphaltene separator. To recover a resin fraction, the overhead from the asphaltene separator is heated to near the critical temperature of the butane. At the elevated, near-critical temperature, the solvent power of the compressed liquid butane decreases and the resins precipitate from solution. The remaining fraction would consist of deasphalted light oils dissolved in butane. The butane is typically recovered using steam.

Figure 3.8.3. Supercritical Extraction Process Flow Diagram



The DAO may be sent to FCC, blended into lubricating oil, or sold as finished product. The asphaltene and resins are reported to be blended into No. 6 fuel oil. The solvent and steam are condensed and collected in a surge drum where the solvent is recycled back to the process. This surge drum accumulates sludges during process upsets that are removed during routine process turnarounds and disposed as nonhazardous wastes.

Asphalt Emulsion

Residuals from the vacuum tower may be upgraded to an asphalt emulsion by milling soap (or shear mixing) with the asphalt. These emulsions are used for road oils, where good adhesion is required.

This process generated residuals from the cleanout of the soap tanks and from the generation of off-spec emulsions. The soap tank cleanout residuals are typically sent to the wastewater treatment plant, and the off-spec emulsions are sent to a pit where heat is applied to break the emulsion. The soap fraction is sent the wastewater treatment system and the oil fraction is recycled back to the coker feed.

3.8.2 Off-specification Product from Residual Upgrading

3.8.2.1 Description

This residual was identified in the consent decree based on an incorrect characterization of data in a supporting document generated from 1983 PRDB data. After conducting a review of the underlying data, it was determined that volumes associated with the category of “off-specification product from residual upgrading” were actually process sludges generated during process upset conditions. The Agency's finding regarding this category was corroborated during its field investigation where this residual category was not identified and in the §3007 survey results. Generally, refineries re-work any residuum that does not initially meet product specifications within the upgrading process and rarely (one reported in 1992 in the §3007 survey) generate off-specification product for disposal.

3.8.2.2 Generation and Management

Off-spec product from residual upgrading includes material generated from asphalt oxidation, solvent deasphalting, and other upgrading processes. Residuals were assigned to be “off-specification product from residual upgrading” if they were assigned a residual identification code of “off-specification product” or “fines” and were generated from a process identified as a residual upgrading unit. These correspond to residual codes “05” and “06” in Section VII.2 of the questionnaire and process code “13” in Section IV-1.C of the questionnaire.

Based on the results of the questionnaire, 47 facilities use residual upgrading processes and thus could potentially generate off-specification product from residual upgrading. Only one facility reported this residual, generating 800 MT that was recovered within the process. The base year, 1992, was expected to be a typical year for residual upgrading processes and the survey results are in keeping with the Agency's understanding of this process. Table 3.8.1 provides a description of the quantity generated and number of reporting facilities.

Table 3.8.1. Generation Statistics for Off-Specification Product from Residual Upgrading, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Other recovery onsite: reuse in extraction process	1	0	800	800

3.8.2.3 Plausible Management

The Agency does not find it necessary to consider other management practices because off-spec product from residual upgrading had been classified as a residual of concern based on erroneous old data and in fact is not generated for disposal.

3.8.2.4 Characterization

Only one source of residual characterization data were developed during the industry study:

- Table 3.8.2 summarizes the physical properties of the off-specification product as reported in Section VII.A of the §3007 survey.

Because it is rarely generated, no record samples of this residual were available during record sampling for analysis.

Table 3.8.2. Off-Specification Product from Residual Upgrading: Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	50th %	90th %
Flash Point, °C	1	2	99.00	99.00	99.00
Specific Gravity	1	2	1.02	1.02	1.02
Aqueous Liquid, %	1	2	40.00	40.00	40.00
Organic Liquid, %	1	2	60.00	60.00	60.00
Solid, %	1	2	100.00	100.00	100.00
Other, %	1	2	100.00	100.00	100.00

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

3.8.2.5 Source Reduction

No source reduction techniques were reported by industry or found in the literature search for this residual.

3.8.3 Process Sludge from Residual Upgrading

3.8.3.1 Description

Process sludge is generated from miscellaneous parts of the various residual upgrading processes. This category is neither uniform nor routinely generated. 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.

Three residuals were reported to be managed “as hazardous”, accounting for 25 percent of the volume of this category generated in 1992.¹

3.8.3.2 Generation and Management

Twenty-one facilities reported generating a total quantity of 241 MT of this residual in 1992, according to the 1992 survey. Residuals were assigned to be “process sludge from residual upgrading” if they were assigned a residual identification code of “process sludge” and were generated from a process identified as a “residual upgrading” unit. These correspond to residual code “02-D” in Section VII.2 of the questionnaire and process code “13” in Section IV-1.C of the questionnaire.

Based on the results of the questionnaire, 47 facilities use residual upgrading units and thus may generate process sludge from residual upgrading. Due to the infrequent generation of this residual, not all of these 47 facilities generated sludge in 1992. However, there was no reason to expect that 1992 would not be a typical year with regard to this residual's generation and management. Table 3.8.3 provides a description of the quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

Table 3.8.3. Generation Statistics for Process Sludge from Residual Upgrading, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Discharge to onsite wastewater treatment facility	3	0	3.94	1.31
Disposal in offsite Subtitle D landfill	12	0	137.56	11.46
Disposal in offsite Subtitle C landfill	1	0	0.10	0.10
Disposal in onsite Subtitle C landfill	4	0	62.00	15.50
Disposal in onsite Subtitle D landfill	2	0	7.30	3.65
Offsite incineration	1	0	9.00	9.00
Other recycling, reclamation, or reuse: onsite road material	4	0	0.22	0.06
Recovery onsite via distillation	1	0	16.00	16.00
Transfer with coke product or other refinery product	4	0	5.44	1.36
TOTAL	32	0	241.56	7.55

¹These percentages do not match up directly with any one of the management scenarios because the number of streams and the volume are a combination of several management scenarios (i.e., managed in WWTP, Subtitle C landfill, etc.).

3.8.3.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.8.3. The Agency gathered information suggesting that “recovery onsite in an asphalt production unit” (3.6 MT) and “transfer to offsite entity: unspecified” (unreported quantity) were used in other years. This non-1992 management practice is comparable with other recovery practices reported in 1992.

3.8.3.4 Characterization

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

- Table 3.8.4 summarizes the physical properties of the sludge as reported in Section VII.A of the §3007 survey.
- One record sample of process sludge from residual upgrading was collected and analyzed by EPA. This sample is summarized in Table 3.8.5.

The sample was analyzed for total and TCLP levels of volatiles, semivolatiles, metals, and ignitability. The sample was found to exhibit the toxicity characteristic for benzene. A summary of the results is presented in Table 3.8.6. Only constituents detected in the sample are shown in this table.

3.8.3.5 Source Reduction

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.

Table 3.8.4. Process Sludge from Residual Upgrading: Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	50th %	90th %
pH	11	38	5.50	6.30	7.60
Reactive CN, ppm	8	41	0.01	0.74	50.00
Reactive S, ppm	7	42	0.01	15.00	4400.00
Flash Point, °C	14	35	82.22	94.17	315.56
Oil and Grease, vol%	7	42	0.10	9.00	100.00
Total Organic Carbon, vol%	16	33	50.00	98.50	100.00
Specific Gravity	12	37	0.90	1.08	1.85
BTU Content, BTU/lb	3	46	11.00	5,000.00	10,000.00
Aqueous Liquid, %	23	26	0.00	0.00	25.00
Organic Liquid, %	23	26	0.00	5.00	90.00
Solid, %	34	15	10.00	99.00	100.00
Other, %	18	31	0.00	0.00	2.00
Particle >60 mm, %	12	37	20.00	50.00	100.00
Particle 1-60 mm, %	9	40	1.00	49.00	80.00
Particle 100 µm-1 mm, %	5	44	0.00	1.00	1.00
Particle 10-100 µm, %	1	48	0.00	0.00	0.00
Particle <10 µm, %	1	48	0.00	0.00	0.00
Median Particle Diameter, microns	1	48	60.00	60.00	60.00

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

Table 3.8.5. Process Sludge from Residual Upgrading Record Sampling Locations

Sample Number	Location	Description
R1-RU-01	Marathon, Indianapolis, IN	ROSE unit scale/sludge

Table 3.8.6. Process Sludge from Residual Upgrading Characterization

Volatile Organics - Method 8260A µg/kg			
	CAS No.	R1-RU-01	Comments
Acetone	67641	B 120,000	
Benzene	71432	73,000	
Ethylbenzene	100414	130,000	
Methylene chloride	75092	64,000	
4-Methyl-2-pentanone	108101	63,000	
n-Propylbenzene	103651	65,000	
Toluene	108883	310,000	
1,2,4-Trimethylbenzene	95636	570,000	
1,3,5-Trimethylbenzene	108678	150,000	
o-Xylene	95476	230,000	
m,p-Xylenes	108383 / 106423	690,000	
Naphthalene	91203	160,000	
TCLP Volatile Organics - Methods 1311 and 8260A µg/L			
	CAS No.	R1-RU-01	Comments
Benzene	71432	2,600	
Ethylbenzene	100414	570	
Toluene	108883	4,100	
1,2,4-Trimethylbenzene	95636	990	
o-Xylene	95476	1,300	
m,p-Xylene	108383 / 106423	2,800	
Semivolatile Organics - Method 8270B µg/kg			
	CAS No	R1-RU-01	Comments
Acenaphthene	83329	J 38,000	
Anthracene	120127	J 13,000	
Dibenzofuran	132649	J 13,000	
Fluorene	86737	J 39,000	
Phenanthrene	85018	120,000	
Pyrene	129000	J 19,000	
1-Methylnaphthalene	90120	390,000	
2-Methylnaphthalene	91576	570,000	
Naphthalene	91203	190,000	
TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L			
	CAS No.	R1-RU-01	Comments
Bis(2-ethylhexyl)phthalate	117817	J 30	
2,4-Dimethylphenol	105679	J 52	
Indene	95136	J 16	
1-Methylnaphthalene	90120	J 96	
2-Methylnaphthalene	91576	130	

Table 3.8.6. Process Sludge from Residual Upgrading Characterization (continued)

TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L (continued)			
	CAS No.	R1-RU-01	Comments
2-Methylphenol	95487	J 65	
3/4-Methylphenol	NA	J 85	
Naphthalene	91203	190	
Phenol	108952	J 57	
Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg			
	CAS No.	R1-RU-01	Comments
Aluminum	7429905	150	
Antimony	7440360	14.0	
Arsenic	7440382	43.0	
Barium	7440393	41.0	
Cadmium	7440439	1.10	
Calcium	7440702	15,000	
Chromium	7440473	86.0	
Cobalt	7440484	13.0	
Copper	7440508	92.0	
Iron	7439896	200,000	
Lead	7439921	20.0	
Magnesium	7439954	6,500	
Manganese	7439965	770	
Mercury	7439976	0.11	
Molybdenum	7439987	24.0	
Nickel	7440020	90.0	
Vanadium	7440622	100	
Zinc	7440666	40.0	
TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L			
	CAS No.	R1-RU-01	Comments
Calcium	7440702	130	
Iron	7439896	120	
Manganese	7439965	3.90	
Zinc	7440666	0.24	
Miscellaneous Characterization			
		R1-RU-01	Comments
Ignitability (oF)		199	

Notes:

- B Analyte also detected in the associated method blank.
- J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.

3.9 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.

3.9.1 Process Descriptions

The manufacture of lubricating oil base stocks consists of five basic steps:

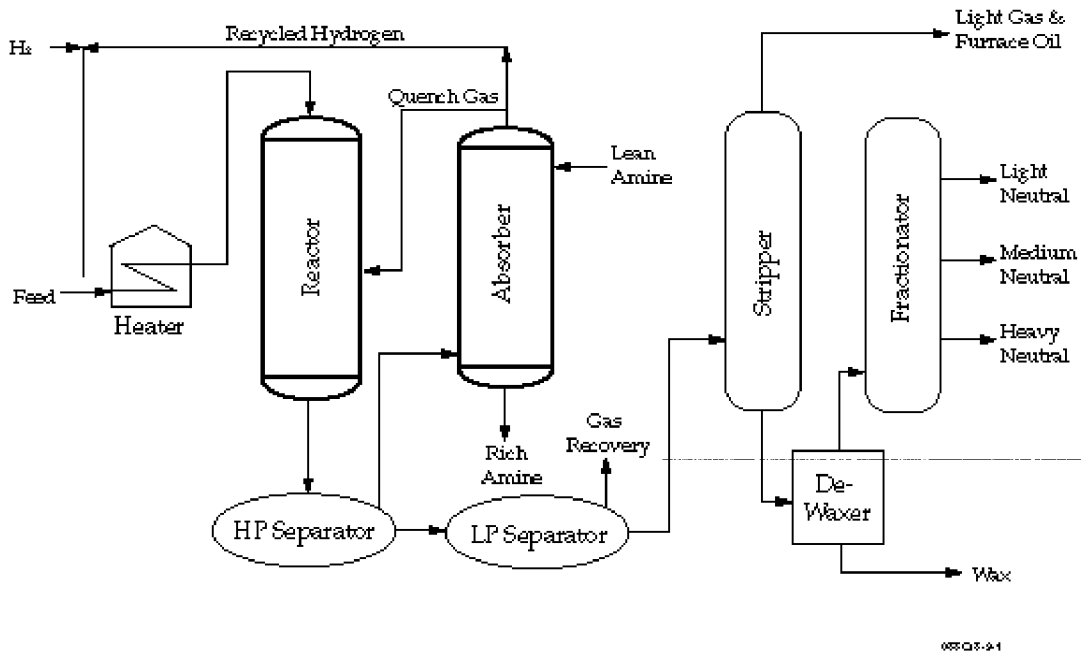
- 1) Distillation
- 2) Deasphalting to prepare the feedstocks
- 3) Solvent or hydrogen refining to improve viscosity index and quality
- 4) Solvent or catalytic dewaxing to remove wax and improve low temperature properties of paraffinic lubes
- 5) Clay or hydrogen finishing to improve color, stability, and quality of the lube base stock.

Based on results of the 1992 survey, 22 facilities reported conducting lube oil processing. The finished lube stocks are blended with each other and additives using batch and continuous methods to produce formulated lubricants. The most common route to finishing lube feedstocks consists of solvent refining, solvent dewaxing, and hydrogen finishing. The solvent and clay processing route or the hydrogen refining and solvent dewaxing route are also used. The all-hydrogen processing (lube hydrocracking-catalytic dewaxing-hydrorefining) route is used by two refiners for the manufacture of a limited number of paraffinic base oils. Figure 3.9.1 provides a general process flow diagram for lube oil processing.

Lube Distillation

Lube processing may be the primary production process at some facilities, while at others it is only one of many operations. The initial step is to separate the crude into the fractions which are the raw stocks for the various products to be produced. The basic process consists of an atmospheric distillation unit and a vacuum distillation unit. The majority of the lube stocks boil in the range between 580°F and 1000°F and are distilled in the vacuum unit to the proper viscosity and flash specifications. Caustic solutions are sometimes introduced to the feed to neutralize organic acids present in some crude oils. This practice reduces or eliminates corrosion in downstream processing units, and improves color, stability, and refining response of lube distillates.

Figure 3.9.1. Lube Oil Processing Flow Diagram



Lube Deasphalting

Other facilities incorporate lube deasphalting to process vacuum residuum into lube oil base stocks. Propane deasphalting is most commonly used to remove asphaltenes and resins which contribute an undesirable dark color to the lube base stocks. This process typically uses baffle towers or rotating disk contactors to mix the propane with the feed. Solvent recovery is accomplished with evaporators, and supercritical solvent recovery processes are also used in some deasphalting units. Another deasphalting process is the Duo-Sol Process that is used to both deasphalt and extract lubricating oil feedstocks. Propane is used as the deasphalting solvent and a mixture of phenol and cresylic acids are used as the extraction solvent. The extraction is conducted in a series of batch extractors followed by solvent recovery in multistage flash distillation and stripping towers. See the section on Residual Upgrading for additional discussion on these processes.

Lube Refining Processes

Chemical, solvent, and hydrogen refining processes have been developed and are used to remove aromatics and other undesirable constituents, and to improve the viscosity index and quality of lube base stocks. Traditional chemical processes that use sulfuric acid and clay refining have been replaced by solvent extraction/refining and hydrotreating which are more effective, cost efficient, and environmentally more acceptable. Chemical refining is used most often for the reclamation of used lubricating oils or in combination with solvent or hydrogen refining processes for the manufacture of specialty lubricating oils and by-products.

Chemical Refining Processes: Acid-alkali refining, also called “wet refining”, is a process where lubricating oils are contacted with sulfuric acid followed by neutralization with

alkali. Oil and acid are mixed and an acid sludge is allowed to coagulate. The sludge is removed or the oil is decanted after settling, and more acid is added and the process repeated.

Acid-clay refining, also called “dry refining” is similar to acid-alkali refining with the exception that clay and a neutralizing agent are used for neutralization. This process is used for oils that form emulsions during neutralization.

Neutralization with aqueous and alcoholic caustic, soda ash lime, and other neutralizing agents is used to remove organic acids from some feedstocks. This process is conducted to reduce organic acid corrosion in downstream units or to improve the refining response and color stability of lube feedstocks.

Hydrogen Refining Processes: Hydrogen refining, also called hydrotreating, has since been replaced with solvent refining processes which are more cost effective. Hydrotreating consists of lube hydrocracking as an alternative to solvent extraction, and hydrorefining to prepare specialty products or to stabilize hydrocracked base stocks. Hydrocracking catalysts are proprietary to the licensors and consist of mixtures of cobalt, nickel, molybdenum, and tungsten on an alumina or silica-alumina-based carrier. Hydrorefining catalysts are proprietary but usually consist of nickel-molybdenum on alumina.

Lube hydrocracking are used to remove nitrogen, oxygen, and sulfur, and convert the undesirable polynuclear aromatics and polynuclear naphthenes to mononuclear naphthenes, aromatics, and isoparaffins which are typically desired in lube base stocks. Feedstocks consist of unrefined distillates and deasphalted oils, solvent extracted distillates and deasphalted oils, cycle oils, hydrogen refined oils, and mixtures of these hydrocarbon fractions.

Lube hydrorefining processes are used to stabilize or improve the quality of lube base stocks from lube hydrocracking processes and for manufacture of specialty oils. Feedstocks are dependent on the nature of the crude source but generally consist of waxy or dewaxed-solvent-extracted or hydrogen-refined paraffinic oils and refined or unrefined naphthenic and paraffinic oils from some selected crudes.

Solvent Refining Processes: Feedstocks from solvent refining processes consist of paraffinic and naphthenic distillates, deasphalted oils, hydrogen refined distillates and deasphalted oils, cycle oils, and dewaxed oils. The products are refined oils destined for further processing or finished lube base stocks. The by-products are aromatic extracts which are used in the manufacture of rubber, carbon black, petrochemicals, FCCU feed, fuel oil, or asphalt. The major solvents used today are N-methyl-2-pyrrolidone (NMP) and furfural, with phenol and liquid sulfur dioxide used to a lesser extent.

The solvents are typically recovered in a series of flash towers. Steam or inert gas strippers are used to remove traces of solvent, and a solvent purification system is used to remove water and other impurities from the recovered solvent.

Lube Dewaxing Processes

Lube feedstocks typically contain increased wax content resulting from deasphalting and refining processes. These waxes are normally solid at ambient temperatures and must be removed to manufacture lube oil products with the necessary low temperature properties. Catalytic dewaxing and solvent dewaxing (the most prevalent) are processes currently in use; older technologies include cold settling, pressure filtration, and centrifuge dewaxing.

Catalytic Dewaxing: Because solvent dewaxing is relatively expensive for the production of low pour point oils, various catalytic dewaxing (selective hydrocracking) processes have been developed for the manufacture of lube oil base stocks. The basic process consists of a reactor containing a proprietary dewaxing catalyst followed by a second reactor containing a hydrogen finishing catalyst to saturate olefins created by the dewaxing reaction and to improve stability, color and demulsibility of the finished lube oil.

Solvent Dewaxing: Solvent dewaxing consists of the following steps: crystallization, filtration, and solvent recovery. In the crystallization step, the feedstock is diluted with the solvent and chilled, solidifying the wax components. The filtration step removes the wax from the solution of dewaxed oil and solvent. Solvent recovery removes the solvent from the wax cake and filtrate for recycle by flash distillation and stripping. The major processes in use today are the ketone dewaxing processes. Other processes that are used to a lesser degree include the Di/Me Process and the propane dewaxing process.

The most widely used ketone processes are the Texaco Solvent Dewaxing Process and the Exxon Dilchill Process. Both processes consist of diluting the waxy feedstock with solvent while chilling at a controlled rate to produce a slurry. The slurry is filtered using rotary vacuum filters and the wax cake is washed with cold solvent. The filtrate is used to prechill the feedstock and solvent mixture. The primary wax cake is diluted with additional solvent and filtered again to reduce the oil content in the wax. The solvent recovered from the dewaxed oil and wax cake by flash vaporization and recycled back into the process. The Texaco Solvent Dewaxing Process (also called the MEK process) uses a mixture of MEK and toluene as the dewaxing solvent, and sometimes uses mixtures of other ketones and aromatic solvents. The Exxon Dilchill Dewaxing Process uses a direct cold solvent dilution-chilling process in a special crystallizer in place of the scraped surface exchangers used in the Texaco process.

The Di/Me Dewaxing Process uses a mixture of dichloroethane and methylene dichloride as the dewaxing solvent. This process is used by a few refineries in Europe. The Propane Dewaxing Process is essentially the same as the ketone process except for the following: propane is used as the dewaxing solvent and higher pressure equipment is required, and chilling is done in evaporative chillers by vaporizing a portion of the dewaxing solvent. Although this process generates a better product and does not require crystallizers, the temperature differential between the dewaxed oil and the filtration temperature is higher than for the ketone processes (higher energy costs), and dewaxing aids are required to get good filtration rates.

Lube Oil Finishing Processes

Today, hydrogen finishing processes (also referred to as hydrorefining) have largely replaced the more costly acid and clay finishing processes. Hydrogen finishing processes are mild hydrogenation processes used to improve the color, odor, thermal, and oxidative stability, and demulsibility of lube base stocks. The process consists of fixed bed catalytic reactors that typically use a nickel-molybdenum catalyst to neutralize, desulfurize, and denitrify lube base stocks. These processes do not saturate aromatics or break carbon-carbon bonds as in other hydrogen finishing processes. Sulfuric acid treating is still used by some refiners for the manufacture of specialty oils and the reclamation of used oils. This process is typically conducted in batch or continuous processes similar to the chemical refining processes discussed earlier, with the exception that the amount of acid used is much lower than used in acid refining. Clay contacting involves mixing the oil with fine bleaching clay at elevated temperature followed by separation of the oil and clay. This process improves color and chemical, thermal, and color stability of the lube base stock, and is often combined with acid finishing. Clay percolation is a static bed absorption process used to purify, decolorize, and finish lube stocks and waxes. It is still used in the manufacture of refrigeration oils, transformer oils, turbine oils, white oils, and waxes.

3.9.2 Treating Clay from Lube Oil Processing

3.9.2.1 Description

The majority of treating clays (including other sorbents) generated from lube oil processing are from acid-clay treating in refining or lube oil finishing. The average volume is approximately 40 metric tons.

3.9.2.2 Generation and Management

The spent clay is vacuumed or gravity dumped from the vessels into piles or into containers such as drums and roll-off bins. Only one residual was reported to be managed “as hazardous” from this category in 1992.

Seven facilities reported generating a total quantity of approximately 733 metric tons of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residual were assigned to be “treating clay from lube oil processes” if they were assigned a residual identification code of “spent sorbent” and were generated from a lube oil process. These correspond to residual code “05” in Section VII.A of the questionnaire and process code “17” in Section IV.C of the questionnaire. Table 3.9.1 provides a description of the 1992 management practices, quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

Table 3.9.1. Generation Statistics for Treating Clay from Lube Oil, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Disposal in offsite Subtitle D landfill	1	1	36.7	36.7
Disposal in offsite Subtitle C landfill	2	0	78.7	39.4
Disposal in onsite Subtitle C landfill	1	0	5	5
Onsite land treatment	1	0	9.8	9.8
Other recycling, reclamation, or reuse: cement plant	1	0	249.2	249.2
Other recycling, reclamation, or reuse: onsite regeneration	12	0	354	29.5
TOTAL	18	1	733.4	40.7

3.9.2.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.9.1. No data were available to the Agency suggesting any other management practices. In addition, EPA compared the management practice reported for lube oil treating clay to those reported for treating clays from extraction, alkylation, and isomerization² based on expected similarities. No additional management practices were reported.

3.9.2.4 Characterization

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

- Table 3.9.2 summarizes the physical and chemical properties of treating clay from lube oil processes as reported in Section VII.A of the §3007 survey.
- One record sample of treating clay from lube oil processes was collected and analyzed by EPA. Sampling information is summarized in Table 3.9.3.

The collected sample is expected to be generally representative of treating clay from lube oil processes. The sample was analyzed for total and TCLP levels of volatiles, semi-volatiles, and metals. The sample did not exhibit any of the hazardous waste characteristics. A summary of the analytical results is presented in Table 3.9.4. Only constituents detected in the sample are reported.

²EPA did not compare these management practices to those reported for the broader category of “treating clay from clay filtering” due to the diverse types of materials included in this miscellaneous category.

Table 3.9.2. Treating Clay from Lube Oil: Physical Properties

Properties	# of Values	# of Unreported Values	10th %	50th %	90th %
pH	3	17	3.80	7.40	7.40
Flash Point, °C	2	18	95.00	95.00	95.00
Oil and Grease, vol%	12	8	1.00	1.00	1.00
Total Organic Carbon, vol%	12	8	1.00	1.00	1.00
Specific Gravity	15	5	0.90	3.20	3.20
Aqueous Liquid, %	4	16	0.00	0.00	0.00
Organic Liquid, %	4	16	0.00	0.00	0.00
Solid, %	7	13	100.00	100.00	100.00
Particle >60 mm, %	2	18	0.00	0.00	0.00
Particle 1-60 mm, %	2	18	0.00	45.80	91.60
Particle 100 µm-1 mm, %	2	18	8.40	54.20	100.00
Particle 10-100 µm, %	4	16	0.00	50.00	100.00
Particle <10 µm, %	2	18	0.00	0.00	0.00
Median Particle Diameter, microns	2	18	0.00	400.00	800.00

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

Table 3.9.3. Treating Clay from Lube Oil Processing Record Sampling Locations

Sample Number	Location	Description
R13-CL-01	Shell, Deer Park, TX	Pellets from wax treating

3.9.3.5 Source Reduction

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

Table 3.9.4. Treating Clay from Lube Oil Processing Characterization

Volatile Organics - Method 8260A µg/kg			
	CAS No.	R13-CL-01	Comments
Benzene	71432	11	
Ethylbenzene	100414	J 8	
Methylene chloride	75092	24	
n-Propylbenzene	103651	J 8	
Toluene	108883	31	
1,2,4-Trimethylbenzene	95636	78	
1,3,5-Trimethylbenzene	108678	34	
o-Xylene	95476	18	
m,p-Xylenes	108383 / 106423	52	
TCLP Volatile Organics - Methods 1311 and 8260A µg/L			
	CAS No.	R13-CL-01	Comments
Methylene chloride	75092	B 2,600	
Semivolatile Organics - Method 8270B µg/kg			
	CAS No	R13-CL-01	Comments
Bis(2-ethylhexyl)phthalate	117817	38,000	
Di-n-butyl phthalate	84742	J 390	
N-Nitrosodiphenylamine	86306	J 470	
TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L			
	CAS No.	R13-CL-01	Comments
2-Methylphenol	95487	J 18	
3/4-Methylphenol	NA	J 18	
Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg			
	CAS No.	R13-CL-01	Comments
Aluminum	7429905	140,000	
Barium	7440393	53.0	
Calcium	7440702	1,300	
Chromium	7440473	100	
Copper	7440508	260	
Iron	7439896	19,000	
Lead	7439921	36.0	
Manganese	7439965	180	
Vanadium	7440622	130	
Zinc	7440666	120	

Table 3.9.4. Treating Clay from Lube Oil Processing Characterization (continued)

TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L			
	CAS No.	R13-CL-01	Comments
Aluminum	7429905	12.0	
Copper	7440508	0.90	
Manganese	7439965	1.50	
Zinc	7440666	B	0.94
Miscellaneous Characterization			
		R13-CL-01	Comments
Ignitability (oF)		NA	

Comments:

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

Notes:

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

3.10 H₂S REMOVAL AND SULFUR COMPLEX

3.10.1 Process Description

All crude oil contains sulfur, which must be removed at various points of the refining process. The predominant technique for treating light petroleum gases is (1) amine scrubbing followed by (2) recovery of elemental sulfur in a Claus unit followed by (3) final sulfur removal in a tail gas unit. This dominance is shown in Table 3.10.1, which presents the sulfur complex/removal processes reported in the RCRA §3007 Survey.

Table 3.10.1. Sulfur Removal Technologies Reported in RCRA §3007 Questionnaire

Technique	Number of Facilities	Percentage of Facilities ¹
Amine-based sulfur removal	106	86
Claus sulfur recovery ²	101	82
Other sulfur removal or recovery	16	13
SCOT®-type tail gas unit ³	50	41
Other tail gas treating unit ⁴	19	15

¹Percentage of the 123 facilities reporting any sulfur removal/complex technique.

²Note that more facilities perform sulfur removal than perform sulfur recovery. Some refineries transfer their H₂S-containing amine offsite to another nearby refinery.

³Shell and other companies license similar technologies. All are included here as "SCOT®-type."

⁴14 facilities use the Beavon-Stretford process for tail gas treating.

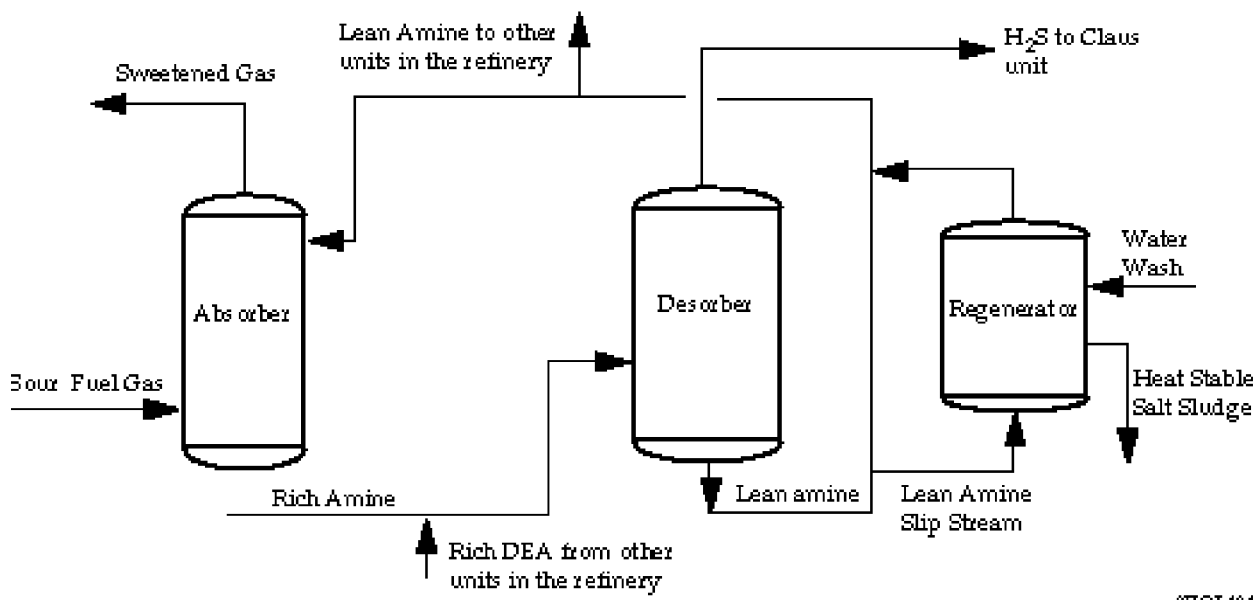
Caustic or water is often used in conjunction with, or instead of, amine solution to remove sulfur, particularly for liquid petroleum fractions. These processes, however, are generally not considered sulfur removal processes because either (1) the sulfur is not further complexed from these solutions (i.e., is not removed from the solution), or (2) if removed, it occurs in a sour water stripper which is in the domain of the facility's wastewater treatment system. Such processes are considered to be liquid treating with caustic, which was discussed in the Listing Background Document.

The dominant sulfur removal/complex train, amine scrubbing followed by Claus unit followed by SCOT®-type tail gas treating, is discussed below. In addition, the second-most popular tail gas system, the Beavon-Stretford system, is discussed. Finally, other processes reported in the questionnaires are discussed.

3.10.1.1 Amine Scrubbing

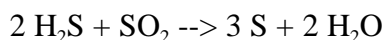
As shown in Table 3.10.1, amine scrubbing is used by most facilities, with 106 refineries reporting this process in the questionnaire. A typical process flow diagram for an amine scrubbing system is shown in Figure 3.10.1. The purpose of the unit is to remove H₂S from refinery fuel gas for economical downstream recovery. Fuel gas from the refinery is fed to a countercurrent absorber with a 25 to 30 percent aqueous solution of amine such as monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA). The H₂S reacts with the amine solution to form a complex, “rich” amine. Typically, a refinery will have several absorbers located throughout the refinery depending on the location of service. These “rich” streams are combined and sent to a common location at the sulfur plant where the H₂S is stripped from the amine in the reverse reaction. The “lean” amine is recycled back to the absorbers.

Figure 3.10.1. Amine Sulfur Removal Process Flow Diagram



3.10.1.2 Claus Unit

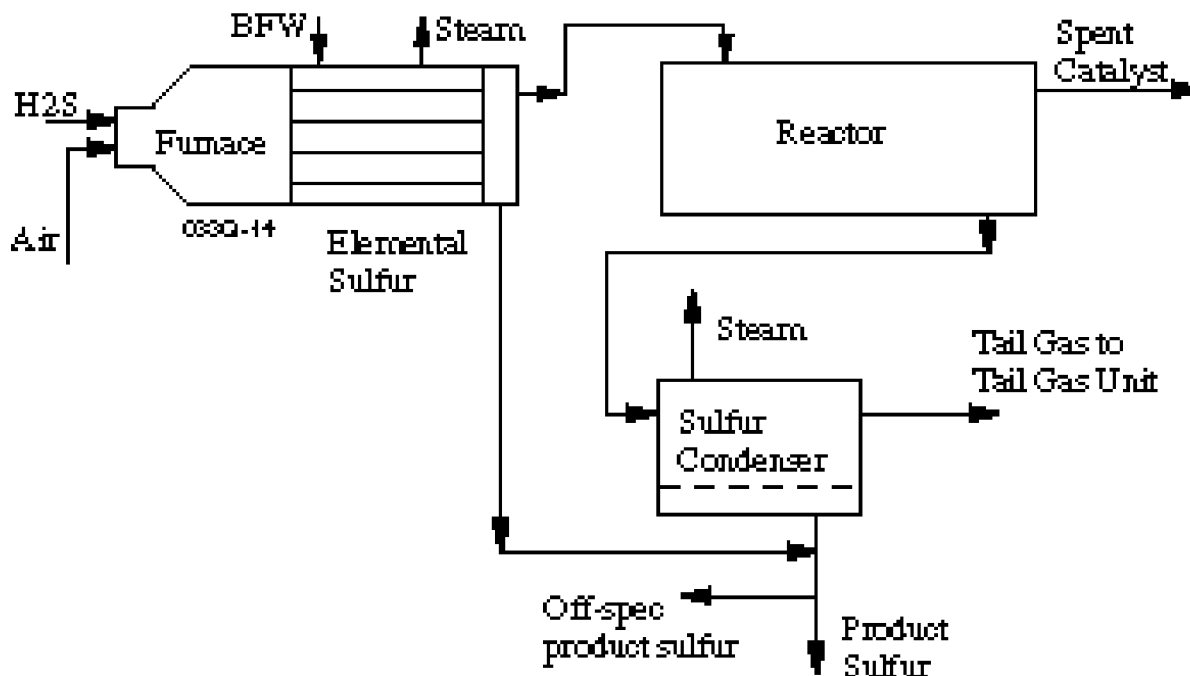
The H₂S from the sulfur removal unit is most often recovered in a Claus system as elemental sulfur. Table 3.10.1 shows that 101 refineries reported this process in the questionnaire. A typical process flow diagram for a Claus unit is shown in Figure 3.10.2. In a Claus unit, the H₂S is partially combusted with air to form a mixture of SO₂ and H₂S. It then passes through a reactor containing activated alumina catalyst to form sulfur by the following endothermic reaction:



The reaction is typically conducted at atmospheric pressure. The resulting sulfur is condensed to its molten state, drained to a storage pit, and reheated. The typical Claus unit consists of three such reactor/condenser/reheaters to achieve an overall sulfur removal yield of 90 to 95 percent.

At this point the tail gas can be (1) combusted and released to the atmosphere, or (2) sent to a tail gas unit to achieve greater sulfur reduction.

Figure 3.10.2. Claus Sulfur Recovery Process Flow Diagram



3.10.1.3 SCOT[®] Tailgas Unit

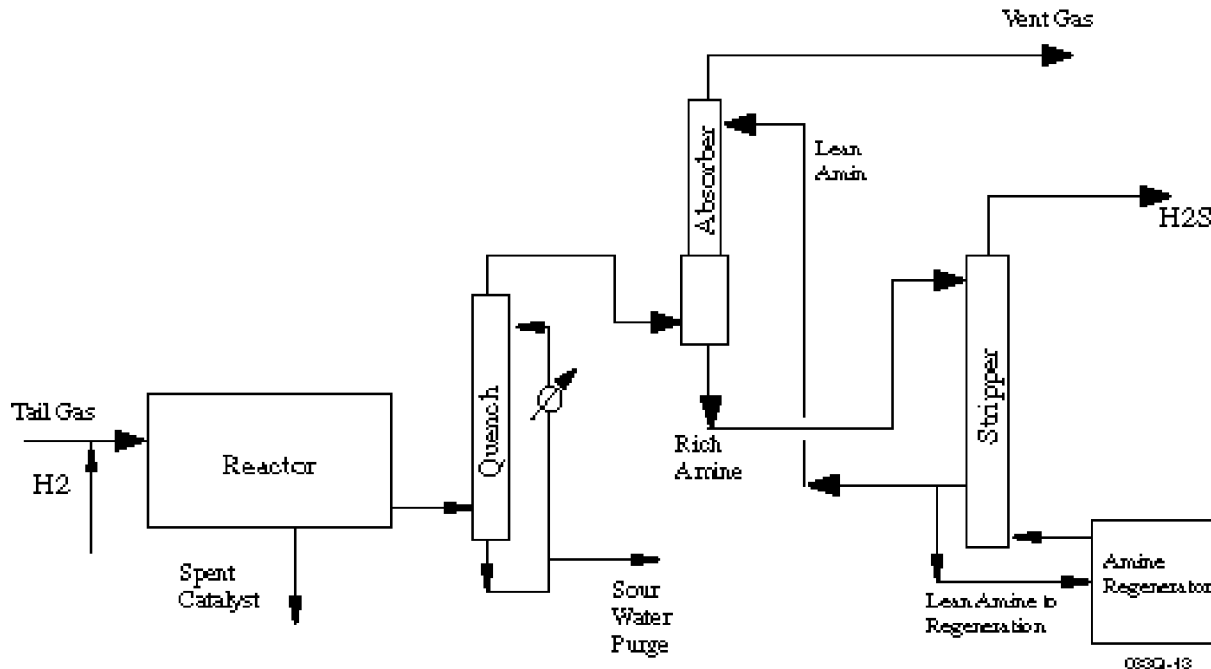
The most common type of tail gas unit uses a hydrotreating reactor followed by amine scrubbing to recover and recycle sulfur, in the form of H₂S, to the Claus unit. Shell licenses this technology as the Shell Claus Offgas Treating (SCOT[®]) unit; many other refineries reported using similar designs licensed by other vendors. All can be represented by the generalized process flow diagram shown in Figure 3.10.3.

Tail gas (containing H₂S and SO₂) is contacted with H₂ and reduced in a hydrotreating reactor to form H₂S and H₂O. The catalyst is typically cobalt/molybdenum on alumina. The gas is then cooled in a water contractor. The water circulates in the column and requires periodic purging due to impurity buildup; filters may be used to control levels of particulates or impurities in the circulating water.

The H₂S-containing gas enters an amine absorber which is typically in a system segregated from the other refinery amine systems discussed above. The purpose of segregation is two-fold: (1) the tail gas treater frequently uses a different amine than the rest of the plant, such as MDEA or diisopropyl amine (DIPA), and (2) the tail gas is frequently cleaner than the refinery fuel gas (in regard to contaminants) and segregation of the systems reduces maintenance requirements for the SCOT[®] unit. Amines chosen for use in the tail gas system tend to be more selective for H₂S and are not affected by the high levels of CO₂ in the offgas.

The “rich” amine generated from this step is desorbed in a stripper; the lean amine is recirculated while the liberated H₂S is sent to the Claus unit. Particulate filters are sometimes used to remove contaminants from lean amine.

Figure 3.10.3. SCOT[®] Tail Gas Sulfur Removal Process Flow Diagram



3.10.1.4 Beavon-Stretford Tail Gas Unit

This system was reported to be used by 14 facilities. A hydrotreating reactor converts SO₂ in the offgas to H₂S. The generated H₂S is contacted with Stretford solution (a mixture of vanadium salt, anthraquinone disulfonic acid (ADA), sodium carbonate, and sodium hydroxide) in a liquid-gas absorber. The H₂S reacts stepwise with sodium carbonate and ADA to produce elemental sulfur, with vanadium serving as a catalyst. The solution proceeds to a tank where oxygen is added to regenerate the reactants. One or more froth or slurry tanks are used to skim the product sulfur from the solution, which is recirculated to the absorber.

3.10.1.5 Other Processes

Although the amine/Claus train followed by a SCOT[®] or Beavon-Stretford tail gas unit is the dominant system used in the industry, it is not exclusive. Some refineries, mostly small asphalt plants, do not require sulfur removal processes at all, while others use alternative technologies. Each of these processes are used by less than five refineries, and most often are used by only one or two facilities. In decreasing order of usage, these other processes are as follows:

Sulfur Removal/Recovery Processes

Sodium Hydrosulfide: Fuel gas containing H₂S is contacted with sodium hydroxide in an absorption column. The resulting liquid is product sodium hydrosulfide (NaHS).

Iron Chelate: Fuel gas containing H₂S is contacted with iron chelate catalyst dissolved in solution. H₂S is converted to elemental sulfur, which is recovered.

Stretford: Similar to iron chelate, except Stretford solution is used instead of iron chelate solution.

Ammonium Thiosulfate: In this process, H₂S is contacted with air to form SO₂. The SO₂ is contacted with ammonia in a series of absorption column to produce ammonium thiosulfate for offsite sale. (Kirk-Othmer, 1983)

Hyperion: Fuel gas is contacted over a solid catalyst to form elemental sulfur. The sulfur is collected and sold. The catalyst is comprised of iron and naphthoquinonsulfonic acid.

Sulfatreat: The Sulfatreat material is a black granular solid powder; the H₂S forms a chemical bond with the solid. When the bed reaches capacity, the Sulfatreat solids are removed and replaced with fresh material. The sulfur is not recovered.

A few facilities report sour water stripping, which was not part of the scope of the survey. The actual number of sour water strippers is likely to be much greater than reported in the questionnaire.

Hysulf: This process is under development by Marathon Oil Company and was not reported by any facilities in the questionnaire. Hydrogen sulfide is contacted with a liquid quinone in an organic solvent such as n-methyl-2-pyrrolidone (NMP), forming sulfur. The sulfur is removed and the quinone reacted to its original state, producing hydrogen gas (*The National Environmental Journal*, March/April 1995).

Tail Gas Processes

Caustic Scrubbing: An incinerator converts trace sulfur compounds in the offgas to SO₂. The gas is contacted with caustic which is sent to the wastewater treatment system.

Polyethylene Glycol: Offgas from the Claus unit is contacted with this solution to generate an elemental sulfur product. Unlike the Beavon Stretford process, no hydrogenation reactor is used to convert SO₂ to H₂S. (Kirk-Othmer, 1983)

Selectox: A hydrogenation reactor converts SO₂ in the offgas to H₂S. A solid catalyst in a fixed bed reactor converts the H₂S to elemental sulfur. The elemental sulfur is recovered and sold. (*Hydrocarbon Processing*, April 1994).

Sulfite/Bisulfite Tail Gas Treating Unit: Following Claus reactors, an incinerator converts trace sulfur compounds to SO₂. The gas is contacted with sulfite solution in an

absorber, where SO₂ reacts with the sulfite to produce a bisulfite solution. The gas is then emitted to the stack. The bisulfite is regenerated and liberated SO₂ is sent to the Claus units for recovery. (Kirk-Othmer, 1983)

3.10.2 Off-Specification Product from Sulfur Complex and H₂S Removal Facilities

3.10.2.1 Description

Elemental sulfur is the most common product from sulfur complex and H₂S removal facilities, although a small number of facilities generate product sodium hydrosulfide or ammonium thiosulfate, as discussed in Section 3.10.1.5. 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.”

Stretford System

Although the Beavon-Stretford system is used by only 14 refineries, off-spec sulfur generated from this process accounts for 2/3 of the refinery-wide 1992 generation of off-spec sulfur. Sources of this volume are as follows:

- **Product sulfur:** Some refineries routinely dispose of their continuously generated product sulfur rather than sell it. Presumably, these refineries have operational difficulties making “on-spec” sulfur from the vanadium-catalyzed process. The small number of refineries managing sulfur this way account for most of the quantity of off-spec sulfur generated industry-wide. Other refineries sell all or most of their product sulfur and only dispose of sulfur generated from spills, etc.
- **Filtered solids from spent Stretford solution:** As discussed further in Section 3.10.3, many refineries report that a portion of the circulating Stretford solution must be purged to remove impurities in the system. After purging, some refineries filter out the solids prior to further managing the spent solution.
- **Turnaround sludge (sediment):** Every few years, the process units are thoroughly cleaned as preparation for maintenance. The principal source of this turnaround sludge is the froth (slurry) tank.
- **Miscellaneous sludges (sediments):** Other solids build up in the system, including tank sludges and process drain pit sludge. They are removed intermittently.

Every residual generated by the Stretford process contains elemental (product) sulfur because sulfur is a reaction product. Most refineries designated the above materials as off-spec product in their questionnaire response, and these residuals are included in statistics discussed later in this Section.

Claus System

Based on database responses, many Claus units generate off-spec sulfur at frequencies ranging from 2 months to 2 years. Sources of such sulfur are spills, process upsets, turnarounds, or maintenance operations. Some refineries generate off-spec sulfur more frequently; one refinery reports that certain spots are drained daily to ensure proper operation.

Other Systems

The amine scrubbing and SCOT[®] units do not generate off-spec sulfur because they do not generate product sulfur (their product is H₂S, an intermediate for the Claus sulfur recovery unit). Other systems generating elemental sulfur or product sulfur compounds can generate off-spec sulfur for the same reasons described above for Claus and Stretford processes.

3.10.2.2 Generation and Management

Most off-spec sulfur from Claus units is solid with little water content. The off-spec sulfur residuals described above from the Stretford process contain varying levels of solution which would give the residual a solid, sludge, or slurry form. Some refineries report filtering this material to generate off-spec sulfur with higher solids levels.

Based on the questionnaire responses, most refineries (regardless of process) reported storing off-spec sulfur onsite in a drum, in a dumpster, or in a pile prior to its final destination. In 1992, five facilities reported classifying this residual as RCRA hazardous (a total quantity of 2,551 MT were reported), however, the hazard waste code was generally not reported.³

Sixty facilities reported generating a total quantity of almost 9,650 MT of this residual in 1992, according to the 1992 RCRA §3007 Survey. As stated in Section 3.10.1, 123 facilities reported sulfur complex/removal processes. The remaining 63 facilities either report never generating this residual, or reported generation in years other than 1992 (due to intermittent generation). There was no reason to expect that 1992 would not be a typical year with regard to this residual's generation and management. Because most of the generation quantity is concentrated at a small number of facilities using the Stretford process, however, future operational changes at those sites could greatly impact the industry-wide residual generation rate.

Residuals were assigned to be “off-spec sulfur” if they were assigned a residual identification code of “off-spec product” and were generated from a process identified as a sulfur removal or complex unit. These correspond to residual code 05 in Section VII.A of the questionnaire and process code 15 in Section IV.C of the questionnaire. Table 3.10.2 provides a description of the 1992 management practices, quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

³These percentages do not match up directly with any one of the management scenarios because the number of streams and the volume are a combination of several management scenarios (i.e., Subtitle C landfill, transfer to offsite entity, etc.).

Table 3.10.2. Generation Statistics for Off-Spec Sulfur, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Disposal in offsite Subtitle D landfill	41	10	5,043.53	123.01
Disposal in offsite Subtitle C landfill	6	2	3,575.50	510.79
Disposal in onsite Subtitle C landfill	3	0	289.07	96.36
Disposal in onsite Subtitle D landfill	10	3	225.50	22.55
Other disposal offsite (anticipated to be Subtitle C landfill)	1	0	0.10	0.10
Offsite incineration	1	0	0.70	0.70
Offsite land treatment	1	0	0.95	0.95
Other recovery onsite: sulfur plant	1	1	2.00	2.00
Transfer for use as an ingredient in products placed on the land	1	0	15.00	15.00
Transfer to other offsite entity	1	2	487.80	487.80
Transfer with coke product or other refinery product	4	0	6.52	1.63
TOTAL	70	21	9,646.57	137.8

3.10.2.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.10.2. No data were available to the Agency suggesting any other management practices.

3.10.2.4 Characterization

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

- Table 3.10.3 summarizes the physical and chemical properties of off-spec sulfur as reported in Section VII.A of the §3007 survey.
- Four record samples of off-spec sulfur were collected and analyzed by EPA. All of these were collected from the Claus process. Sampling information is summarized in Table 3.10.4.

The collected samples are expected to be representative of off-spec sulfur generated from Claus units, the sulfur recovery process used by most refineries. They are not expected to represent off-spec sulfur from the Stretford process because vanadium would be present in off-spec sulfur from this process at levels higher than those found in off-spec sulfur from Claus units. Concentrations of other contaminants may also differ.

All four record samples were analyzed for total and TCLP levels of volatiles, semivolatiles and metals. None of the samples were found to exhibit a hazardous waste characteristic. A summary of the analytical results is presented in Table 3.10.5. Only constituents detected in at least one sample are shown in this table.

3.10.2.5 Source Reduction

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.

Table 3.10.3. Off-Specification Sulfur: Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	50th %	90th %
pH	45	62	2.80	5.50	9.00
Reactive CN, ppm	20	87	0.00	0.25	20.85
Reactive S, ppm	35	72	0.00	1.23	92.00
Flash Point, °C	30	77	60.00	93.33	187.78
Oil and Grease, vol%	28	78	0.00	0.54	13.10
Total Organic Carbon, vol%	12	95	0.00	0.00	1.00
Vapor Pressure, mm Hg	9	98	0.00	0.10	11.00
Vapor Pressure Temperature, °C	9	98	20.00	140.00	284.00
Specific Gravity	35	72	0.80	1.36	2.07
Specific Gravity Temperature, °C	11	96	4.00	15.60	21.10
BTU Content, BTU/lb	15	92	0.00	4,606.00	4,606.00
Aqueous Liquid, %	46	61	0.00	0.00	5.00
Organic Liquid, %	44	63	0.00	0.00	100.00
Solid, %	82	25	60.00	100.00	100.00
Particle >60 mm, %	28	79	0.00	80.00	100.00
Particle 1-60 mm, %	24	83	0.00	22.50	100.00
Particle 100 µm-1 mm, %	23	84	0.00	0.00	100.00
Particle 10-100 µm, %	14	93	0.00	0.00	0.00
Particle <10 µm, %	14	93	0.00	0.00	0.00
Median Particle Diameter, microns	7	100	0.00	0.00	200.00

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

Table 3.10.4. Off-Specification Sulfur Record Sampling Locations

Sample number	Facility	Description
R1-SP-01	Marathon, Indianapolis, IN	Claus unit: contents of product tank destined for disposal
R2-SP-01	Shell, Wood River, IL	Claus unit: generated daily from unit "low spots"
R7B-SP-01	BP, Belle Chase, LA	Claus unit: from cleaning and turnaround of product tank
R23-SP-01	Chevron, Salt Lake City, UT	Claus unit: from loading spills, connection leaks, and sumps

Table 3.10.5. Residual Characterization Data for Off-Specification Sulfur

Volatile Organics - Method 8260A µg/kg								
	CAS No.	R1-SP-01	R2-SP-01	R7B-SP-01	R23-SP-01	Average Conc	Maximum Conc	Comments
Acetone	67641	< 25	< 25	< 5	2,000	514	2,000	
TCLP Volatile Organics - Methods 1311 and 8260A µg/L								
	CAS No.	R1-SP-01	R2-SP-01	R7B-SP-01	R23-SP-01	Average Conc	Maximum Conc	Comments
Acetone	67641	B 2,300	< 50	< 50	B 160	640	2,300	
Semivolatile Organics - Method 8270B µg/kg								
	CAS No.	R1-SP-01	R2-SP-01	R7B-SP-01	R23-SP-01	Average Conc	Maximum Conc	Comments
Bis(2-ethylhexyl) phthalate	117817	J 75	< 165	880	460	395	880	
Benzo(a)pyrene	50328	< 165	< 165	< 165	J 110	110	110	1
Benzo(g,h,i) perylene	191242	< 165	< 165	< 165	J 130	130	130	1
Chrysene	218019	< 165	< 165	< 165	J 270	191	270	
Di-n-butyl phthalate	84742	< 165	< 165	J 140	< 165	140	140	1
Di-n-octyl phthalate	117840	< 165	< 165	J 180	< 165	169	180	
Pyridine	110861	< 165	J 160	< 165	< 165	160	160	1
Fluorene	86737	< 165	< 165	J 280	< 165	194	280	
2-Methylchrysene	3351324	< 330	< 330	< 330	J 230	230	230	1
1-Methylnaphthalene	90120	< 330	< 330	680	< 330	418	680	
2-Methylnaphthalene	91576	< 165	< 165	760	< 165	314	760	
Phenanthrene	85018	< 165	< 165	J 140	< 165	140	140	1
TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L								
	CAS No.	R1-SP-01	R2-SP-01	R7B-SP-01	R23-SP-01	Average Conc	Maximum Conc	Comments
Bis(2-ethylhexyl) phthalate	117817	< 50	J 11	< 50	< 50	11	11	1

Table 3.10.5. Residual Characterization Data for Off-Specification Sulfur (continued)

Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg								
	CAS No.	R1-SP-01	R2-SP-01	R7B-SP-01	R23-SP-01	Average Conc	Maximum Conc	Comments
Aluminum	7429905	< 20	< 20	780	350	293	780	
Barium	7440393	< 20	< 20	90.0	< 20	37.5	90.0	
Calcium	7440702	< 500	< 500	3,400	< 500	1,225	3,400	
Chromium	7440473	2.70	< 1.00	62.0	4.70	17.6	62.0	
Copper	7440508	< 2.50	< 2.50	68.0	8.40	20.4	68.0	
Iron	7439896	62.0	610	22,000	710	5,846	22,000	
Lead	7439921	< 0.30	0.83	4.30	3.40	2.21	4.30	
Manganese	7439965	< 1.50	< 1.50	91.0	3.20	24.3	91.0	
Molybdenum	7439987	< 6.50	< 6.50	15.0	< 6.50	8.63	15.0	
Nickel	7440020	< 4.00	< 4.00	21.0	< 4.00	8.25	21.0	
Zinc	7440666	< 2.00	< 2.00	140	34.0	44.5	140	
TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L								
	CAS No.	R1-SP-01	R2-SP-01	R7B-SP-01	R23-SP-01	Average Conc	Maximum Conc	Comments
Aluminum	7429905	< 1.00	< 1.00	5.90	< 1.00	2.23	5.90	
Calcium	7440702	< 25.0	< 25.0	62.0	< 25.0	34.3	62.0	
Chromium	7440473	< 0.05	< 0.05	0.43	< 0.05	0.15	0.43	
Iron	7439896	< 0.50	16.0	44.0	1.50	15.5	44.0	
Manganese	7439965	< 0.08	0.26	0.77	< 0.08	0.30	0.77	
Zinc	7440666	0.31	< 0.10	B 2.90	B 0.87	1.05	2.90	

Comments:

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

Notes:

- B Analyte also detected in the associated method blank.
- J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.

3.10.3 Off-Specification Treating Solution from Sulfur Complex and H₂S Removal Facilities

3.10.3.1 Description

All treating solutions used in refinery sulfur removal systems are regenerative, meaning the solution is used over and over in a closed system (for example, amines use multiple absorption/desorption cycles, while Stretford solution undergoes multiple reversible reactions). In the following instances the treating solution becomes “off-spec” and cannot be reused:

- **Amine systems.** At most refineries, amine continuously leaves the closed system through entrainment in overhead gas, leaks, and other routes. The amine is collected in various locations such as sumps and either returned to the process or discharged to the refinery's wastewater treatment (possibly due to purity constraints).

At some refineries, the circulating amine must be replaced in whole or in part due to contamination or process upset. Rarely, a refinery may change from one amine to another and completely remove the existing amine from the system prior to introducing the new solution.

- **Stretford systems.** Many refineries report that a portion of the circulating Stretford solution must be purged to remove impurities in the system. After purging, some refineries filter out the solids prior to further managing the spent solution. Stretford systems are used at a smaller number (15) of facilities. Unlike amine systems, Stretford solution is generally used only in tail gas treating.

During operation, the treating solution alternatively becomes “rich” (i.e., containing H₂S) and “lean” (i.e., containing low levels or no H₂S). In all observed cases, a refinery will generate off-spec treating solution when it is “lean.”

Approximately 800 MT of off-spec treating solution generated in 1992 was identified by 6 facilities as displaying hazardous characteristics.⁴ The facilities designated the wastes with hazardous waste codes D002 (corrosive), D003 (reactive), D010 (TC selenium), and D018 (TC benzene). No single hazardous waste code was reported by more than one facility.

3.10.3.2 Generation and Management

Spent Amine Solution

As discussed in Section 3.10.1, the amine sulfur removal process is the dominant sulfur removal process for gas streams used in the industry. Amine solutions are aqueous and are typically stored in covered sumps, tanks, etc. In the 1992 questionnaire, most facilities did not

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

report how their off-spec treating solution is stored prior to final management; those that did indicated storage in a tank (most common), storage in a container, or storage in a sump.

Forty-four facilities reported generating a total quantity of 4,627 MT of spent amine in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be “off-spec treating solution (spent amine)” if they were assigned a residual identification code of “treating solution” and were generated from a sulfur complex or H₂S removal process. These correspond to residual codes of “04-B” or “04-C” in Section VII.A and process code “15-A” and “15-D” in Section IV-1.C of the questionnaire. Based on the results of the questionnaire, approximately 123 facilities employ some type of sulfur removal system (most of these systems employ treating solution). Many facilities generate this residual on an intermittent basis, or only during unusual circumstances such as upsets. Therefore, not all of these 123 facilities are expected to generate off-spec treating solution.

Table 3.10.6 provides a description of the 1992 management practices, quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

Table 3.10.6. Generation Statistics for Spent Amine for H₂S Removal, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Discharge to onsite wastewater treatment facility	40	16	1,224.2	30.6
Discharge to offsite privately-owned WWT facility	1	0	152	152
Disposal in onsite or offsite underground injection	4	0	673.3	168.3
Disposal in offsite Subtitle D landfill	1	0	200	200
Disposal in offsite Subtitle C landfill	1	0	39	39
Disposal in onsite surface impoundment	3	0	0.8	0.3
Neutralization	1	0	0.2	0.2
Onsite boiler	1	0	9.1	9.1
Other recovery onsite: recycle to the process	3	4	12.8	4.27
Recovery onsite in catalytic cracker	1	0	1,150	1,150
Transfer to other offsite entity/amine reclaimer	3	0	166	55.3
TOTAL	59	20	4,627.4	78.4

Spent Stretford Solution

The second most frequently used process is the Stretford sulfur removal/complex process. Stretford solutions are aqueous and are typically stored in covered sumps, tanks, etc.

Twelve facilities reported generating a total quantity of 19,254.5 MT of spent Stretford solution in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be “spent Stretford solution” if they were assigned a residual identification code of “treating solution” and were generated from a sulfur complex or H₂S removal process. These correspond to residual codes of “04-B” or “04-C” in Section VII.A and process code “15-B” and “15-E” in Section IV-1.C of the questionnaire.

Table 3.10.7 provides a description of the 1992 management practices, quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

Table 3.10.7. Generation Statistics for Stretford Solution for H₂S Removal, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Discharge to onsite wastewater treatment facility	4	2	4,830	1,207.5
Discharge to offsite privately-owned WWT facility	3	0	6,111.5	2,037.2
Disposal in onsite Subtitle D landfill	1	0	711	711
Transfer metal catalyst for reclamation or regeneration	2	0	5,127	2563.5
Transfer of acid or caustic for reclamation, regeneration, or recovery	3	0	2,475	825
TOTAL	13	2	19,254.5	1,481

3.10.3.3 Plausible Management

Spent Amine

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.10.6. The Agency gathered information suggesting other management practices have been used in other years including: “onsite Subtitle D landfill” (200 MT) and “offsite incineration” (120 MT). These non-1992 practices are generally comparable to practices reported in 1992 (i.e., off-site Subtitle D landfilling and on-site boiler, respectively).

Spent Stretford Solution

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.10.7. Even though spent Stretford solution has different properties, it is possible that the solution could be managed as the spent amine in Table 3.10.6.

3.10.3.4 Characterization

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

- Tables 3.10.8 and 3.10.9 summarize the physical properties of spent amine and spent Stretford solution as reported in Section VII.A of the §3007 survey.
- Four record samples of spent amine solution were collected and analyzed by EPA. The sample locations are summarized in Table 3.10.10.
- No samples of spent Stretford solution were available from the randomly selected facilities during record sampling.

Table 3.10.8. Spent Amine: Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	50th %	90th %
pH	36	67	4.5	9.1	11.8
Reactive CN, ppm	5	98	0	5	12
Reactive S, ppm	10	93	1.41	280	7,500
Flash Point, °C	16	87	-10	90.6	168.9
Oil and Grease, vol%	11	92	0	0.1	1
Total Organic Carbon, vol%	16	87	0	10	15
Vapor Pressure, mm Hg	12	91	1	30	300
Vapor Pressure Temperature, °C	13	90	15	25	50
Viscosity, lb/ft-sec	10	93	0	0	10
Specific Gravity	34	69	1	1.1	1.1
Specific Gravity Temperature, °C	16	87	15	17.5	38
Aqueous Liquid, %	61	42	0	100	100
Organic Liquid, %	43	60	0	0	100
Solid, %	36	67	0	0	20

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

Table 3.10.9. Spent Stretford Solution: Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	50th %	90th %
pH	10	12	8.3	8.8	9.7
Reactive CN, ppm	2	19	1	1.35	1.7
Reactive S, ppm	2	19	0.1	3,190	6,380
Oil and Grease, vol%	1	20	1	1	1
Total Organic Carbon, vol%	4	17	0	0	1
Vapor Pressure, mm Hg	3	18	1.5	10	20
Specific Gravity	8	14	1	1.1	1.5
COD, mg/L	4	17	100	6,930	6,930
Aqueous Liquid, %	9	13	0	90	100
Organic Liquid, %	3	19	0	0	0
Solid, %	10	12	0.5	10	100

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

Table 3.10.10. Off-Specification Treating Solution Record Sampling Locations

Sample Number	Facility	Description
R11-SA-01	ARCO, Ferndale, WA	Refinery DEA system: circulating amine
R13-SA-01	Shell, Deer Park, TX	Refinery DEA system: circulating amine
R14-SA-01	BP, Toledo, OH	Refinery DEA system: from sump collecting knock-out pot liquid, etc, prior to its exiting the system
R15-SA-01	Total, Ardmore, OK	Refinery MDEA system: circulating amine

All of the samples were taken from refinery amine systems and are believed to represent the various types of spent amine generated by refineries. No samples from the tail gas system units were collected. Tail gas residuals are expected to be cleaner because the feeds are cleaner. Therefore, the tail gas treating residuals are expected to exhibit levels of contaminants no higher than those found in the sampled residuals. No samples of Stretford solution were taken. Stretford systems were not used by the facilities randomly selected by the Agency for record sampling. Samples of Stretford solution are expected to exhibit higher levels of vanadium than amine solution because vanadium is present in new Stretford solution; levels of some organic contaminants may be lower because most refineries use their Stretford system to treat low-organic Claus unit tail gas.

Several of the samples were taken from the process line (i.e., at the time of sampling, the refinery had no immediate plans to remove the sampled treating solution from the system).

However, these refineries indicated they do remove all or part of their circulating amine on an infrequent basis due to process upset or excessive contaminant levels. The sampled amine is expected to have contaminant concentrations at least as high as when the circulating amine is removed from the system. Physical properties such as pH and flash point are expected to be similar as well.

All four samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals, pH, total amines, and ignitability. Two samples were also analyzed for reactive sulfides. One sample exhibited the characteristic of ignitability. A summary of the results is presented in Table 3.10.11. Only constituents detected in at least one sample are shown in this table.

3.10.3.5 Source Reduction

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.

Reference	Waste Minimization/Management Methods
Stewart, E.J. and Lanning, R.A. "Reduce Amine Plant Solvent Losses, Part 2." <i>Hydrocarbon Processing</i> . June, 1994.	Process modification.
"Liquid Catalyst Efficiently Removes H ₂ S From Liquid Sulfur." <i>Oil & Gas Journal</i> . July 17, 1989.	Lower catalyst quantities needed to remove H ₂ S in the sulfur degassing process.
Stewart, E.J. and Lanning, R.A. "Reduce Amine Plant Solvent Losses, Part 1." <i>Hydrocarbon Processing</i> . May, 1994.	Process modification.

Table 3.10.11. Characterization Data for Off-Specification Treating Solution from Sulfur Complex and H₂S Removal

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Volatile Organics - Method 8260A µg/L										
	CAS No.	R11-SA-01	R13-SA-01	R14-SA-01	R15-SA-01	Average Conc	Maximum Conc	Comments		
Acetone	67641	< 25	< 50	< 25	10	10	10	1		
Benzene	71432	< 25	< 50	88	< 5	42	88			
Toluene	108883	< 25	< 50	220	< 5	75	220			
o-Xylene	95476	< 25	< 50	J 24	< 5	15	24	1		
m,p-Xylenes	108383 / 106423	< 25	< 50	69	< 5	37	69			
Naphthalene	91203	< 25	< 50	J 32	< 5	19	32	1		
Semivolatile Organics - Method 8270B µg/L										
	CAS No.	R11-SA-01	R13-SA-01	R14-SA-01	R15-SA-01	Average Conc	Maximum Conc	Comments		
Acenaphthene	83329	< 50	< 545	180	< 575	115	180	1		
Anthracene	120127	J 18	< 545	250	< 575	134	250	1		
Aniline	62553	< 50	J 540	< 50	< 575	213	540	1		
Benz(a)anthracene	56553	< 50	< 545	J 34	< 575	34	34	1		
Bis(2-ethylhexyl)phthalate	117817	JB 26	< 545	J 17	< 575	22	26	1		
Carbazole	86748	J 80	< 1,090	< 100	< 1,150	80	80	1		
Chrysene	218019	< 50	< 545	J 71	< 575	61	71	1		
Dibenzofuran	132649	< 50	< 545	160	< 575	105	160	1		
2,4-Dimethylphenol	105679	110	< 545	J 86	< 575	98	110	1		
Fluoranthene	206440	J 17	< 545	< 50	< 575	17	17	1		
Fluorene	86737	< 50	< 545	1,100	< 575	568	1,100			
2-Methylchrysene	3351324	< 100	< 1,090	J 84	< 1,150	84	84	1		
1-Methylnaphthalene	90120	< 100	< 1,090	2,500	< 1,150	1,210	2,500			
2-Methylnaphthalene	91576	< 50	< 545	3,400	< 575	1,143	3,400			
2-Methylphenol	95487	360	< 545	210	< 575	285	360	1		
3/4-Methylphenol	NA	1,200	< 545	1,000	< 575	830	1,200			
Phenanthrene		J 50	< 545	3,000	< 575	1,043	3,000			
Phenol	108952	4,400	< 545	3,100	< 575	2,155	4,400			
Pyrene		J 25	< 545	430	< 575	228	430	1		
1-Naphthylamine	134327	< 50	< 545	< 50	J 230	110	230	1		
Naphthalene	91203	< 50	< 545	150	< 575	100	150	1		

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Table 3.10.11. Characterization Data for Off-Specification Treating Solution from Sulfur Complex and H₂S Removal (continued)

Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/L								
	CAS No.	R11-SA-01	R13-SA-01	R14-SA-01	R15-SA-01	Average Conc	Maximum Conc	Comments
Aluminum	7429905	0.39	< 0.10	< 0.10	< 0.10	0.17	0.39	
Antimony	7440360	0.81	< 0.03	< 0.03	0.62	0.37	0.81	
Cadmium	7440439	0.035	< 0.003	< 0.003	0.025	0.016	0.035	
Chromium	7440473	0.26	0.99	0.021	0.031	0.326	0.990	
Cobalt	7440484	0.11	< 0.025	< 0.025	0.099	0.065	0.110	
Copper	7440508	< 0.013	< 0.013	0.034	< 0.013	0.018	0.034	
Iron	7439896	39.0	14.0	1.10	0.11	13.6	39.0	
Manganese	7439965	0.31	2.30	0.043	< 0.008	0.67	2.30	
Potassium	7440097	21.0	< 2.50	< 2.50	22.0	12.0	22.0	
Selenium	7782492	0.031	0.61	0.038	0.99	0.42	0.99	
Sodium	7440235	8.40	< 2.50	< 2.50	2,300	578	2,300	
Zinc	7440666	< 0.01	< 0.01	0.039	< 0.01	0.017	0.039	
Miscellaneous Characterization								
		R11-SA-01	R13-SA-01	R14-SA-01	R15-SA-01	Average Conc	Maximum Conc	Comments
Ignitability (oF)		> 211	NA	> 210	90	NA	NA	
Corrosivity (pH units)		10	10	8.9	11.5	NA	NA	
Reactivity - Total ReleasableH ₂ S (mg/L)		< 20	NA	48	NA	NA	NA	
Amines - Methyldiethanolamine (mg/L)		ND	ND	ND	36,000	36,000	36,000	
Amines - Ethanolamine (mg/L)		4,400	4,500	ND	ND	4,450	4,500	
Amines - Diethanolamine (mg/L)		330,000	280,000	41,300	ND	217,100	330,000	

Comments:

- 1 Detection limits greater than the highest detected concentration are excluded from the calculations. TCLP was not performed because these were liquid samples

Notes:

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

3.11 CLAY FILTERING

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. All solid materials discussed in Section 3.11.1 are termed as “solid sorbents” for the purposes of defining this residual category.

3.11.1 Process Description

Clay or other adsorbents are used to remove impurities from many hydrocarbon streams. Some of these applications are associated with isomerization, extraction, alkylation, and lube oil processing; such processes are discussed in the respective sections of this document. Other solid media remove impurities from amine solutions used in hydrogen sulfide removal systems; such media were discussed in the *Listing Background Document*. Solid media used in all other refinery processes are summarized and discussed in this section. The principal applications are described below.

Kerosene Clay Filtering: Clay treatment removes diolefins, asphaltic materials, resins, and acids; this improves the color of the product and removes gum-forming impurities (Speight, 1991). The RCRA §3007 Survey indicates that approximately 90 facilities use this process; some facilities have multiple treaters or treat different streams, so that an estimated 150 processes exist. Most clay treatment is conducted as a fixed bed. A typical clay volume is 2,000 ft³, distributed in 1 or more vessels. Alternatively to the fixed bed process, the clay can be mixed with the hydrocarbon and filtered in a belt press. In addition to kerosene, some facilities identify filtering furnace oils through clay and generating spent clay in a similar manner.

Catalyst Support in Merox and Minalk Systems: The Merox and Minalk caustic treatment systems convert mercaptans to disulfides using oxygen and an organometallic catalyst in an alkaline environment. Depending on the process configuration, the disulfides can remain in the hydrocarbon product (a “sweetening” process) or the disulfides can be removed by settling (an “extractive” process). These treatment processes are commonly applied to gasoline, but refinery streams ranging from propane to diesel undergo this treatment.

The catalyst can either be dissolved in the caustic or can be supported on a fixed bed. Either activated carbon, coal, or charcoal are typically used as support material for solid supported catalyst (the hydrocarbon passes over the catalyst, where reaction occurs). These materials provide contact area for reaction when the catalyst is dissolved in the caustic. The RCRA §3007 survey indicates that approximately 25 facilities (using 40 processes) reported generating spent carbon, coal, or charcoal from these processes; additional facilities likely generate this residual but did not report generation in the questionnaire because the residual is typically generated infrequently.

Drying: Water is removed from many hydrocarbon streams ranging from diesel fuel to propane. Water must be removed for reasons including: (1) product specifications (e.g., jet fuel

has low tolerances for water content), and (2) reactor feed preparation (e.g., precious metal catalysts are often poisoned by water). Salt and sand are commonly used for the first application, while molecular sieve is commonly used for the second application.

When hydrocarbon is passed through a fixed bed of sand, the moisture collects on the sand particles and eventually settles to the bottom of the vessel, where the water is removed. In a salt drier, water in the stream dissolves salt (e.g., sodium chloride) which then collects in the vessel bottom and is periodically removed. As a result, the vessel requires periodic topping with solid salt.

Salt and sand treaters can be found throughout the refinery to treat hydrocarbons ranging from diesel to propane. They are commonly found following aqueous treatments such as caustic washing, water washing, or Merox caustic treatment. In these treatments, the hydrocarbon is contacted with the aqueous stream; the hydrocarbon then passes through salt or sand to remove residual moisture. The RCRA §3007 questionnaire indicates that approximately 60 facilities (using 150 processes) reported generating spent salt or sand from these processes; additional facilities likely generate this residual but did not report generation in the questionnaire because it was not generated in 1992.

Molecular sieves are most commonly used to selectively adsorb water and sulfur compounds from light hydrocarbon fractions such as propane and propylene. The hydrocarbon passes through a fixed bed of molecular sieve. After the bed is saturated, water is desorbed by passing heated fuel gas over the bed to release the adsorbed water and sulfur compounds into the regeneration gas stream, which is commonly sent to a flare stack. Molecular sieves are often used for drying feed to the isomerization unit and HF acid alkylation unit, applications that are discussed in Sections 3.4 and 3.5, respectively, of this document. Other applications include drying propane or propylene prior to entering the Dimersol unit, drying naphtha entering the reformer, and feed preparation for other reaction units. Molecular sieves are also used to dry light-end product streams from the hydrocracker, catalytic reformer, and light-ends recovery unit. Less common uses also exist for molecular sieves including the separation of light-end fractions such as methanol, butane, and butylene. In total, the RCRA §3007 questionnaire indicates that approximately 70 facilities (using 150 processes) reported generating spent molecular sieve; this includes the applications of HF acid alkylation and isomerization that are discussed elsewhere in this document, but excludes additional facilities that are likely generate this residual but did not report 1992 generation in the questionnaire.

Sulfur and Chloride Guards in Catalytic Reforming: As discussed in the *Listing Background Document*, catalytic reforming units require a platinum catalyst; this catalyst is readily poisoned by sulfur compounds. To prolong catalyst life, many refineries install sulfur traps to remove sulfur compounds prior to the reforming catalyst bed. This material can consist of granular or pelletized metal oxides, such as copper or magnesium. These materials (1) remove H₂S, (2) convert mercaptans to H₂S and organic sulfides, and (3) remove generated H₂S. The material can be desorbed, reactivated, and reused (Perry's, 1950). Alumina also is used to treat light naphtha prior to isomerization (which also uses precious metal catalyst). The RCRA §3007 questionnaire indicates that approximately 20 facilities reported generating spent sulfur guards from 35 applications, most often as guards for reforming and isomerization reactors.

Additional facilities may employ sulfur guards but did not report generation in the questionnaire because the residual is typically generated infrequently.

Alumina beds may be used to remove chlorides from the hydrogen produced from the reforming process. The hydrogen is then used throughout the refinery. The alumina bed is expected to last for 24-30 months prior to chloride breakthrough, when replacement of the alumina is required. Reformate from the reformer may also be passed through alumina to remove chloride. The RCRA §3007 questionnaire indicates that approximately 15 facilities reported generating spent chloride guards from 25 applications, most often in the reforming process.

Propane Treating by Alumina: An activated alumina bed is used to de-fluorinate propane generated from a propane stripper. The propane then is dried in a sand tower and a drier which also contains alumina. Both the defluorinator and drier periodically generate spent alumina.

Particulate Filters: Entrained solids can be removed by in-line cartridge filters. These cartridges are commonly used for finishing kerosene, diesel fuel, etc., prior to sale. Approximately 10 facilities reported generating spent cartridges from 20 applications, according to the questionnaire results.

In most of the applications discussed above, the use of solid media such as clay, sand, etc. are not the only options refineries have in imparting the desired properties on a product. For example, drying can be conducted by simple distillation. Hydrotreating and caustic treating are common alternatives to the clay treatment of jet fuel by removing undesirable contaminants from the kerosene/jet fuel fraction. And, as discussed above, the Merox process can be conducted with or without solid supported catalyst.

3.11.2 Treating Clay from Clay Filtering

3.11.2.1 Description

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.

3.11.2.2 Generation and Management

The spent clay is vacuumed or gravity dumped from the vessels into piles or into containers such as drums and roll-off bins. The RCRA §3007 questionnaire and site visits indicate that very few other interim storage methods are used.

In 1992, approximately 30 facilities reported that 1,700 MT of this residual was managed as hazardous. The most commonly designated waste codes were D001 (ignitable), D008 (TC lead), and D018 (TC benzene).⁵ This is consistent with how the residual was reported to be managed in other years.

One hundred facilities reported generating a total quantity of approximately 9,000 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. There was no reason to expect that 1992 would not be a typical year with regard to this residual's generation and management. Residuals were assigned to be "treating clay from clay filtering" if they were assigned a residual identification code of "spent sorbent" (residual coded "07") and were **not** generated from a process identified as an alkylation, isomerization, extraction, sulfur removal, or lube oil unit (process codes "09," "10," "12," "15," and "17," respectively) (sorbents from these units are discussed elsewhere in this document or in the *Listing Background Document*). The frequency of generation is highly variable as discussed in Section 3.11.1. Table 3.11.1 provides a description of the 1992 management practices, quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

The wide array of management methods reflect the numerous applications of sorbents. For example, disposed salt from salt driers can be managed in onsite wastewater treatment plants, cement plants can accept spent alumina, and catalyst reclaimers can accept sulfur sorbers having recoverable metals. The large quantity disposed, however, demonstrates that for most applications and refineries the spent clay is seen as a low value solid waste.

3.11.2.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.11.1. The Agency gathered information suggesting other management practices have been used in other years including: "other recycling, reclamation, or reuse: unknown" (1 MT), "other recycling, reclamation, or reuse: onsite road material" (13.5 MT) and "reuse as a replacement catalyst for another unit" (5 MT). These non-1992 very small management practices are comparable to the recycling practices reported in 1992.

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

Table 3.11.1. Generation Statistics for Treating Clay from Clay Filtering, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Discharge to onsite wastewater treatment facility	14	3	514	36.7
Disposal in offsite Subtitle D landfill	91	0	3,642.1	40
Disposal in offsite Subtitle C landfill	42	0	1,735	41.3
Disposal in onsite Subtitle C landfill	1	1	52.4	52.4
Disposal in onsite Subtitle D landfill	15	0	1,031.9	68.8
Evaporation	1	0	7.9	7.9
Offsite incineration	7	0	42.1	6
Offsite land treatment	9	0	198.3	22
Onsite land treatment	16	0	923.1	57.7
Other disposal onsite: bioremediation, fill material, or onsite berms	5	0	57.4	11.5
Other recovery onsite: recycle to process	1	0	20.1	20.1
Other recycling, reclamation, or reuse: cement plant	5	0	161.4	32.3
Offsite filter recycling	2	0	38	19
Storage in pile	2	0	128	64
Recovery in coker	1	0	20	20
Transfer for direct use as a fuel or to make a fuel	1	0	95	95
Transfer for use as an ingredient in products placed on the land	6	0	175.8	29.3
Transfer metal catalyst for reclamation or regeneration	10	0	89.4	8.9
Transfer to other offsite entity/carbon regeneration	2	0	53.6	26.8
Transfer with coke product or other refinery product	1	0	4.5	4.5
TOTAL	232	4	8,990	38.8

3.11.2.4 Characterization

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

- Table 3.11.2 summarizes the physical properties of the spent clay as reported in Section VII.A of the §3007 survey.
- Four record samples of spent clay were collected and analyzed by EPA. These spent clays represent some of the various types of applications used by the industry. Sampling information is summarized in Table 3.11.3.

Table 3.11.2. Treating Clay from Clay Filtering: Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	50th %	90th %
pH	171	334	4.6	7.6	10.4
Reactive CN, ppm	100	405	0	0.5	50
Reactive S, ppm	106	399	0	10	125
Flash Point, °C	132	373	57.2	93.3	200
Oil and Grease, vol%	94	411	0	1	17.5
Total Organic Carbon, vol%	50	455	0	1	55
Specific Gravity	167	338	0.7	1.3	2.6
Specific Gravity Temperature, °C	50	455	15	20	25
BTU Content, BTU/lb	31	474	0	2,000	13,500
Aqueous Liquid, %	230	275	0	0	10.3
Organic Liquid, %	240	265	0	0	5
Solid, %	346	159	89.0	100	100
Particle >60 mm, %	59	446	0	0	100
Particle 1-60 mm, %	91	414	0	100	100
Particle 100 µm-1 mm, %	70	435	0	10	100
Particle 10-100 µm, %	54	451	0	0	20
Particle <10 µm, %	49	456	0	0	0
Median Particle Diameter, microns	48	457	0	1,000	3,000

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

Table 3.11.3. Treating Clay Record Sampling Locations

Sample #	Facility	Description
R1-CF-01	Marathon Indianapolis, IN	kerosene/jet treating clay (fixed bed process)
R6-CF-01	Shell Norco, LA	kerosene/jet treating clay (bag filter process, generated daily)
R11-CF-01	ARCO Ferndale, WA	reformer unit sulfur trap
R23-CF-01	Chevron, Salt Lake City, UT	kerosene/jet treating clay

The collected samples are expected to be representative of treating clay from kerosene treatment. Section 3.11.1 shows that kerosene clay treatment represents the highest single use of sorbents in refineries (outside of the sulfur recovery, isomerization, and alkylation processes that are not included in the scope of this study residual). In addition, a cursory review of the 1992 generation data presented in Section 3.11.2.2 shows that the 1992 generation rate of spent kerosene treating clay represents at least half of the total 1992 quantity from all sources identified in Section 3.11.1.

One of the samples is representative of a sulfur guard bed. Other applications of spent sorbents (discussed in Section 3.11.1) are not well represented by the record sampling. Specifically:

- Spent activated carbon from Merox treatment, salt and sand from product drying, particulate filters, and chloride removal beds are not expected to resemble these materials.
- Spent molecular sieves and alumina are not represented by the collected record samples. However, they may be represented by the record samples of isomerization treating clay and alkylation treating clay, discussed in Sections 3.4 and 3.5, respectively.

All four record samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. Two samples were analyzed for ignitability and all were analyzed for reactivity (pyrophoricity). One of the samples was found to exhibit the ignitability characteristic. High manganese concentrations in one sample result from the adsorbent make-up. A summary of the results is presented in Table 3.11.4. Only constituents detected in at least one sample are shown in this table.

3.11.2.5 Source Reduction

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.

Table 3.11.4. Residual Characterization Data for Treating Clay

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Volatile Organics - Method 8260A µg/kg									
	CAS No.	R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments	
Acetone	67641	260,000	< 565	< 25	< 1,250	65,460	260,000		
Benzene	71432	< 125,000	8,500	540	< 1,250	3,430	8,500	1	
n-Butylbenzene	104518	< 125,000	94,000	< 25	< 1,250	31,758	94,000	1	
sec-Butylbenzene	135988	< 125,000	54,000	< 25	< 1,250	18,425	54,000	1	
Ethylbenzene	100414	< 125,000	76,000	J 28	2,800	26,276	76,000	1	
Isopropylbenzene	98828	< 125,000	44,000	< 25	< 1,250	15,092	44,000	1	
p-Isopropyltoluene	99876	< 125,000	59,000	< 25	< 1,250	20,092	59,000	1	
n-Propylbenzene	103651	< 125,000	70,000	< 25	< 1,250	23,758	70,000	1	
Methylene chloride	75092	< 125,000	< 565	100	< 1,250	100	100	1	
Toluene	108883	< 125,000	140,000	340	3,600	67,235	140,000		
1,2,4-Trimethylbenzene	95636	580,000	620,000	< 25	32,000	308,006	620,000		
1,3,5-Trimethylbenzene	108678	< 125,000	210,000	< 25	13,000	87,006	210,000		
o-Xylene	95476	< 125,000	180,000	89	7,200	78,072	180,000		
m,p-Xylenes	108383 / 106423	300,000	380,000	130	23,000	175,783	380,000		
Naphthalene	91203	310,000	350,000	< 25	9,800	167,456	350,000		
TCLP Volatile Organics - Methods 1311 and 8260A µg/L									
	CAS No.	R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments	
Acetone	67641	43,000	< 50	< 50	B 100	10,800	43,000		
Benzene	71432	< 1,250	100	J 44	< 50	65	100	1	
Ethylbenzene	100414	< 1,250	190	< 50	< 50	97	190	1	
Methylene chloride	75092	2,600	< 50	1,700	< 50	1,100	2,600		
Toluene	108883	< 1,250	850	210	< 50	370	850	1	
1,2,4-Trimethylbenzene	95636	4,900	840	< 50	J 62	1,463	4,900		
1,3,5-Trimethylbenzene	108678	< 1,250	270	< 50	< 50	123	270	1	
o-Xylene	95476	< 1,250	610	< 50	J 44	235	610	1	
m,p-Xylene	108383 / 106423	< 1,250	1,200	< 50	110	453	1,200	1	
Naphthalene	91203	< 1,250	650	< 50	J 71	257	650	1	
Semivolatile Organics - Method 8270B µg/kg									
	CAS No.	R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments	
Bis(2-ethylhexyl) phthalate	117817	< 6,600	< 4,125	J 100	< 4,150	100	100	1	
Carbazole	86748	< 13,200	< 8,250	< 330	J 6,000	3,165	6,000	1	
Di-n-butyl phthalate	57976	< 6,600	< 4,125	420	< 4,150	420	420	1	
Dibenzofuran	132649	< 6,600	J 24,000	< 165	< 4,150	8,729	24,000		
Fluorene	86737	< 6,600	< 4,125	< 165	20,000	7,723	20,000		
2,4-Dimethylphenol	105679	< 6,600	< 4,125	2,500	< 4,150	2,500	2,500	1	

Table 3.11.4. Residual Characterization Data for Treating Clay (continued)

Semivolatile Organics - Method 8270B µg/kg (continued)									
	CAS No.	R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments	
2-Methylphenol	95487	< 6,600	< 4,125	9,000	< 4,150	5,969	9,000		
3/4-Methylphenol	NA	< 6,600	< 4,125	30,000	< 4,150	11,219	30,000		
1-Methylnaphthalene	90120	980,000	890,000	< 165	78,000	487,041	980,000		
2-Methylnaphthalene	91576	150,000	1,200,000	< 165	92,000	360,541	1,200,000		
Naphthalene	91203	120,000	740,000	< 165	43,000	225,791	740,000		
Phenanthrene	85018	< 6,600	J 4,800	< 165	25,000	9,141	25,000		
Phenol	108952	< 6,600	< 4,125	20,000	< 4,150	8,719	20,000		
TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L									
	CAS No.	R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments	
Bis(2-ethylhexyl) phthalate	117817	290	J 16	< 250	< 50	152	290		
Dibenzofuran	132649	< 50	J 17	< 250	< 50	17	17	1	
Di-n-butyl phthalate	84742	< 50	JB 19	< 250	< 50	19	19	1	
2,4-Dimethylphenol	105679	350	J 73	1,400	< 50	468	1,400		
Fluorene	86737	< 50	J 41	< 250	< 50	41	41	1	
1-Methylnaphthalene	90120	J 190	550	< 250	J 130	280	550		
2-Methylnaphthalene	91576	220	780	< 500	120	405	780		
Naphthalene	91203	600	700	< 250	140	423	700		
2-Methylphenol	95487	310	< 50	7,800	< 50	2,053	7,800		
3/4-Methylphenol (total)	NA	580	< 50	6,300	< 50	1,745	6,300		
Phenol	108952	< 50	< 50	2,300	< 50	613	2,300		
Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg									
	CAS No.	R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments	
Aluminum	7429905	12,000	6,800	110,000	13,000	35,450	110,000		
Arsenic	7440382	3.20	< 1.00	14.0	16.0	8.55	16.0		
Barium	7440393	78.0	< 20.0	< 20.0	59.0	44.3	78.0		
Beryllium	7440417	3.80	< 0.50	< 0.50	2.50	1.83	3.80		
Calcium	7440702	4,500	16,000	< 500	4,400	6,350	16,000		
Chromium	7440473	37.0	24.0	34.0	39.0	33.5	39.0		
Cobalt	7440484	12.0	< 5.00	34.0	11.0	15.5	34.0		
Copper	7440508	< 2.50	< 2.50	5.30	620	158	620		
Iron	7439896	9,400	3,800	97.0	9,800	5,774	9,800		
Lead	7439921	4.80	1.90	2.70	6.00	3.85	6.00		
Magnesium	7439954	9,400	10,000	< 500	9,300	7,300	10,000		
Manganese	7439965	130	140	150,000	120	37,598	150,000		
Mercury	7439976	< 0.05	< 0.05	< 0.05	0.26	0.10	0.26		

Table 3.11.4. Residual Characterization Data for Treating Clay (continued)

Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg (continued)								
	CAS No.	R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments
Molybdenum	7439987	< 6.50	< 6.50	14.0	< 6.50	8.38	14.0	
Nickel	7440020	16.0	< 4.00	< 4.00	31.0	13.8	31.0	
Potassium	7440097	1,400	< 500	< 500	1,300	925	1,400	
Selenium	7782492	< 0.50	< 0.50	22.0	< 0.50	5.88	22.0	
Silver	7440224	< 1.00	< 1.00	70.0	< 1.00	18.3	70.0	
Sodium	7440235	34,000	< 500	< 500	< 500	8,875	34,000	
Vanadium	7440622	37.0	21.0	34.0	35.0	31.8	37.0	
Zinc	7440666	47.0	19.0	< 2.00	55.0	30.8	55.0	
TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L								
	CAS No.	R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments
Aluminum	7429905	< 1.00	< 1.00	< 1.00	3.90	1.73	3.90	
Arsenic	7440382	< 0.05	< 0.05	< 0.05	0.13	0.07	0.13	
Calcium	7440702	54	590	< 25.0	60.0	182	590	
Copper	7440508	< 0.13	< 0.13	< 0.13	0.89	0.32	0.89	
Iron	7439896	< 0.50	< 0.50	< 0.50	1.00	0.63	1.00	
Magnesium	7439954	< 25.0	91	< 25.0	< 25.0	41.5	91.0	
Manganese	7439965	< 0.08	2.60	1,400	0.85	351	1,400	
Silver	7440224	< 0.05	< 0.05	0.10	< 0.05	0.06	0.10	
Zinc	7440666	< 0.10	B 0.76	< 0.10	B 0.27	0.31	0.76	
Miscellaneous Characterization								
		R1-CF-01	R6-CF-01	R11-CF-01	R23-CF-01	Average Conc	Maximum Conc	Comments
Ignitability (oF)		185	131	NA	NA	NA	NA	

Comments:

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

Notes:

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

3.12 RESIDUAL OIL TANK STORAGE

Almost every refinery stores its feed and products in tanks onsite. Occasionally (every 10 to 20 years), tanks require sediment removal due to maintenance, inspection, or sediment buildup. These tank bottoms are removed by techniques ranging from manual shoveling to robotics and filtration. Residual oil tank sludge is a study residual of concern.

Residual oil is generally considered to be equivalent to No. 6 fuel oil which is a heavy residue oil sometimes called Bunker C when used to fuel ocean-going vessels. Preheating is required for both handling and burning. It is typically produced from units such as atmospheric and vacuum distillation, hydrocracking, delayed coking, and visbreaking. The fluid catalytic cracking unit also contributes to the refinery's heavy oil pool, but EPA terms this material "clarified slurry oil," or CSO, and discussed this product separately in the *Listing Background Document* (October 31, 1995).

According to DOE's *Petroleum Supply Annual*, approximately 400 million barrels of "residual oil" was domestically used in 1992 (including imports and exports). The use profile in 1994 was as follows (DOE's *Fuel Oil and Kerosene Sales 1994*):

<u>Sector</u>	<u>1990 Consumption of Residual Fuel Oil</u>
Electric Utility	40%
Shipping	35%
Industrial	15%
Commercial and Other	10%

The larger utilities often have their own specifications when purchasing residual fuel oil. These can include sulfur, nitrogen, ash, and vanadium. The current ASTM standard for No. 6 oil (D-396) specifies only three parameters: minimum flash point (of 150°F), maximum water and sediment (of 2 percent), and a viscosity range (Bonnet, 1994). Thus, the characteristics of residual oil, and the generated tank sludge, can vary greatly depending on the buyer and the refinery.

3.12.1 Residual Oil Storage Tank Sludge

In 1992, 125 U.S. refineries reported approximately 717 residual oil storage tanks. From the survey, tank volume was reported for about 10 percent (73) of these tanks (excluding outliers); the average tank volume was approximately 77,000 barrels. DOE's *Petroleum Supply Annual 1992* reported that refineries produced about 327 million barrels of No. 6 fuel oil or residual oil or approximately 900,000 barrels per day (this likely includes CSO).

3.12.1.1 Description

Residual oil tank sludge consists of heavy hydrocarbons, rust and scale from process pipes and reactors, and entrapped oil that settles to the bottom of the tank. It can be manually removed directly from the tank after drainage of the residual oil or, commonly, removed using a variety of oil recovery techniques. The recovered oil is returned generally to slop oil storage while the remaining solids are collected and discarded as waste.

Once a tank is taken out of service, many refineries use *in situ* and *ex situ* oil recovery techniques. Common *in situ* oil recovery techniques include hot distillate washing, and steam stripping. This allows entrapped oil to float to the top of the sediment layer and be recovered prior to removal of the sediment from the tank. *Ex situ* recovery methods are usually performed by a contractor at the tank site and include filtration, centrifuging, and settling. Separated oil is recycled back to the process or sent to the slop oil tanks, and the water phase is sent to the wastewater treatment plant (WWTP). The solids are managed in a variety of ways, but primarily are disposed of in Subtitle C and D landfills (78 percent in 1992).

Many refineries reduce tank bottom buildup with in-tank mixers. Mixers keep the sediments or solids continuously in suspension so that they travel with the residual oil.

In 1992, less than one percent of the volume of residual oil tank bottom sludge was reported to be managed as hazardous.⁶ Of the few refineries that reported a hazardous waste designation for this residual in 1992, only one reported a hazardous waste code (the others specified handling the sludge as hazardous without designating a code).

3.12.1.2 Generation and Management

The refineries reported generating 9,107 MT of residual oil tank bottom sludge in 1992. Residual oil tank sludge includes sludges from No. 6 oil and similar product tanks. Sludges from tanks identified as containing a mixture of residual oil and clarified slurry oil were included in the scope of K170 and are omitted here. Residuals were assigned to be “residual oil tank sludge” if they were assigned a residual identification code of “residual oil tank sediment,” corresponding to residual code “01-B” in Section VII.1 of the questionnaire. Process wastewaters, decantates, and recovered oils (e.g., from deoiling or dewatering operations) were eliminated from the analysis. These correspond to residual codes “09,” “10,” and “13” (newly added “recovered oil”) in the questionnaire. Quality assurance was conducted by ensuring that all residual oil tank sludges previously identified in the questionnaire (i.e., in Section V.D) were assigned in Section VII.1. Table 3.12.1 provides a description of the 1992 management practices, quantity generated, number of streams reported, number of streams not reporting volumes, and average volumes.

When cleaning a tank, it is common for refineries to use some type of *in situ* treatment, such as washing with lighter fuel, to recover oil from the top layers of sludge where there is a high percentage of free oil. However, treatment or recovery practices after this depend on the refinery's planned final management method. If land disposed (as most residual oil tank sludge was in 1992), low free liquid must be achieved; such levels can be achieved by sludge deoiling/dewatering or stabilization. A refinery may conduct this

⁶These percentages do not match up directly with any one of the management scenarios because the number of streams and the volume are a combination of several management scenarios (i.e., managed in WWTP, Subtitle C landfill, recovery onsite in coker, etc.).

Table 3.12.1. Generation Statistics for Residual Oil Tank Sludge, 1992

Final Management	# of Streams	# of Streams w/ Unreported Volume	Total Volume (MT)	Average Volume (MT)
Discharge to onsite wastewater treatment facility	1	0	47	47
Disposal in offsite Subtitle D landfill	13	4	6,458	496.8
Disposal in offsite Subtitle C landfill	8	0	622	77.8
Disposal in onsite Subtitle C landfill	2	0	4	2
Disposal in onsite Subtitle D landfill	3	0	30.4	10.1
Disposal in onsite surface impoundment	1	0	132	132
Offsite land treatment	1	1	4	4
Onsite land treatment	2	0	530.4	265.2
Other recycling, reclamation, or reuse: cover for onsite landfill	1	0	7.2	7.2
Recovery onsite via distillation	1	3	310	310
Transfer for use as an ingredient in products placed on the land	1	0	35	35
Transfer to another petroleum refinery	1	0	927	927
TOTAL	35	8	9,107	260.2

treatment for only some of the waste (e.g., the top layers); in the deeper sections of sludge where free liquid levels are lower no treatment may be performed. In addition to lower liquid levels, treatment or deoiling may be used to achieve lower levels of benzene or other hazardous properties.

3.12.1.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.12.1. The Agency gathered information suggesting other management practices have been used in other years including: “recovery onsite in an asphalt production unit” (9.2 MT), “transfer for direct use as a fuel or to make a fuel” (380.8 MT), “transfer with coke product or other refinery product” (5 MT), “onsite industrial furnace” (39 MT), “recycle to process” (unknown quantity), “recovery in coker” (unknown quantity), and “recovery in a catalytic cracker” (unknown quantity). These non-1992 management practices are generally comparable to the recycling practices reported in 1992.

3.12.1.4 Characterization

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

- Table 3.12.2 summarizes the physical properties of residual oil tank sludges as reported in Section VII.A of the §3007 survey.
- Two record samples of actual residual oil sludge were collected and analyzed by EPA. These sludges represent the various types of treatment typically used by the industry and are summarized in Table 3.12.3.

Table 3.12.4 provides a summary of the characterization data collected under this sampling effort. The record samples collected are believed to be representative of residual oil tank sludges generated by the industry.

The samples collected of the composite of oily and de-oiled sediment are representative of industry treatment practices. As reported in the RCRA 3007 questionnaires, 10 of the 34 residual oil tank sludges (30 percent) that were ultimately managed in a land treatment or landfill in 1992 were deoiled in some manner, most often by filtration or centrifuge. This management resulted in volume reduction averaging 55 percent. Another 7 (20 percent) were stabilized, resulting in the volume increasing by an average of 55 percent. The remaining 17 residuals (50 percent) were not reported to be treated *ex situ* in any manner. The sampled refineries represent two alternative interim management procedures: free liquid reduction using stabilization (Amoco), and *ex situ* deoiling (Star). Therefore, the record samples represent the various types of *ex situ* treatment typically performed for residual oil tank sludge, but may not represent cases in which no treatment is performed. However, the same contaminants will be present in all three types of sludge (i.e., deoiled, stabilized, and untreated), but their levels may differ.

As illustrated in Table 3.12.4, none of the record samples exhibited a hazardous waste characteristic. Only constituents detected in at least one sample are shown in this table.

3.12.1.5 Source Reduction

Only a small quantity of sludge was reported to be deoiled in 1992, as reported in the §3007 survey. Of the 34 residuals disposed in landfills or land treatment units in 1992, 10 residuals, totaling approximately 1,000 MT. The remaining 24 residuals, totaling approximately 7,600 MT, were reported to be untreated or underwent volume addition treatment (such as stabilization. As stated in Section 3.12.1.3, the average volume reduction achieved by deoiling was 55 percent (as calculated from those facilities providing sludge quantities prior to and following deoiling in 1992).

Table 3.12.2. Residual Oil Tank Sludge: Physical Properties

Properties	# of Values	# of Unreported Values ¹	10th %	Mean	90th %
pH	39	87	5.5	7	8.5
Reactive CN, ppm	27	99	0	0.3	5
Reactive S, ppm	27	99	0	2.5	15
Flash Point, °C	42	84	60	93.3	140
Oil and Grease, vol%	36	90	9	34.1	99
Total Organic Carbon, vol%	20	106	3.5	51	85.3
Vapor Pressure, mm Hg	11	115	0	0.1	10
Vapor Pressure Temperature, °C	9	117	25	37.8	38
Viscosity, lb/ft-sec	6	120	0.01	50.2	500
Specific Gravity	30	96	0.9	1.2	2.4
BTU Content, BTU/lb	16	110	600	5,000	20,000
Aqueous Liquid, %	78	48	0	0	50
Organic Liquid, %	82	44	0	18	86
Solid, %	91	35	1	60	100
Other, %	65	61	0	0	0
Particle >60 mm, %	4	122	0	0	0
Particle 1-60 mm, %	6	120	0	50	100
Particle 100 µm-1 mm, %	5	121	0	50	100
Particle 10-100 µm, %	4	122	0	0	1
Particle <10 µm, %	4	122	0	0	0
Median Particle Diameter, microns	3	123	0	0	15,000

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

Table 3.12.3. Residual Oil Tank Sludge Record Sampling Locations

Sample No.	Facility	Description:
R8B-RS-01	Amoco, Texas City, TX	Residual oil and CSO mixed. ¹ Cleaning procedure: pumped down, mixed with diatomaceous earth, removed with backhoe.
R22-RS-01	Star, Port Arthur, TX	Residual oil. ² Cleaning procedure: washed with lighter oil, centrifuged to generate cake.

¹The refinery has a fluid catalytic cracking unit and generates CSO. An unknown quantity of CSO was stored in the sampled tank.

²The refinery has a fluid catalytic cracking unit and generates CSO. It is unknown if, or to what extent, CSO was stored in the sampled tank.

Table 3.12.4. Residual Oil Tank Sludge Characterization

Volatile Organics - Method 8260A µg/kg						
	CAS No.	R8B-RS-01	R22-RS-01	Average Conc	Maximum Conc	Comments
n-Butylbenzene	104518	< 6,250	3,600	3,600	3,600	1
Ethylbenzene	100414	13,000	J 1,600	7,300	13,000	
p-Isopropyltoluene	99876	< 6,250	J 470	470	470	1
n-Propylbenzene	103651	J 6,850	J 1,600	4,225	6,850	
Toluene	108883	26,000	< 1,250	13,625	26,000	
1,2,4-Trimethylbenzene	95636	43,000	18,000	30,500	43,000	
1,3,5-Trimethylbenzene	108678	J 11,000	4,200	7,600	11,000	
o-Xylene	95476	19,000	J 1,800	10,400	19,000	
m,p-Xylenes	108383 / 106423	51,000	7,400	29,200	51,000	
Naphthalene	91203	64,000	19,000	41,500	64,000	
TCLP Volatile Organics - Methods 1311 and 8260A µg/L						
	CAS No.	R8B-RS-01	R22-RS-01	Average Conc	Maximum Conc	Comments
Benzene	71432	110	< 50	80	110	
Ethylbenzene	100414	J 55	< 50	53	55	
Toluene	108883	690	< 50	370	690	
1,2,4-Trimethylbenzene	95636	J 79	< 50	65	79	
Methylene chloride	75092	B 1,200	< 50	625	1,200	
o-Xylene	95476	J 96	< 50	73	96	
m,p-Xylene	108383 / 106423	220	JB 28	124	220	
Naphthalene	91203	J 91	J 46	69	91	
Semivolatile Organics - Method 8270B µg/kg						
	CAS No	R8B-RS-01	R22-RS-01	Average Conc	Maximum Conc	Comments
Acenaphthene	83329	60,000	27,000	43,500	60,000	
Anthracene	120127	150,000	< 4,125	77,063	150,000	
Benz(a)anthracene	56553	480,000	9,200	244,600	480,000	
Benzofluoranthene (total)	NA	130,000	34,000	82,000	130,000	
Benzo(g,h,i)perylene	191242	450,000	36,000	243,000	450,000	
Benzo(a)pyrene	50328	250,000	87,000	168,500	250,000	
Bis(2-ethylhexyl)phthalate	117817	< 10,313	10,000	10,000	10,000	1
Carbazole	86748	< 20,625	J 16,000	16,000	16,000	1
Chrysene	218019	800,000	170,000	485,000	800,000	
Dibenzofuran	132649	25,000	8,700	16,850	25,000	
Dibenz(a,h)anthracene	53703	65,000	J 8,000	36,500	65,000	
3,3'-Dichlorobenzidine	91941	< 10,313	87,000	48,656	87,000	
Fluoranthene	206440	120,000	< 4,125	62,063	120,000	
Fluorene	86737	160,000	38,000	99,000	160,000	
Indeno(1,2,3-cd)pyrene	193395	58,000	< 4,125	31,063	58,000	
Phenanthrene	85018	1,000,000	220,000	610,000	1,000,000	
Pyrene	129000	3,500,000	46,000	1,773,000	3,500,000	
1-Methylnaphthalene	90120	500,000	250,000	375,000	500,000	
2-Methylnaphthalene	91576	650,000	410,000	530,000	650,000	
2-Methylchrysene	3351324	380,000	< 8,250	194,125	380,000	
Naphthalene	91203	230,000	110,000	170,000	230,000	

Table 3.12.4. Residual Oil Tank Sludge Characterization (continued)

TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L							
	CAS No.	R8B-RS-01	R22-RS-01	Average Conc	Maximum Conc	Comments	
Di-n-butylphthalate	84742	< 50	JB 24	24	24	1	
1-Methylnaphthalene	90120	J 28	J 54	41	54		
2-Methylnaphthalene	91576	J 37	J 74	56	74		
Naphthalene	91203	J 37	J 73	55	73		
Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg							
	CAS No.	R8B-RS-01	R22-RS-01	Average Conc	Maximum Conc	Comments	
Aluminum	7429905	9,100	38,000	23,550	38,000		
Arsenic	7440382	3.00	< 1.00	2.00	3.00		
Barium	7440393	< 20.0	230	125	230		
Beryllium	7440417	1.80	< 0.50	1.15	1.80		
Calcium	7440702	< 500	1,400	950	1,400		
Chromium	7440473	11.0	31.0	21.0	31.0		
Cobalt	7440484	130	< 5.00	67.5	130		
Copper	7440508	7.40	110	58.7	110		
Iron	7439896	1,600	11,000	6,300	11,000		
Lead	7439921	6.50	84.0	45.3	84.0		
Magnesium	7439954	< 500	4,300	2,400	4,300		
Manganese	7439965	12.0	67.0	39.5	67.0		
Mercury	7439976	1.50	< 0.05	0.78	1.50		
Molybdenum	7439987	330	18.0	174	330		
Nickel	7440020	410	83.0	247	410		
Sodium	7440235	< 500	3,200	1,850	3,200		
Vanadium	7440622	1,400	480	940	1,400		
Zinc	7440666	75.0	200	138	200		
TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L							
	CAS No.	R8B-RS-01	R22-RS-01	Average Conc	Maximum Conc	Comments	
Aluminum	7429905	< 1.00	3.70	2.35	3.70		
Iron	7439896	< 0.50	10.0	5.25	10.0		
Manganese	7439965	< 0.08	1.10	0.59	1.10		
Zinc	7440666	B 0.26	1.20	0.73	1.20		

Comments:

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

Notes:

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

In situ oil recovery techniques can greatly reduce the total amount of residual oil tank sludge to be disposed as well as reduce volatile constituents such as benzene. As discussed above, recovery methods include distillate washing, nonpetroleum solvent washing, water wash with surfactant, and steam stripping. These operations allow entrapped oil to float to the top of the sediment layer and be recovered prior to removal from the tank. Separated oil is recycled back to the process or sent to the slop oil tanks, and the water phase is sent to the WWTP.

Oily sludges are emulsions formed due to a surface attraction among oily droplets, water droplets, and solid particles. If the solids are large and dense, the resultant material will settle and become a sludge. The surface charge interactions between the solid particles and oil droplets cause the sludge to become stable and difficult to separate. However, the sludge can be separated into its individual components by mechanically removing the solids or by neutralizing the surface charge on the solids and oil droplets.

The predominant method of minimizing the formation of tank sludge is the use of mixers to keep the sludges continuously in suspension. A common mixer configuration is a sweeping mixer that automatically oscillates to produce a sweeping motion over the floor of the tank, keeping the heavy oil and particles suspended.

Of the twenty facilities that EPA visited, eight listed methods in recovering oil from tank sludges. Several facilities wash the tanks with light oils and water, whereas another facility washes with a surfactant followed by pressure filtration.

Reference	Waste Minimization/Management Methods
"Re-refiner Fluidizes Tank Residue Using Portable Mixer." <i>Oil & Gas Journal</i> . September 5, 1994.	A portable mixer was used to cut lighter oil into the partially gelled residue.
Kuriakose, A.P., Manjooran, S. Jochu Baby. "Utilization of Refinery Sludge for Lighter Oils and Industrial Bitumen." <i>Energy & Fuels</i> . vol.8, no.3. May-June, 1994.	Utilizing waste sludge.
"Environmental Processes '93: Challenge in the '90s." <i>Hydrocarbon Processing</i> . August, 1993.	A variety of technologies described, such as bioslurry treatment of oily wastes, oily-waste recovery, and evaporation/solvent extraction.
"Waste Minimization in the Petroleum Industry: A Compendium of Practices." API. November, 1991.	Sludge formation can be minimized by mixing contents of tank.

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