

**STUDY OF SELECTED  
PETROLEUM REFINING RESIDUALS  
  
INDUSTRY STUDY**

Part 2

August 1996

U.S. ENVIRONMENTAL PROTECTION AGENCY  
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### 3.4 ISOMERIZATION

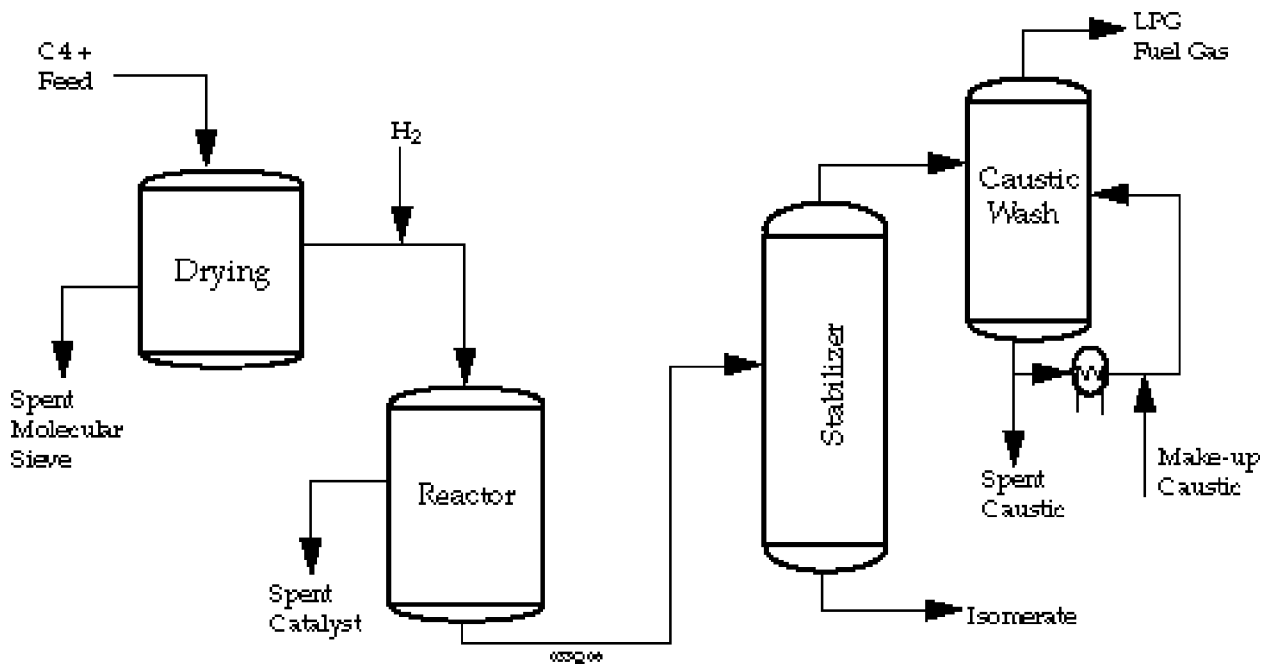
The purpose of isomerization is to increase the refinery's production of high octane, low aromatic gasoline. Gasoline with low benzene and aromatics is newly specified in the California market and is expected to be adopted by other states in the future (*Oil & Gas Journal*, 1995)<sup>1</sup>.

#### 3.4.1 Isomerization Process Description

Principal applications of isomerization at refineries are naphtha isomerization, which produces a gasoline blending component, and butane isomerization, which produces isobutane feed for the alkylation unit. Figure 3.4.1 depicts a generic process flow diagram for isomerization. Based on the results of the RCRA §3007 questionnaire, 65 facilities reported having isomerization units, distributed as follows (some facilities have more than one type of isomerization unit):

- 47 facilities have naphtha isomerization units
- 15 facilities have butane isomerization units
- 7 facilities have other types of isomerization units.

**Figure 1.1.1. Isomerization Process Flow Diagram**



<sup>1</sup>*Oil & Gas Journal*, "Deadline Looming for California Refineries to Supply Phase II RFG," December 11, 1995, pages 21-25.

### 3.4.1.1 Naphtha Isomerization

Gasoline, or naphtha, is generated throughout the refinery and consists of a mix of C<sub>5</sub> and higher hydrocarbons in straight, branched, or ring configuration. Naphtha isomerization converts the straight chains to branched, significantly raising their octane number. A common source of such “low grade” naphtha is light straight run, which consists of the lighter fraction (C<sub>5</sub>/C<sub>6</sub>) of naphtha from atmospheric crude distillation. The reduction of lead in gasoline in the 1970s increased the demand for isomerization technology; prior to that time naphtha isomerization was not widely used (Meyers, 1986).

As found from the RCRA §3007 questionnaire results, the most common naphtha isomerization processes presently used in the industry are UOP's Penex process and Union Carbide's Total Isomerization Process (TIP). Other licensed processes used include the Union Carbide Hysomer process and the BP Isomerization process. In these four processes, naphtha is combined with hydrogen and flows through one or two fixed bed reactors in series; the catalyst consists of a precious metal catalyst on a support (non-precious metal catalysts are rarely, if ever, used for naphtha isomerization). The reactor effluent is sent to a series of columns where hydrogen and fuel gas are separated from the isomerate product. The isomerate, having a significantly higher octane number than the light straight run feed, is charged to the gasoline blending pool. Although the isomerization reaction is not a net consumer or producer of hydrogen, the presence of hydrogen prevents coking and subsequent deactivation of the catalyst (Meyers, 1986).

From a solid waste generation perspective, the principal differences between the various processes relate to the catalyst used; this will in turn affect the feed pretreatment steps and spent catalyst characterization. The two principal types of catalyst identified in the industry are: (1) platinum on zeolite, which operates at temperatures above 200°C, and (2) platinum chloride on alumina, which operates at temperatures below 200°C. The higher temperatures are characteristic of the TIP and Hysomer processes, while the lower temperatures are characteristic of the Penex process and the BP process. The effect of these two different precious metal catalysts on the process are as follows:

- **Dioxin formation.** To maintain an environment of hydrogen chloride in the reactor required for catalyst activity, the platinum chloride catalyst requires a small but continuous addition of a chlorinated organic compound (e.g., carbon tetrachloride) to the feed. Although no oxygen is present during operating conditions, the conditions encountered during unit turnaround and catalyst removal (see Section 3.4.3) could result in dioxin formation. During sampling and analysis, the Agency tested for dioxin and the results are presented in Table 3.4.4.

Unlike reforming unit catalyst (a platinum catalyst discussed in the *Listing Background Document*), the isomerization unit catalyst apparently does not undergo *in situ* regeneration. One refinery stated that they do not conduct regeneration because coke does not form and contaminate the catalyst (making regeneration unnecessary), and design information for these units does not mention *in situ* regeneration.

- **Feed pretreatment.** The platinum chloride catalyst, operating at the lower temperatures, provides better conversion of paraffins to isomers. However, this catalyst is susceptible to water, sulfur, and nitrogen as catalyst poisons (Meyers, 1986). To combat these contaminants, the feed is commonly desulfurized over a cobalt/molybdenum or similar catalyst and generated  $H_2S$  is removed prior to the isomerization reactor. To further protect against sulfur poisoning, some processes include a guard column between the hydrodesulfurization reactor and the isomerization reactor to remove additional sulfur-containing compounds. Rather than consisting of Co/Mo (like many hydrotreating catalysts), this guard column often consists of zinc oxide, nickel on alumina, or copper oxide.

To remove water from the desulfurized naphtha, the hydrocarbon feed is typically dried using molecular sieve. When the molecular sieve is saturated, it is taken off-line for water desorption while the hydrocarbon is rerouted to a parallel molecular sieve vessel. In a similar way, water is removed from the hydrogen feed. Certain molecular sieves can remove both sulfur compounds and water from hydrogen or hydrocarbon feeds.

The platinum on zeolite catalyst is less susceptible to poisoning by these contaminants and reportedly requires none, or significantly less, pretreatment (Meyers, 1986).

Another difference in operating practices found among individual refineries is product stream recycling to increase yield and octane. These qualities can be increased by (1) recycling the paraffins to the reactor following their separation from the isomerized product, or (2) separating (and effectively concentrating) low octane paraffins from other high octane feed components such as isomers and aromatics. These steps can be performed using either conventional fractionation or an adsorbent. In the latter case, the normal paraffins are adsorbed onto zeolite or another adsorbent while the isomers pass through. The paraffins are desorbed and introduced as isomerization reactor feed, while the isomers bypass the isomerization reactor and are introduced to a post reactor stabilizer. Not all refineries conduct such separation, although separation of the feed or product using molecular sieve is integral to the Union Carbide Total Isomerization Process.

#### 3.4.1.2 Butane Isomerization

The purpose of butane isomerization is to generate feed material for a facility's alkylation or MTBE production unit; alkylation unit feed includes isobutane and olefins, while the raw materials used in making MTBE are isobutylene and methanol. Butane isomerization is a much older process than naphtha isomerization, having been used in refineries since World War II. Presently, the most prevalent method of producing isobutane from n-butane is the UOP Butamer process, similar in many ways to the isomerization of naphtha over platinum chloride catalyst. In the Butamer process, normal butane, generated from throughout the refinery and separated from other butanes by distillation, is combined with hydrogen and a chlorinated organic compound. The hydrogen is used to suppress the polymerization of olefin intermediates, while the chlorine source is used to maintain catalyst activity. The feed flows through one or two fixed bed reactors in series, containing platinum chloride on alumina catalyst. The isobutane

product is recovered and used as alkylation unit feed. Butane isomerization takes place at lower temperatures than naphtha isomerization.

Like platinum chloride catalyst used in naphtha isomerization, the Butamer catalyst is poisoned by water and sulfur, as well as fluoride (Meyers, 1986). These compounds are removed from the hydrogen and hydrocarbon feed by molecular sieve.

Although the Butamer process and others using platinum chloride on alumina as a catalyst dominate the industry, other technologies are also used. Three facilities conducting butane isomerization do not use platinum catalysts. Instead, the catalyst is aluminum chloride/hydrochloric acid and generates an almost continuous spent catalyst waste stream in slurry or sludge form.

#### 3.4.1.3 Other Isomerization Processes

Seven facilities reported using isomerization for purposes other than naphtha or butane isomerization. Such applications demonstrate the integration of petroleum refining and chemical production at many refineries. Some of these processes more closely represent petrochemical production than refining processes because they are not widely reported by refineries as a refining step, are not used for fuel production, and produce commodity chemicals. The processes reported by these seven facilities can be classified into three areas:

- **Xylene Isomerization.** Four facilities report processes to convert xylene isomers (e.g., from an extraction process) to p- and/or o-xylene. Unlike the naphtha and butane isomerization units described above, the catalyst is not precious metal. The xylene products are sold.
- **Cyclohexane Isomerization.** Two facilities produce cyclohexane from raw materials that include benzene and hydrogen. Unlike the naphtha and butane isomerization units described above, the catalyst is not precious metal.
- **Butylene Isomerization.** Two facilities produce butylene from various C<sub>4</sub> olefins. Butylene is used for feed to the alkylation unit. A precious metal (palladium) catalyst is used.

### 3.4.2 Isomerization Catalyst

#### 3.4.2.1 Description

As discussed in Section 3.4.1, the most prevalent catalyst used for both butane and naphtha isomerization is platinum or platinum chloride on alumina or zeolite. When the catalyst loses activity, it is removed from the reactor and replaced with fresh catalyst. Prior to removal, the reactor may be swept to remove hydrocarbons from the catalyst. These preparation steps can include one or more of the following:

- Nitrogen sweep (to remove hydrocarbon)
- Oxygen sweep (to burn hydrocarbon)

- Steam stripping (to remove hydrocarbon).

This procedure of catalyst preparation, removal, and replacement is relatively lengthy (typically one week or more) and requires the unit, or at least the reactor, to be shut down such that no hydrocarbon is processed during the time of catalyst replacement.

There are a handful of isomerization processes used at domestic refineries that do not use platinum or platinum chloride catalyst. At these facilities, spent catalyst is generated in one of the following two methods:

- A method similar to the generation of spent platinum/platinum chloride catalyst described above. Fixed-bed processes are used in both palladium and non-precious metal catalyst applications and spent solid catalyst is infrequently removed.
- A method where catalyst is removed from the fixed-bed reactor frequently (up to once a day) in liquid/semi-solid form, presumably with little to no disruption of the process. This method is used only for one process which uses aluminum chloride/hydrochloric acid catalyst.

Another type of catalyst seen in conjunction with an isomerization unit is desulfurization catalyst. In many naphtha isomerization processes, the feed typically contains high levels of mercaptans which are converted to H<sub>2</sub>S over a non-precious metal catalyst, such as cobalt/molybdenum. Such catalysts were discussed in the Listing Background Document under the broad name of “hydrotreating catalysts” and will not be discussed here.

#### 3.4.2.2 Generation and Management

The spent catalyst is vacuumed or gravity dumped from the reactors. Based on information from site visits, most refineries place the material directly into closed containers such as 55-gallon drums, flow-bins, or 1 cubic yard “supersacks.” The frequency of generation is typically between 2 and 10 years, with a small number of facilities generating a slurry/sludge continuously. In 1992, only one facility reported classifying this residual as RCRA hazardous (this facility classified 2 MT as D001).<sup>2</sup> In other years, some facilities reported that this residual carried a RCRA hazardous waste code of D018 (TCLP benzene).

Eighteen facilities reported generating a total quantity of 337 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. The questionnaire reported that 65 facilities have isomerization units and thus are likely to generate spent isomerization catalyst at some time. Due to the infrequent generation of this residual, not all of these 65 facilities generated spent catalyst 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.

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<sup>2</sup>These percentages do not match up directly with any one of the management scenarios because the number of streams and the volume are a combination of several management scenarios (i.e., Subtitle C landfill, transfer for metals reclamation, etc.).



Residuals were assigned to be “spent isomerization catalyst” if they were assigned a residual identification code of “spent solid catalyst” and were generated from a process identified as an isomerization unit. These correspond to residual code 03-A in Section VII.A of the questionnaire and process code 10 in Section IV.C of the questionnaire. The small volume of continuously generated residuals (discussed in Section 3.4.3.1) were typically omitted from these statistics, because they were most often characterized as sludges. However, as stated in Section 3.4.1, some nonprecious metal catalysts are also used in fixed bed processes and are included in these statistics. Table 3.4.1 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 3.4.1. Generation Statistics for Catalyst from Isomerization, 1992**

| <b>Final Management</b>                                 | <b># of Streams</b> | <b># of Streams w/ Unreported Volume</b> | <b>Total Volume (MT)</b> | <b>Average Volume (MT)</b> |
|---|---------------------|--|--------------------------|----------------------------|
| Disposal in offsite Subtitle C landfill                 | 3                   | 0  | 43.79                    | 14.60                      |
| Transfer metal catalyst for reclamation or regeneration | 17                  | 0  | 293.40                   | 17.26                      |
| <b>TOTAL</b>  | <b>20</b>           | <b>0</b>                                 | <b>337.19</b>            | <b>16.86</b>               |

### 3.2.2.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized above in Table 3.4.1. The Agency assessed information reported for other years but no additional management practices were reported for this residual. In addition, EPA compared the management practice reported for isomerization catalysts to those reported for reforming catalysts (a listing residual described in the Listing Background Document) based on expected similarities. The vast majority of both wastes are reclaimed due to their precious metal content.

### 3.4.2.4 Characterization

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

- Table 3.4.2 summarizes the physical properties of the spent catalyst as reported in Section VII.A of the §3007 survey.
- Four record samples of spent isomerization catalyst were collected and analyzed by EPA. These spent catalysts represent the majority of processes used by the industry. Sampling information is summarized in Table 3.4.3.



**Table 3.4.2. Catalyst from Isomerization: Physical Properties**

| Properties                        | # of Values | # of Unreported Values <sup>1</sup> | 10th % | 50th %   | 90th %   |
|-----------------------------------|-------------|-------------------------------------|--------|----------|----------|
| pH                                | 20          | 51                                  | 3.35   | 4.50     | 7.75     |
| Reactive CN, ppm                  | 14          | 57                                  | 0.04   | 1.00     | 11.60    |
| Reactive S, ppm                   | 16          | 55                                  | 0.90   | 3.00     | 100.00   |
| Flash Point, °C                   | 15          | 56                                  | 60.00  | 100.00   | 200.00   |
| Oil and Grease, vol%              | 14          | 56                                  | 0.00   | 0.50     | 1.00     |
| Total Organic Carbon, vol%        | 13          | 58                                  | 0.00   | 0.20     | 3.00     |
| Specific Gravity                  | 23          | 48                                  | 0.65   | 1.08     | 3.00     |
| Aqueous Liquid, %                 | 32          | 39                                  | 0.00   | 0.00     | 0.00     |
| Organic Liquid, %                 | 32          | 39                                  | 0.00   | 0.00     | 1.00     |
| Solid, %                          | 52          | 19                                  | 95.00  | 100.00   | 100.00   |
| Other, %                          | 29          | 42                                  | 0.00   | 0.00     | 0.00     |
| Particle >60 mm, %                | 11          | 60                                  | 0.00   | 0.00     | 100.00   |
| Particle 1-60 mm, %               | 22          | 49                                  | 0.00   | 100.00   | 100.00   |
| Particle 100 µm-1 mm, %           | 13          | 58                                  | 0.00   | 0.00     | 1.00     |
| Particle 10-100 µm, %             | 13          | 58                                  | 0.00   | 0.00     | 5.00     |
| Particle <10 µm, %                | 11          | 60                                  | 0.00   | 0.00     | 0.00     |
| Median Particle Diameter, microns | 9           | 62                                  | 0.00   | 1,590.00 | 2,000.00 |

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

**Table 3.4.3. Spent Isomerization Catalyst Record Sampling Locations**

| Sample number | Facility                    | Description: Process Name/Catalyst Type                                |
|---------------|-----------------------------|--|
| R5B-IC-01     | Marathon, Garyville LA      | Butane isomerization (UOP Butamer process), platinum chloride catalyst |
| R8B-IC-01     | Amoco, Texas City TX        | Naphtha isomerization (UOP Penex process), platinum chloride catalyst  |
| R18-IC-01     | Ashland, Canton OH          | Naphtha isomerization (UOP Penex process), platinum chloride catalyst  |
| R23B-IC-01    | Chevron, Salt Lake City, UT | Butane isomerization (UOP Butamer process), platinum chloride catalyst |

The collected samples are expected to be representative of processes using platinum chloride catalyst. Other processes use platinum catalyst or (rarely) non-precious metal catalysts. Because similar feeds are processed by most isomerization processes, these spent catalysts are expected to display similar characteristics, with the following exceptions: (1) spent platinum chloride catalysts (and possibly aluminum chloride/hydrogen chloride catalysts) are the only catalysts expected to contain dioxins, because of the presence of chlorine in the process, (2) platinum chloride catalysts require cleaner feed (i.e., water and sulfur are catalyst poisons), and thus concentrations of some contaminants may be greater in spent catalysts from processes not using platinum chloride catalysts.

All four record samples were analyzed for total and TCLP levels of volatiles, semivolatiles, metals, and reactivity (pyrophoricity). Three samples were analyzed for total levels of dioxins/furans. Three of the four samples were found to exhibit the toxicity characteristic for benzene (i.e., the level of benzene in these samples' TCLP extracts exceeded the corresponding regulatory level). A summary of the analytical results is presented in Table 3.4.4. Only constituents detected in at least one sample are shown in this table.

#### 3.4.2.5 Source Reduction

As in the case of the hydrocracking catalyst, source reduction methods are those that extend the life of the catalyst. Currently, recycling of the spent catalyst by sending to metals reclamation is a common practice since the catalyst is platinum.

| Reference   | Waste Minimization Methods  |
|---|---|
| J. Liers, J. Mensinger, A. Mosch, W. Reschefilowski. "Reforming Using Erionite Catalysts." <i>Hydrocarbon Processing</i> . Aug. 1993. | The platinum catalyst together with erionite increases isomerization. |

**Table 3.4.4. Residual Characterization Data for Spent Isomerization Catalyst**

Petroleum Refining Industry Study

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| Volatile Organics - Method 8260A µg/kg               |                 |           |           |           |            |              |              |          |  |  |
|--|-----------------|-----------|-----------|-----------|------------|--------------|--------------|----------|--|--|
|  | CAS No.         | R5B-IC-01 | R8B-IC-01 | R18-IC-01 | R23B-IC-01 | Average Conc | Maximum Conc | Comments |  |  |
| Acetone  | 67641           | < 625     | < 625     | B 1,200   | < 15,625   | 817          | 1,200        | 1        |  |  |
| Benzene  | 71432           | 24,000    | 19,000    | 280,000   | < 15,625   | 84,656       | 280,000      |          |  |  |
| tert-Butylbenzene                                    | 98066           | < 625     | < 625     | 1,900     | < 15,625   | 1,050        | 1,900        | 1        |  |  |
| Chlorobenzene  | 108907          | < 625     | 15,000    | J 580     | < 15,625   | 5,402        | 15,000       | 1        |  |  |
| Chloromethane  | 74873           | 3,700     | 1,900     | 2,800     | 150,000    | 39,600       | 150,000      |          |  |  |
| 2-Chlorotoluene                                      | 95498           | < 625     | < 625     | 1,900     | < 15,625   | 1,050        | 1,900        | 1        |  |  |
| 4-Chlorotoluene                                      | 106434          | < 625     | < 625     | 1,300     | < 15,625   | 850          | 1,300        | 1        |  |  |
| 1,4-Dichlorobenzene                                  | 106467          | < 625     | J 730     | < 600     | < 15,625   | 652          | 730          | 1        |  |  |
| Ethylbenzene   | 100414          | < 625     | < 625     | 63,000    | < 15,625   | 19,969       | 63,000       |          |  |  |
| Isopropylbenzene                                     | 98828           | < 625     | < 625     | J 520     | < 15,625   | 520          | 520          | 1        |  |  |
| n-Propylbenzene                                      | 103651          | < 625     | < 625     | 1,800     | < 15,625   | 1,017        | 1,800        | 1        |  |  |
| Methyl ethyl ketone                                  | 78933           | < 625     | < 625     | B 1,200   | < 15,625   | 817          | 1,200        | 1        |  |  |
| Toluene  | 108883          | < 625     | J 500     | 270,000   | < 15,625   | 71,688       | 270,000      |          |  |  |
| 1,2,4-Trimethylbenzene                               | 95636           | < 625     | 1,500     | 3,800     | < 15,625   | 1,975        | 3,800        | 1        |  |  |
| 1,3,5-Trimethylbenzene                               | 108678          | < 625     | J 540     | < 600     | < 15,625   | 540          | 540          | 1        |  |  |
| o-Xylene   | 95476           | < 625     | < 625     | 29,000    | < 15,625   | 11,469       | 29,000       |          |  |  |
| m,p-Xylenes  | 108383 / 106423 | < 625     | J 720     | 190,000   | < 15,625   | 51,743       | 190,000      |          |  |  |
| Naphthalene  | 91203           | < 625     | 1,900     | < 600     | J 9,800    | 3,231        | 9,800        |          |  |  |
| TCLP Volatile Organics - Methods 1311 and 8260A µg/L |                 |           |           |           |            |              |              |          |  |  |
|  | CAS No.         | R5B-IC-01 | R8B-IC-01 | R18-IC-01 | R23B-IC-01 | Average Conc | Maximum Conc | Comments |  |  |
| Acetone  | 67641           | < 50      | < 50      | B 180     | < 50       | 83           | 180          |          |  |  |
| Benzene  | 71432           | 1,700     | 1,400     | 8,800     | < 50       | 2,988        | 8,800        |          |  |  |
| Chlorobenzene  | 108907          | < 50      | 220       | < 50      | < 50       | 93           | 220          |          |  |  |
| 2-Chlorotoluene                                      | 95498           | < 50      | < 50      | J 33      | < 50       | 33           | 33           | 1        |  |  |
| 4-Chlorotoluene                                      | 106434          | < 50      | < 50      | J 21      | < 50       | 21           | 21           | 1        |  |  |
| Ethylbenzene   | 100414          | < 50      | < 50      | 1,500     | < 50       | 413          | 1,500        |          |  |  |
| Methylene chloride                                   | 75092           | < 50      | B 3,500   | J 23      | < 50       | 906          | 3,500        |          |  |  |
| Methyl ethyl ketone                                  | 78933           | < 50      | < 50      | J 42      | < 50       | 42           | 42           | 1        |  |  |
| Toluene  | 108883          | < 50      | J 48      | 8,300     | < 50       | 2,112        | 8,300        |          |  |  |
| 1,2,4-Trimethylbenzene                               | 95636           | < 50      | < 50      | J 55      | < 50       | 51           | 55           |          |  |  |
| o-Xylene   | 95476           | < 50      | < 50      | 930       | < 50       | 270          | 930          |          |  |  |
| m,p-Xylene   | 108383 / 106423 | < 50      | < 50      | 3,800     | < 50       | 988          | 3,800        |          |  |  |
| Naphthalene  | 91203           | < 50      | < 50      | < 50      | J 26       | 26           | 26           | 1        |  |  |

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**Table 3.3.4. Residual Characterization Data for Spent Isomerization Catalyst (continued)**

| Semivolatile Organics - Method 8270B µg/kg                              |         |           |           |           |            |              |              |          |
|---|---------|-----------|-----------|-----------|------------|--------------|--------------|----------|
|   | CAS No. | R5B-IC-01 | R8B-IC-01 | R18-IC-01 | R23B-IC-01 | Average Conc | Maximum Conc | Comments |
| Bis(2-ethylhexyl) phthalate   | 117817  | < 165     | J 410     | 710       | < 165      | 363          | 710          |          |
| 7,12-Dimethylbenz(a)anthracene  | 57976   | J 73      | J 600     | < 165     | < 165      | 251          | 600          |          |
| Isophorone  | 78591   | 1,200     | 15,000    | J 220     | 2,700      | 4,780        | 15,000       |          |
| 2,4-Dimethylphenol  | 105679  | < 165     | < 413     | 1,000     | < 165      | 436          | 1,000        |          |
| 2-Methylphenol  | 95487   | < 165     | < 413     | 640       | < 165      | 346          | 640          |          |
| 3/4-Methylphenol  | NA      | < 165     | < 413     | 1,500     | < 165      | 561          | 1,500        |          |
| Phenol  | 108952  | < 165     | < 413     | 1,700     | < 165      | 611          | 1,700        |          |
| TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L                |         |           |           |           |            |              |              |          |
|   | CAS No. | R5B-IC-01 | R8B-IC-01 | R18-IC-01 | R23B-IC-01 | Average Conc | Maximum Conc | Comments |
| Bis(2-ethylhexyl) phthalate   | 117817  | < 50      | < 25,000  | J 18      | < 50       | 18           | 18           | 1, 2     |
| Di-n-butyl phthalate  | 84742   | J 31      | < 25,000  | J 50      | < 50       | 44           | 50           | 2        |
| 2,4-Dimethylphenol  | 105679  | < 50      | 320,000   | J 53      | < 50       | 51           | 53           | 2        |
| 2-Methylphenol  | 95487   | < 50      | 140,000   | 140       | < 50       | 80           | 140          | 2        |
| 3/4-Methylphenol (total)  | NA      | < 50      | 870,000   | 240       | < 50       | 113          | 240          | 2        |
| Phenol  | 108952  | < 50      | < 25,000  | 840       | < 50       | 313          | 840          | 2        |
| Isophorone  | 78591   | < 50      | J 6,700   | < 50      | < 50       | NA           | NA           | 2        |
| Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg     |         |           |           |           |            |              |              |          |
|   | CAS No. | R5B-IC-01 | R8B-IC-01 | R18-IC-01 | R23B-IC-01 | Average Conc | Maximum Conc | Comments |
| Aluminum  | 7429905 | 460,000   | 130,000   | 260,000   | 230,000    | 270,000      | 460,000      |          |
| Arsenic   | 7440382 | < 1.00    | < 1.00    | 26.0      | < 1.00     | 7.25         | 26.0         |          |
| Chromium  | 7440473 | 20.0      | 17.0      | 17.0      | 17.0       | 17.8         | 20.0         |          |
| Copper  | 7440508 | < 2.50    | < 2.50    | < 2.50    | 5.50       | 3.25         | 5.50         |          |
| Iron  | 7439896 | < 10.0    | 54.0      | 190       | 73.0       | 81.8         | 190          |          |
| Nickel  | 7440020 | 14.0      | 10.0      | < 4.00    | < 4.00     | 8.00         | 14.0         |          |
| Zinc  | 7440666 | < 2.00    | < 2.00    | < 2.00    | 9.2        | 3.80         | 9.20         |          |
| TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L |         |           |           |           |            |              |              |          |
|   | CAS No. | R5B-IC-01 | R8B-IC-01 | R18-IC-01 | R23B-IC-01 | Average Conc | Maximum Conc | Comments |
| Aluminum  | 7429905 | 620       | 560       | 380       | 450        | 503          | 620          |          |
| Chromium  | 7440473 | < 0.05    | < 0.05    | 0.13      | < 0.05     | 0.07         | 0.13         |          |
| Iron  | 7439896 | 2.40      | < 0.50    | 7.60      | < 0.50     | 2.75         | 7.60         |          |
| Lead  | 7439921 | < 0.015   | < 0.015   | 0.045     | < 0.015    | 0.023        | 0.045        |          |
| Manganese   | 7439965 | < 0.08    | < 0.08    | 0.42      | < 0.08     | 0.16         | 0.42         |          |
| Zinc  | 7440666 | B 0.45    | B 0.41    | B 0.70    | B 0.53     | 0.52         | 0.70         |          |

**Table 3.3.4. Residual Characterization Data for Spent Isomerization Catalyst (continued)**

| Dioxins/Furans - Method 8290 ng/kg |          |           |           |           |            |              |              |          |  |
|------------------------------------|----------|-----------|-----------|-----------|------------|--------------|--------------|----------|--|
|                                    | CAS No.  | R5B-IC-01 | R8B-IC-01 | R18-IC-01 | R23B-IC-01 | Average Conc | Maximum Conc | Comments |  |
| 2,3,7,8-TCDF                       | 51207319 | < 0.13    | < 0.20    | B 0.69    | NA         | 0.34         | 0.69         |          |  |
| Total TCDF                         | 55722275 | < 0.13    | < 0.20    | B 0.69    | NA         | 0.34         | 0.69         |          |  |
| 2,3,4,6,7,8-HxCDF                  | 60851345 | 0.32      | < 0.34    | < 0.50    | NA         | 0.32         | 0.32         | 1        |  |
| Total HxCDF                        | 55684941 | B 0.32    | < 0.34    | < 0.50    | NA         | 0.32         | 0.32         | 1        |  |
| 1,2,3,4,6,7,8-HpCDF                | 67562394 | 0.42      | < 0.26    | < 0.37    | NA         | 0.35         | 0.42         |          |  |
| Total HpCDF                        | 38998753 | 2.10      | < 0.26    | < 0.37    | NA         | 0.91         | 2.10         |          |  |
| 1,2,3,4,6,7,8-HpCDD                | 35822469 | 3.00      | < 0.60    | < 0.50    | NA         | 1.37         | 3.00         |          |  |
| Total HpCDD                        | 37871004 | B 3.00    | < 0.60    | < 0.50    | NA         | 1.37         | 3.00         |          |  |
| OCDF                               | 39001020 | 3.70      | < 0.80    | < 0.55    | NA         | 1.68         | 3.70         |          |  |
| OCDD                               | 3268879  | B 43.0    | B 1.70    | B 1.70    | NA         | 15.47        | 43.00        |          |  |
| 2,3,7,8-TCDD Equivalence           | 1746016  | 0.11      | 0.0017    | 0.071     | NA         | 0.06         | 0.11         |          |  |

Comments:

- 1 Detection limits greater than the highest detected concentration are excluded from the calculations.
- 2 TCLP Semivolatile Organic results for sample R8B-IC-01 are excluded from the calculations.

Notes:

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

### 3.4.3 Isomerization Treating Clay

#### 3.4.3.1 Description

Not all facilities with isomerization units use “treating clay,” or adsorbents. However, solid adsorbents can be used in three places in the isomerization process:

- **Hydrocarbon feed purification.** Processes using platinum chloride catalysts require a purified feed. Both spent molecular sieve (for drying) and spent metal-alumina (for sulfur removal) are generated.
- **Hydrogen feed purification.** Processes using platinum chloride catalysts require dry hydrogen gas. Spent molecular sieve is generated.
- **Paraffin separation of the feed or product.** Various types of processes use adsorbents for paraffin separation. Molecular sieve is the most common adsorbent for this application.

All of these adsorbents go through adsorption/desorption cycles. Over time, the adsorbent loses its capacity or efficiency and is removed from the vessel and replaced with fresh adsorbent. Prior to removal, the vessel can be swept to remove light hydrocarbons and hydrogen sulfide from the vessel. Typically, processes use adsorbent beds in parallel so that one bed can be on-line (adsorption mode) while the second is off-line for desorption or replacement.

#### 3.4.3.2 Generation and Management

When spent, adsorbents from isomerization are vacuumed or gravity dumped from the vessels. Interim storage can include 55-gallon drums, flow-bins, dumpsters, or piles. The frequency of generation is highly dependent on the generating process: isomerization adsorbents are typically generated approximately every 5 years, while extraction clay is typically generated once per year or less. According to questionnaire results, 6 facilities reported classifying 39.5 MT of this residual as RCRA hazardous in 1992 (most typically as D018, D001, and D006).<sup>3</sup> This is consistent with reporting for other years.

Twenty-two facilities reported generating a total quantity of approximately 597 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. The questionnaire reported that 65 facilities have isomerization units. However, not all of these facilities use clay, molecular sieve, or other adsorbents in their process; 25 percent of facilities with isomerization units did not report generating any clay residual for their process in any year, indicating either that clay is either not used, has not yet been replaced, or is generated so infrequently that respondents could not recall when, if ever, the clay was last replaced. In addition, these adsorbents may be replaced less often than once per year or not in 1992, particularly those

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<sup>3</sup>These percentages do not match up directly with any one of the management scenarios because the number of streams and the volume are a combination of several management scenarios (i.e., Subtitle C landfill, transfer for metals reclamation, etc.).

associated with the isomerization process. However, 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 “spent clay from isomerization” if they were assigned a residual identification code of “spent sorbent” and were generated from a process identified as an isomerization or extraction unit. These correspond to residual code 07 in Section VII.A of the questionnaire and process code 10 in Section IV.C of the questionnaire. Table 3.4.5 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 3.4.5. Generation Statistics for Treating Clay from Isomerization, 1992**

| <b>Final Management</b>                                 | <b># of Streams</b> | <b># of Streams w/ Unreported Volume</b> | <b>Total Volume (MT)</b> | <b>Average Volume (MT)</b> |
|---|---------------------|--|--------------------------|----------------------------|
| Disposal in offsite Subtitle D landfill                 | 14                  | 0  | 202                      | 14.4                       |
| Disposal in offsite Subtitle C landfill                 | 6                   | 0  | 140                      | 23.3                       |
| Disposal in onsite Subtitle C landfill                  | 1                   | 0  | 18                       | 18                         |
| Disposal in onsite Subtitle D landfill                  | 2                   | 0  | 46.8                     | 23.4                       |
| Other discharge or disposal offsite: broker             | 2                   | 0  | 14                       | 7                          |
| Other recycling, or reuse: cement plant                 | 2                   | 0  | 2.5                      | 1.25                       |
| Other recycling, or reuse: onsite road material         | 4                   | 0  | 138                      | 34.5                       |
| Storage in pile   | 7                   | 0  | 19.7                     | 2.8                        |
| Transfer metal catalyst for reclamation or regeneration | 5                   | 0  | 15                       | 3                          |
| <b>TOTAL</b>  | <b>43</b>           | <b>0</b>                                 | <b>596</b>               | <b>13.8</b>                |

### 3.4.3.3 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 3.4.5. The Agency gathered information from other years but no additional management practices were reported for this residual. In addition, EPA compared the management practice reported for isomerization treating clay to those reported for treating clays from extraction, alkylation, and lube oil<sup>4</sup> based on expected similarities. Land treatment was reported for these other types of treating clays, therefore it is likely that land treatment is a plausible management practice for clays from isomerization.

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<sup>4</sup>EPA 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.

#### 3.4.3.4 Characterization

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

- Table 3.4.6 summarizes the physical properties of the spent adsorbents as reported in Section VII.A of the §3007 survey.
- One record sample of spent adsorbents from isomerization were collected and analyzed by EPA. The isomerization treating clay was categorized with the extraction clay in the consent decree, therefore, the sampling information is summarized with the extraction clay in Table 3.4.7.

The one record sample was analyzed for total and TCLP levels of volatiles, semivolatiles, and metals, and ignitability. The sample was not found to exhibit a hazardous waste characteristic. A summary of the results is presented in Table 3.4.7. Only constituents detected in at least one sample are shown in this table.

#### 3.4.3.5 Source Reduction

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



**Table 3.4.6. Treating Clay from Isomerization: Physical Properties**

| Properties                        | # of Values | # of Unreported Values <sup>1</sup> | 10th % | 50th % | 90th % |
|-----------------------------------|-------------|-------------------------------------|--------|--------|--------|
| pH                                | 37          | 71                                  | 5.9    | 7      | 9.4    |
| Reactive CN, ppm                  | 22          | 86                                  | 0      | 1      | 10     |
| Reactive S, ppm                   | 27          | 81                                  | 0      | 1      | 100    |
| Flash Point, °C                   | 20          | 88                                  | 19.17  | 60     | 131.7  |
| Oil and Grease, vol%              | 20          | 85                                  | 0      | 0.75   | 1.5    |
| Total Organic Carbon, vol%        | 18          | 87                                  | 0      | 0.18   | 2      |
| Specific Gravity                  | 31          | 77                                  | 0.8    | 1.2    | 2.2    |
| Aqueous Liquid, %                 | 50          | 58                                  | 0      | 0      | 3.5    |
| Organic Liquid, %                 | 51          | 57                                  | 0      | 0      | 0.1    |
| Solid, %                          | 75          | 33                                  | 97.5   | 100    | 100    |
| Particle >60 mm, %                | 22          | 86                                  | 0      | 0      | 100    |
| Particle 1-60 mm, %               | 32          | 76                                  | 0      | 100    | 100    |
| Particle 100 µm-1 mm, %           | 23          | 85                                  | 0      | 0      | 7.5    |
| Particle 10-100 µm, %             | 20          | 88                                  | 0      | 0      | 0      |
| Particle <10 µm, %                | 20          | 88                                  | 0      | 0      | 0      |
| Median Particle Diameter, microns | 9           | 98                                  | 0      | 2      | 3000   |

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

**Table 3.4.7. Isomerization Spent Sorbent Record Sampling Locations**

| Sample number | Facility                   | Description  |
|---------------|----------------------------|--|
| R23B-CI-01    | Chevron, Salt Lake City UT | Molecular sieve, drying butane feed prior to isomerization |

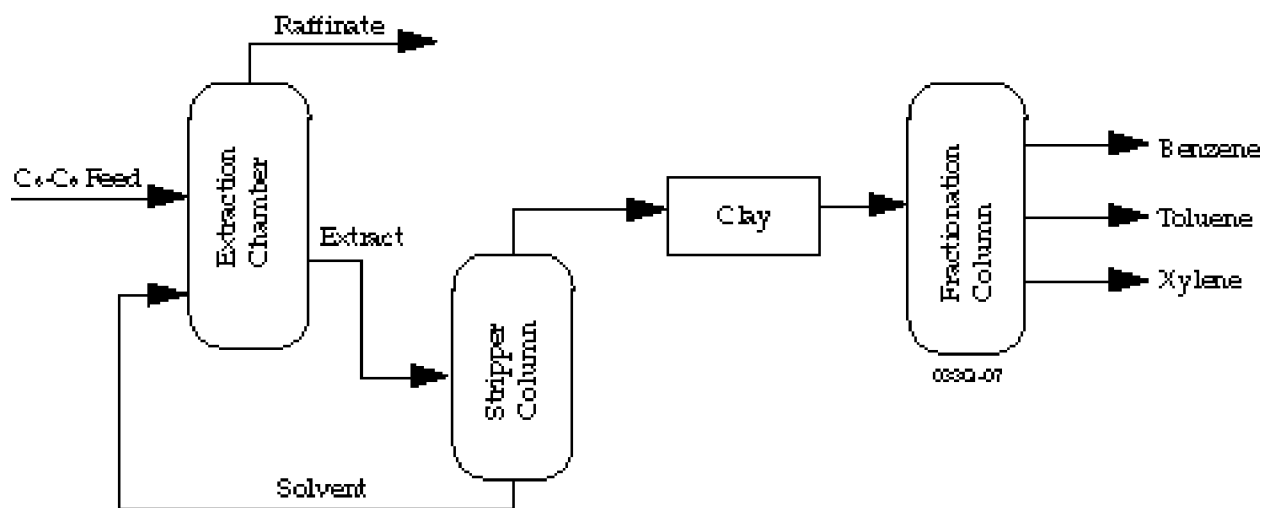
### 3.5 EXTRACTION

Extraction processes separate more valuable chemical mixtures from a mixed aromatic and paraffinic stream. At refineries, extraction processes most commonly fall into two types: (1) “heavy end” extraction, commonly used in lube oil manufacture and deasphalting operations to upgrade and further process gas oils, and (2) gasoline component extraction, commonly used to separate some of the more valuable aromatics from naphtha. “Heavy end” extraction is discussed with other residual upgrading technologies in Section 3.8 of this document. The gasoline component extraction processes are discussed here.

#### 3.5.1 Extraction Process Description

Thirty facilities reported using gasoline component extraction processes in their refineries. By far the most common type of gasoline component extraction process conducted at refineries, according to the RCRA §3007 questionnaire, is the recovery of benzene, toluene, and mixed xylenes from reformat (i.e., the product from a catalytic reforming unit) for sales or further processing. Most extraction units actually consist of two sections in series: an extraction section, which separates aromatics from non-aromatics using continuous liquid-liquid extraction, and a distillation section, which separates the various aromatic compounds from each other in a series of fractionation towers. Figure 3.5.1 depicts a generic extraction process flow diagram.

Figure 1.2.1. Extraction Process Flow Diagram



In the extraction section, the charge is countercurrently contacted with a solvent. The solvent is most commonly sulfolane,  $C_4H_8SO_2$ , or tetraethylene glycol,  $O(CH_2CH_2OCH_2CH_2OH)_2$ , although a small number of facilities use diglycol amine,  $O(CCO)CCN$ . The raffinate is separated from the aromatic-rich solvent in a tower. The aromatic-poor raffinate is water-washed to remove solvent and used elsewhere in the refinery. The aromatic-rich extract is also water-washed to remove solvent and the aromatics sent to the distillation section for separation into benzene, toluene, and xylenes.

In the distillation section, the aromatic extract is distilled to remove benzene from the top of the column; the bottoms are sent to the next column. In successive columns, toluene and finally xylene are removed. The bottoms from the xylene tower (C<sub>9</sub> aromatics) are sent to gasoline blending. Some facilities omit the distillation section altogether, using their extraction unit simply to produce low and high octane blending stocks.

To decrease the unit's loading, the feed can be separated prior to extraction so that only the most desirable fractions, such as C<sub>6</sub> to C<sub>8</sub>, are upgraded. This eliminates a final distillation step and eliminates a heavy aromatic stream as a product from the benzene-toluene-xylene separation.

Several other gasoline component extraction processes are each reported by only 1 or 2 refineries in the industry. Other refineries may use these processes, but did not report them because of their resemblance to petrochemical operations of solvent manufacture, etc., which some refineries considered out of the survey scope. As a result, the database may not accurately reflect the incidence of these processes. These processes are as follows:

- The UOP Parex process separates p-xylene from mixed C<sub>8</sub> aromatics. C<sub>8</sub> feed is injected countercurrently to a bed of solid adsorbent, which adsorbs p-xylene. The bed is then desorbed and the p-xylene is recovered in the extract for use in petrochemical production. This process is typically associated with a xylene isomerization process (Meyers, 1986). This arrangement differs from the overwhelming majority of extraction processes, which are associated with reforming processes.
- The Union Carbide IsoSiv process separates normal C<sub>6</sub>-C<sub>8</sub> paraffins from the other branched and ring compounds present in light straight run. In this process, the paraffins are adsorbed onto a fixed bed of molecular sieve. The paraffins are desorbed and used as petrochemical feedstock, solvents, etc., while the branched and ring compounds are used for gasoline blending (Meyers, 1986).
- One facility uses a process similar to the gasoline component extraction process described above, but with a slightly heavier feed.
- Heavy naphtha is fed to a fixed bed of silica gel. Aromatics are adsorbed while paraffins pass through. When saturated, the bed is desorbed with benzene and the product distilled to form various solvents. No other adsorbents are used in the process.

### 3.5.2 Extraction Treating Clay

#### 3.5.2.1. Description

Wastes generated from the reformate extraction processes include the following:

- **"Fuel side."** Treating clay is used to remove impurities from the hydrocarbon following extraction; the most common application is the filtering of the aromatic fraction prior to benzene distillation (to keep impurities out of the downstream fractions), although a small number of facilities use the clay to filter the benzene

product stream only. The purpose of the clay is to remove olefins, suspended solids, and trace amount of solvent by a combination of adsorption and catalytic processes. A few facilities also treat the raffinate (non-aromatic) stream with clay. Many facilities did not report a clay treating step anywhere in their reformate extraction process. For these facilities, clay treating is evidently not required to achieve the target product limits.

- **”Solvent side.”** Various treatment methods are used to remove impurities such as polymers and salts from the lean solvent. A slip stream of lean solvent is processed using ion-exchange, sock filters, carbon adsorption, or regeneration. This is similar to the methods used to treat amine in sulfur-removal systems. An intermittent stream of spent solvent can sometimes be generated.

Only the “fuel side” residuals are discussed and evaluated in Section 3.4.4. The “solvent side” residuals are generally classified as miscellaneous sludges in the database and their volumes were not tabulated in Table 3.5.1 (below).

As stated above, reformate extraction is the most common type of gasoline component extraction process, but the small number of other processes also generate spent adsorbents. These processes are unlike reformate extraction because the adsorbent is used for aromatic separation (in reformate extraction, clay treatment occurs following aromatic extraction). In these processes, spent adsorbent is also periodically generated, although generally less frequently so than in the reformate extraction process. These materials were included in the statistics presented in Table 3.5.1.

### 3.5.2.2 Generation and Management

When spent, adsorbents from extraction are vacuumed or gravity dumped from the vessels. Interim storage can include 55-gallon drums, flow-bins, dumpsters, or piles. The frequency of generation is highly dependent on the generating process: extraction clay is typically generated once per year or less. According to questionnaire results, 2 facilities reported classifying 81.3 MT of this residual as RCRA hazardous in 1992 (as D018).<sup>5</sup> This is consistent with reporting for other years.

Fifteen facilities reported generating a total quantity of approximately 1900 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. The questionnaire reported that 30 facilities have extraction units. However, not all of these facilities use clay, molecular sieve, or other adsorbents in their process; 33 percent of facilities with extraction units did not report generating any clay residual for their process in any year, indicating either that clay is either not used, has not yet been replaced, or is generated so infrequently that respondents could not recall when, if ever, the clay was last replaced. However, there was no reason to expect that 1992 would not be a typical year with regard to this residual's generation and management. Extraction clays are generated more frequently and in greater quantity than isomerization clays.

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

Residuals were assigned to be “spent clay from extraction” if they were assigned a residual identification code of “spent sorbent” and were generated from a process identified as an isomerization or extraction unit. These correspond to residual code 07 in Section VII.A and process codes 12 in Section IV.C of the survey. Table 3.5.1 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 3.5.1. Generation Statistics for Treating Clay from Extraction, 1992**

| Final Management  | # of Streams | # of Streams w/ Unreported Volume | Total Volume (MT) | Average Volume (MT) |
|---|--------------|-----------------------------------|-------------------|---------------------|
| Disposal in offsite Subtitle D landfill                 | 10           | 0                                 | 734.8             | 88.4                |
| Disposal in offsite Subtitle C landfill                 | 4            | 0                                 | 376.3             | 94                  |
| Disposal in onsite Subtitle C landfill                  | 1            | 0                                 | 40                | 40                  |
| Disposal in onsite Subtitle D landfill                  | 2            | 0                                 | 448.8             | 224.4               |
| Onsite land treatment                                   | 3            | 0                                 | 231               | 78                  |
| Other recycling, or reuse: cement plant                 | 1            | 0                                 | 26                | 26                  |
| Transfer metal catalyst for reclamation or regeneration | 1            | 0                                 | 18                | 18                  |
| <b>TOTAL</b>  | <b>22</b>    | <b>0</b>                          | <b>1875</b>       | <b>85.2</b>         |

### 3.5.2.3 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 3.5.1. The Agency gathered information suggesting that “offsite land treatment” (95 MT) was used in other years. This practice is comparable to the practice reported for 1992 (i.e., onsite land treatment). In addition, EPA compared the management practice reported for extraction treating clay to those reported for treating clays from isomerization, alkylation, and lube oil<sup>6</sup> based on expected similarities. No additional management practices were reported.

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<sup>6</sup>EPA 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.

#### 3.5.2.4 Characterization

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

- Table 3.5.2 summarizes the physical properties of the spent adsorbents as reported in Section VII.A of the §3007 survey.
- One record sample of spent adsorbents from extraction was collected and analyzed by EPA. The sampling information is summarized in Table 3.5.3.

The record sample was analyzed for total and TCLP levels of volatiles, semivolatiles, and metals, and ignitability. It was not found to exhibit a hazardous waste characteristic. A summary of the results is presented in Table 3.5.4. Only constituents detected in at least one sample are shown in this table. This residual was categorized with isomerization clay in the consent decree, and the characterization information for both residuals is presented in Table 3.5.4.

#### 3.5.2.5 Source Reduction

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

**Table 3.5.2. Treating Clay from Extraction: Physical Properties**

| Properties                        | # of Values | # of Unreported Values <sup>1</sup> | 10th % | 50th % | 90th % |
|-----------------------------------|-------------|-------------------------------------|--------|--------|--------|
| pH                                | 12          | 17                                  | 4.28   | 6.65   | 7.5    |
| Reactive CN, ppm                  | 14          | 15                                  | 0      | 0.5    | 250    |
| Reactive S, ppm                   | 13          | 16                                  | 0      | 1      | 100    |
| Flash Point, °C                   | 10          | 19                                  | 37.78  | 71.1   | 96.1   |
| Oil and Grease, vol%              | 6           | 23                                  | 0      | 0.85   | 1      |
| Total Organic Carbon, vol%        | 5           | 24                                  | 0      | 0.34   | 100    |
| Specific Gravity                  | 9           | 20                                  | 0.9    | 1      | 2      |
| Aqueous Liquid, %                 | 20          | 9                                   | 0      | 0      | 11     |
| Organic Liquid, %                 | 19          | 10                                  | 0      | 0      | 1      |
| Solid, %                          | 25          | 4                                   | 98     | 100    | 100    |
| Particle >60 mm, %                | 10          | 19                                  | 0      | 0      | 100    |
| Particle 1-60 mm, %               | 11          | 18                                  | 0      | 85     | 100    |
| Particle 100 µm-1 mm, %           | 9           | 20                                  | 0      | 0      | 20     |
| Particle 10-100 µm, %             | 8           | 21                                  | 0      | 0      | 20     |
| Particle <10 µm, %                | 9           | 20                                  | 0      | 0      | 100    |
| Median Particle Diameter, microns | 1           | 28                                  | 10     | 10     | 10     |

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

**Table 3.5.3. Extraction Spent Sorbent Record Sampling Locations**

| Sample number | Facility              | Description   |
|---------------|-----------------------|---|
| R8D-CI-01     | Amoco, Texas City, TX | Clay from aromatic extraction unit (reformate feed) |

**Table 3.5.4. Residual Characterization Data for Spent Treating Clay from Extraction/Isomerization**

| Volatile Organics - Method 8260A µg/kg                              |                 |           |            |              |              |          |
|---|-----------------|-----------|------------|--------------|--------------|----------|
|   | CAS No.         | R8D-CI-01 | R23B-CI-01 | Average Conc | Maximum Conc | Comments |
| Acetone   | 67641           | < 600     | 940,000    | 470,300      | 940,000      |          |
| Benzene   | 71432           | 2,500     | < 62,500   | 2,500        | 2,500        | 1        |
| Isopropylbenzene  | 98828           | J 650     | < 62,500   | 650          | 650          | 1        |
| Toluene   | 108883          | 36,000    | < 62,500   | 36,000       | 36,000       | 1        |
| Naphthalene   | 91203           | < 600     | J 29,000   | 14,800       | 29,000       |          |
| TCLP Volatile Organics - Methods 1311 and 8260A µg/L                |                 |           |            |              |              |          |
|   | CAS No.         | R8D-CI-01 | R23B-CI-01 | Average Conc | Maximum Conc | Comments |
| Acetone   | 67641           | 120       | 32,000     | 16,060       | 32,000       |          |
| Benzene   | 71432           | < 50      | J 45       | 45           | 45           | 1        |
| 4-Methyl-2-pentanone  | 108101          | < 50      | 6,100      | 3,075        | 6,100        |          |
| Methyl ethyl ketone   | 78933           | < 50      | 3,800      | 1,925        | 3,800        |          |
| Toluene   | 108883          | < 50      | 110        | 80           | 110          |          |
| 1,2,4-Trimethylbenzene  | 95636           | < 50      | 250        | 150          | 250          |          |
| 1,3,5-Trimethylbenzene  | 95476           | < 50      | 630        | 340          | 630          |          |
| m,p-Xylene  | 108383 / 106423 | < 50      | J 62       | 56           | 62           |          |
| Naphthalene   | 91203           | < 50      | J 30       | 30           | 30           | 1        |
| Semivolatile Organics - Method 8270B µg/kg                          |                 |           |            |              |              |          |
|   | CAS No.         | R8D-CI-01 | R23B-CI-01 | Average Conc | Maximum Conc | Comments |
| Fluoranthene  | 206440          | J 130     | < 165      | 130          | 130          | 1        |
| Fluorene  | 86737           | < 165     | J 220      | 193          | 220          |          |
| Isophorone  | 78591           | < 165     | 130,000    | 65,083       | 130,000      |          |
| 2,4-Dimethylphenol  | 105679          | < 165     | J 2,800    | 1,483        | 2,800        |          |
| 3/4-Methylphenol  | NA              | < 165     | J 150      | 150          | 150          | 1        |
| Naphthalene   | 91203           | J 280     | < 165      | 223          | 280          |          |
| 1-Methylnaphthalene   | 90120           | J 220     | J 650      | 435          | 650          |          |
| 2-Methylnaphthalene   | 91576           | 520       | J 310      | 415          | 520          |          |
| TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L            |                 |           |            |              |              |          |
|   | CAS No.         | R8D-CI-01 | R23B-CI-01 | Average Conc | Maximum Conc | Comments |
| Isophorone  | 78591           | < 50      | 7,300      | 3,675        | 7,300        |          |
| 2-Methylphenol  | 95487           | < 50      | J 34       | 34           | 34           | 1        |
| 3/4-Methylphenol (total)  | NA              | < 50      | J 99       | 75           | 99           |          |
| Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg |                 |           |            |              |              |          |
|   | CAS No.         | R8D-CI-01 | R23B-CI-01 | Average Conc | Maximum Conc | Comments |
| Aluminum  | 7429905         | 8,300     | 110,000    | 59,150       | 110,000      |          |
| Barium  | 7440393         | 250       | < 20.0     | 135          | 250          |          |
| Calcium   | 7440702         | 4,700     | 4,500      | 4,600        | 4,700        |          |
| Chromium  | 7440473         | < 1.00    | 14.0       | 7.50         | 14.0         |          |
| Iron  | 7439896         | 1,800     | 3,000      | 2,400        | 3,000        |          |
| Lead  | 7439921         | 13.0      | 1.60       | 7.30         | 13.0         |          |



**Table 3.5.4. Residual Characterization Data for Spent Treating Clay from Extraction/Isomerization (continued)**

| Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg (continued) |         |           |            |              |              |          |
|---|---------|-----------|------------|--------------|--------------|----------|
|   | CAS No. | R8D-CI-01 | R23B-CI-01 | Average Conc | Maximum Conc | Comments |
| Magnesium   | 7439954 | 4,300     | 9,600      | 6,950        | 9,600        |          |
| Manganese   | 7439965 | 350       | 43.0       | 197          | 350          |          |
| Potassium   | 7440097 | < 500     | 1,300      | 900          | 1,300        |          |
| Sodium  | 7440235 | < 500     | 81,000     | 40,750       | 81,000       |          |
| Vanadium  | 7440622 | 20.0      | 10.0       | 15.0         | 20.0         |          |
| Zinc  | 7440666 | 8.80      | 28.0       | 18.4         | 28.0         |          |
| TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L         |         |           |            |              |              |          |
|   | CAS No. | R8D-CI-01 | R23B-CI-01 | Average Conc | Maximum Conc | Comments |
| Aluminum  | 7429905 | < 1.00    | 17.0       | 9.00         | 17.0         |          |
| Calcium   | 7440702 | 160       | < 25.0     | 92.5         | 160.0        |          |
| Iron  | 7439896 | 18.0      | 1.30       | 9.65         | 18.0         |          |
| Lead  | 7439921 | 0.04      | < 0.015    | 0.03         | 0.04         |          |
| Magnesium   | 7439954 | 82.0      | 50.0       | 66.0         | 82.0         |          |
| Manganese   | 7439965 | 12.0      | < 0.08     | 6.04         | 12.0         |          |

Comments:

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

Notes:

- B Analyte also detected in the associated method blank.
- C 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.

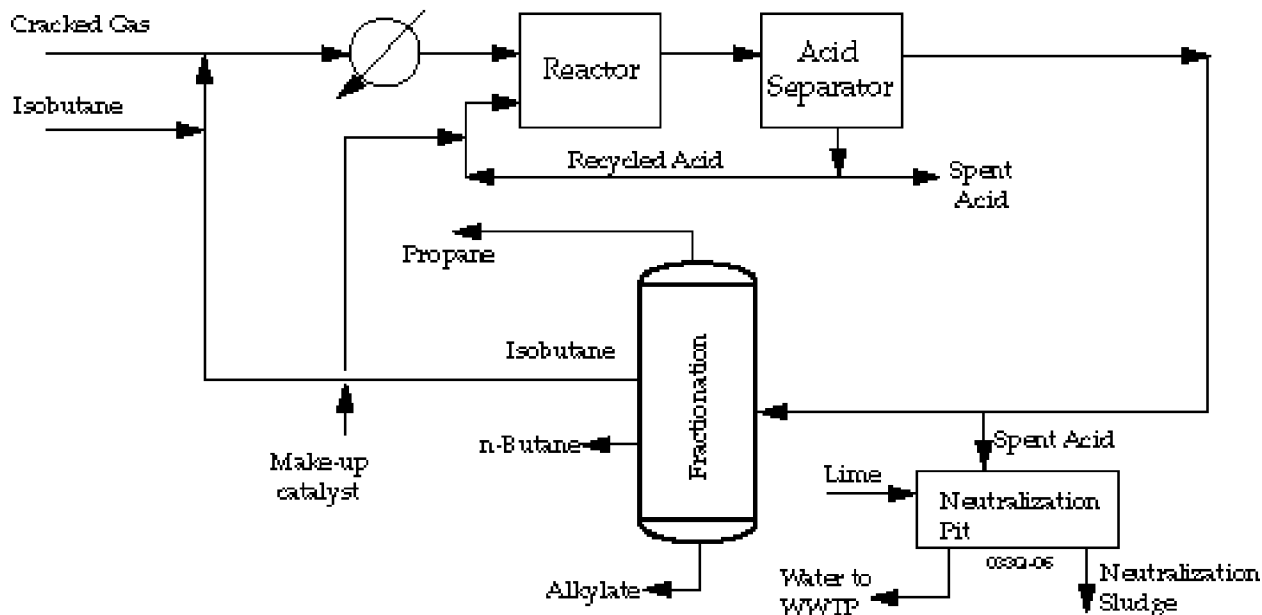
### 3.6 ALKYLATION

The petroleum refining industry uses both hydrofluoric and sulfuric acid catalyzed alkylation processes to form high octane products. DOE reported that 103 facilities operated almost 1.1 million BPSD of alkylation capacity; 49 facilities used sulfuric acid and 59 used HF. While the general chemistry of these processes is the same, the HF process includes a closed loop and integral recycling step for the HF acid, while the sulfuric acid process requires a separate acid regeneration process, which generally occurs off site. Study residuals are generated from both alkylation processes.

#### 3.6.1 Sulfuric Acid Alkylation Process Description

In the sulfuric acid alkylation process, olefin and isobutane gases are contacted over concentrated sulfuric acid ( $H_2SO_4$ ) catalyst to synthesize alkylates for octane-boosting. The reaction products are separated by distillation and scrubbed with caustic. Alkylate product has a Research Octane Number in the range of 92 to 99. Figure 3.6.1 provides a generic process flow diagram for  $H_2SO_4$  alkylation.

Figure 1.3.1.  $H_2SO_4$  Alkylation Process Flow Diagram



The olefin stream is mixed with isobutane and  $H_2SO_4$  in the reactor. To prevent polymerization and to obtain a higher quality yield, temperatures for the  $H_2SO_4$  catalyzed reaction are kept between 40 and 50°F (McKetta, 1992). Since the reactions are carried out below atmospheric temperatures during most of the year, refrigeration is required. Pressures are maintained so all reaction streams are in their liquid form. The streams are mixed well during their long residence time in the reactor to allow optimum reaction to occur.

The hydrocarbon/acid mixture then moves to the acid separator, where it is allowed to settle and separate. The hydrocarbons are drawn off the top and sent to a caustic wash to

neutralize any remaining trace acid. The acid is drawn from the bottom and recycled back to the reactor. A portion of the acid catalyst is continuously bled and replaced with fresh acid to maintain the reactor's acid concentration at around 90 percent. This spent  $H_2SO_4$  was a listing residual of concern.

In the fractionator, the hydrocarbon streams are separated into the alkylate and saturated gases. The isobutane is recycled back into the reactor as feed. Light end products may be filtered with sorbents to remove trace  $H_2SO_4$  acid, caustic or water. The sorbents (e.g., treating clays) are study residuals of concern.

Some facilities have neutralization tanks (in and above ground), referred to as pits, which neutralize spent caustic and any acid generated from spills prior to discharge to the WWTP, serving as surge tanks. Neutralizing agents (sodium, calcium, potassium hydroxides) are selected by the refineries. If necessary, the influent to the pit is neutralized and, depending on the neutralizing agent, the precipitated salts form a sludge. This sludge was also a listing residual of concern. Sludge may also be generated in process line junction boxes, in the spent  $H_2SO_4$  holding tank, and during turnaround. However, due to the aqueous solubility of sodium, calcium, and potassium sulfates, sludge generation rates are relatively low and the majority of neutralization salts (e.g., sodium sulfate) are solubilized and discharged to the WWTP.

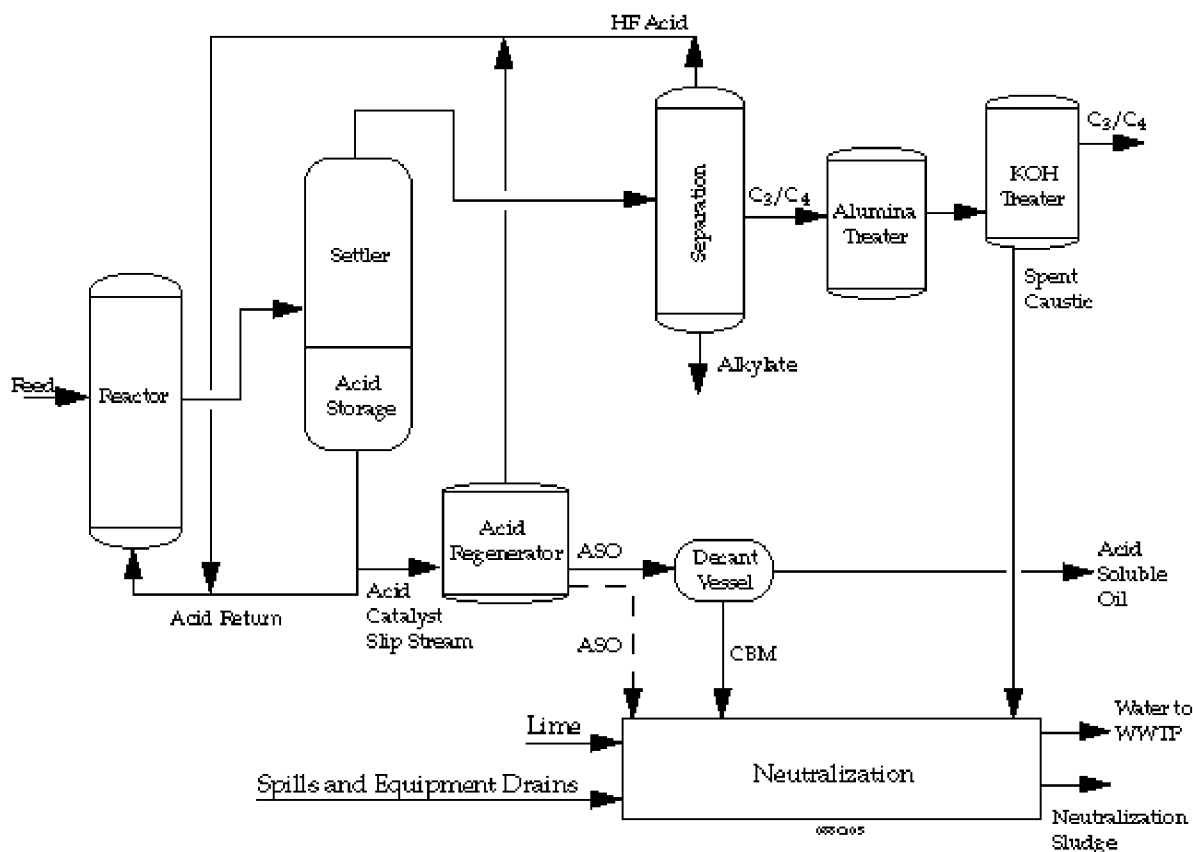
### **3.6.2 Hydrofluoric Acid Alkylation Process Description**

Hydrofluoric acid alkylation is very similar to the  $H_2SO_4$  alkylation process. In the hydrofluoric acid alkylation process, olefin and isobutane gases are contacted over hydrofluoric acid (HF) catalyst to synthesize alkylates for octane-boosting. The reaction products are separated by distillation and scrubbed with caustic. Alkylate product has a research octane number (RON) in the range of 92 to 99. Because it is clean burning and contributes to reduced emissions, alkylate is a highly valued component in premium and reformulated gasolines. The HF process differs from the  $H_2SO_4$  alkylation in that the HF catalyst is managed in a closed-loop process, never leaving the unit for replacement or regeneration. Figure 3.6.2 provides a generic process flow diagram for HF alkylation.

The olefin stream is mixed with the isobutane and HF in the reactor. To prevent polymerization and to receive a higher quality yield, temperatures for the HF catalyzed reaction are maintained at approximately 100°F. Pressures are kept so all reaction streams are in their liquid form (usually 85 to 120 psi). The streams are mixed well in the reactor to allow optimum reaction to occur.

The hydrocarbon/acid mixture then moves to the settler, where it is allowed to settle and phase separate. The hydrocarbons are drawn off the top and sent to a fractionator. The acid is drawn from the bottom and recycled back to the reactor. A slip stream of acid is sent to an acid regenerator where distillation separates the HF acid from by-product contaminants. The HF acid from the regenerator is recycled back to the reactor. Fresh acid is added to replace acid losses at a rate of about 500 pounds per day per 5,000 BPSD alkylation unit capacity (a small to medium size unit).

**Figure 3.6.2. HF Alkylation Process Flow Diagram**



A residual of high molecular-weight reaction by-products dissolves in the HF acid catalyst and lowers its effectiveness. To maintain the catalyst activity, a slip stream of catalyst is distilled, leaving the by-product, acid soluble oil (ASO), as a residue. The ASO is charged to a decanting vessel where an aqueous phase settles out. The aqueous phase, an azeotropic mixture of HF acid and water, is referred to as constant boiling mixture (CBM). The ASO is scrubbed with potassium hydroxide (KOH) to remove trace amounts of HF and either recycled, sold as product (e.g., residual fuel), or burned in the unit's boiler. The CBM is sent to the neutralization tank. In some cases, the ASO from the regenerator is sent directly to the neutralization tank. The ASO is a residual of concern for the petroleum refining study.

A series of fractionators distills the product streams from the reactor into the alkylate, saturated gases, and HF acid. Isobutane and HF are recycled back into the reactor as feed.

The main fractionator overhead is charged to the depropanizer and debutanizer, where high-purity propane and butane are produced. The propane and butane are then passed through the alumina treater for HF removal. Once catalytically defluorinated, they are KOH-treated and sent to LPG storage.

As HF is neutralized by aqueous KOH, soluble potassium fluoride (KF) is produced and the caustic is eventually depleted. Some facilities employ KOH regeneration. Periodically some of the KF-containing neutralizing solution is withdrawn to the KOH regenerator. In this vessel

KF reacts with a lime slurry to produce insoluble calcium fluoride ( $\text{CaF}_2$ ) and thereby regenerates KF to KOH. The regenerated KOH is then returned to the system, and the solid  $\text{CaF}_2$  is routed to the neutralizing tank. The KF, at facilities that do not have a regenerator, is sent directly to the neutralizing tank, where it is reacted with lime to form a sludge.

Spent caustic, KOH scrubbers, acidic waters from acid sewers and, in some cases, CBM are charged to in-ground neutralization tanks (referred to by industry as pits), which neutralize effluent to the WWTP. Neutralizing controls fluoride levels to the WWTP. Neutralizing agents (sodium, calcium, and potassium hydroxide) are selected based on the refineries' WWTP permits. Effluent to the pit is neutralized, generally with lime, which forms a sludge (calcium fluoride) that collects on the bottom of the tank. This sludge was a listing residual of concern.

HF acid is an extremely corrosive and toxic chemical. Refineries go to great lengths to protect their personnel from HF contact. Prior to entrance to an HF alkylation unit, personnel must have special training and wear various levels of personal protective clothing (depending upon the work to be performed). The unit is generally cordoned off and marked as an HF hazard area. Valves, flanges, and any place where leaks can occur are painted with a special paint that will change colors when contacted with HF. The units are continuously monitored and alarms are activated if an HF leak is detected.

### 3.6.3 Spent Treating Clay from Alkylation

#### 3.6.3.1 Description

Treating clay from alkylation predominantly includes (1) molecular sieves used for drying feed and (2) alumina used for removing fluorinated compounds from the product. Both are applications in HF alkylation; clays are little used in sulfuric acid alkylation. Specifically, the industry reported 83 treating clay residuals from alkylation in 1992, accounting for 2,890 metric tons of residuals. Only 7 of these residuals (143 metric tons) were from sulfuric acid alkylation processes.

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

Treating clay becomes spent when breakthrough of  $\text{H}_2\text{SO}_4$  or HF acid, caustic, or water occurs. Depending on the type of clay and the type of service, breakthrough can occur anywhere between 2 months and 5 years (e.g., alumina in HF service is typically 2 months and salt treaters can be as long as 5 years). Prior to removal the clay may undergo one of the following *in situ* treatments:

- Nitrogen sweep
- Propane sweep
- Steam stripping
- Methane sweep

Following removal, the spent clay is placed in closed containers and is typically sent to an offsite landfill. Certain types of treating clay, such as alumina, are more amenable to recycling and may be sent offsite to a smelter or a cement kiln to be used as process feeds.

In 1992, less than 2 percent of the volume of spent treating clay from alkylation was managed as hazardous, with one residual reported to be D004, and three others reported generically to be managed as hazardous (i.e., no specific codes were reported).<sup>7</sup>

### 3.6.3.2 Generation and Management

The RCRA §3007 Survey responses indicated 2,895 MT of spent treating clay were generated in 1992. Residuals were assigned to be “treating clay from alkylation” if they were assigned a residual identification code of “spent sorbent” and was generated from a process identified as a sulfuric acid or HF alkylation unit. This corresponds to residual code “07” in Section VII.1 and process codes “09-A” or “09-B” in Section IV-1.C of the questionnaire. Due to the frequent generation of this residual, not all 103 facilities generated spent treating clay 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 3.6.1 provides a description of the total quantity generated, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

**Table 3.6.1. Generation Statistics for Treating Clay from Alkylation, 1992**

| <b>Final Management</b>   | <b># of Streams</b> | <b># of Streams w/ Unreported Volume</b> | <b>Total Volume (MT)</b> | <b>Average Volume (MT)</b> |
|---|---------------------|--|--------------------------|----------------------------|
| Disposal in offsite Subtitle D landfill   | 28                  | 2  | 633.7                    | 22.6                       |
| Disposal in offsite Subtitle C landfill   | 4                   | 1  | 23.9                     | 6                          |
| Disposal in onsite Subtitle C landfill  | 3                   | 0  | 67.0                     | 22.3                       |
| Disposal in onsite Subtitle D landfill  | 18                  | 0  | 626.3                    | 34.8                       |
| Disposal in onsite wastewater treatment facility  | 0                   | 2  | --                       | --                         |
| Onsite land treatment   | 4                   | 0  | 59.2                     | 14.8                       |
| Other recycling, or reuse: cement plant   | 4                   | 0  | 770.5                    | 154.1                      |
| Other recycling, or reuse: onsite road material   | 1                   | 0  | 3.6                      | 3.6                        |
| Storage in pile   | 6                   | 0  | 30.0                     | 5.0                        |
| Transfer to offsite entity: alumina manufacturer, smelter, or other unspecified recycle | 15                  | 0  | 680.4                    | 45.4                       |
| <b>TOTAL</b>  | <b>83</b>           | <b>5</b>                                 | <b>2,894.6</b>           | <b>34.9</b>                |

<sup>7</sup>These 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 to offsite entity, etc.).

### 3.6.3.3 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 3.6.1. The Agency gathered information suggesting other management practices have been used in other years including: “disposal onsite in surface impoundment” (38.4 MT), “other recycling, reclamation, or reuse: offsite fluoride recovery” (23.6 MT), and “offsite incineration” (3.6 MT). The very small volume reported to have been disposed in a surface impoundment was placed in the surface impoundment the year it was closed, suggesting the inert material was used as fill. The refinery reported the future management of the spent clay would be sent offsite to a cement kiln for reuse. Similarly, the very small volume reported for offsite fluoride recovery was a management practice seen as a trend for fluoride containing residuals during the engineering site visits. The very small volume reported for offsite incineration are comparable to the 1992 practices for other treating clay residuals (e.g., clay filtering)

### 3.6.3.4 Characterization

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

- Table 3.6.2 summarizes the physical properties of the alkylation sorbents as reported in Section VII.A of the §3007 survey.
- Four record samples of actual treating clay were collected and analyzed by EPA. These spent clays are all from HF processes and represent the various types of spent sorbents typically used by the industry as summarized in Table 3.6.3.

The four record samples were analyzed for total and TCLP levels of volatiles, semivolatiles, metals, fluorides, reactivity and ignitability. None of the samples were found to exhibit any of the hazardous waste characteristics. A summary of the results is presented in Table 3.6.4. Only constituents detected in at least one sample are shown in this table.

### 3.6.3.5 Source Reduction

Several solid-acid catalysts used for alkylation are being tested in pilot plants. The solid-catalyst reactor systems are different from the current liquid-acid systems, but for one solid-catalyst operation, the other process equipment is compatible. The three types of new solid catalyst include aluminum chloride, alumina/zirconium halide, and antimony pentafluoride (a slurry system). It is unclear whether these processes will generate more or less treating clays than current processes. Theoretically, these processes would not require filtering for acid and water removal.

The February 1, 1993 issue of the *Oil & Gas Journal* reported that Conoco's Ponca City, Oklahoma refinery sold reclaimed fluorinated alumina to Kaiser Aluminum & Chemical Corporation's plant in Mead, Washington. The fluorinated alumina is substituted for aluminum fluoride, a “bath” chemical used in aluminum manufacturing.

**Table 3.6.2. Treating Clay from Alkylation: Physical Properties**

| Properties                        | # of Values | # of Unreported Values <sup>1</sup> | 10th % | 50th %   | 90th %   |
|-----------------------------------|-------------|-------------------------------------|--------|----------|----------|
| pH                                | 60          | 91                                  | 2.91   | 7.00     | 9.00     |
| Reactive CN, ppm                  | 39          | 112                                 | 0.00   | 0.25     | 250.00   |
| Reactive S, ppm                   | 45          | 106                                 | 0.00   | 4.00     | 170.00   |
| Flash Point, °C                   | 43          | 108                                 | 60.00  | 93.33    | 100.00   |
| Oil and Grease, vol%              | 43          | 108                                 | 0.00   | 0.05     | 1.00     |
| Total Organic Carbon, vol%        | 25          | 126                                 | 0.00   | 0.00     | 1.00     |
| Specific Gravity                  | 54          | 97                                  | 0.70   | 1.24     | 2.24     |
| Specific Gravity Temperature, °C  | 27          | 124                                 | 15.00  | 15.60    | 25.00    |
| BTU Content, BTU/lb               | 12          | 139                                 | 0.00   | 0.00     | 500.00   |
| Aqueous Liquid, %                 | 89          | 62                                  | 0.00   | 0.00     | 8.00     |
| Organic Liquid, %                 | 85          | 66                                  | 0.00   | 0.00     | 1.00     |
| Solid, %                          | 123         | 28                                  | 96.00  | 100.00   | 100.00   |
| Other, %                          | 77          | 74                                  | 0.00   | 0.00     | 0.00     |
| Particle >60 mm, %                | 41          | 110                                 | 0.00   | 0.00     | 100.00   |
| Particle 1-60 mm, %               | 53          | 98                                  | 0.00   | 100.00   | 100.00   |
| Particle 100 µm-1 mm, %           | 37          | 114                                 | 0.00   | 0.00     | 50.00    |
| Particle 10-100 µm, %             | 38          | 113                                 | 0.00   | 0.00     | 3.00     |
| Particle <10 µm, %                | 36          | 115                                 | 0.00   | 0.00     | 0.00     |
| Median Particle Diameter, microns | 21          | 130                                 | 0.00   | 1,200.00 | 9,525.00 |

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

**Table 3.6.3. Alkylation Treating Clay Record Sampling Locations**

| Sample Number | Location                    | Description  |
|---------------|-----------------------------|--|
| R3-CA-01      | Exxon, Billings, MT         | Alumina propane product treater <sup>1</sup>           |
| R15-CA-01     | Total, Ardmore, OK          | Alumina butane product treater <sup>1</sup>            |
| R21-CA-01     | Chevron, Pt. Arthur, TX     | Alumina propane or butane product treater <sup>1</sup> |
| R23-CA-01     | Chevron, Salt Lake City, UT | Alumina propane product treater <sup>1</sup>           |

<sup>1</sup>HF process



**Table 3.6.4. Alkylation Treating Clay Characterization**

Petroleum Refining Industry Study

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| Volatile Organics - Method 8260A µg/kg                              |                 |          |           |           |           |              |              |          |  |
|---|-----------------|----------|-----------|-----------|-----------|--------------|--------------|----------|--|
|   | CAS No.         | R3-CA-01 | R15-CA-01 | R21-CA-01 | R23-CA-01 | Average Conc | Maximum Conc | Comments |  |
| Acetone   | 67641           | 42,000   | 680       | J 880     | 13,000    | 14,140       | 42,000       |          |  |
| Benzene   | 71432           | J 67     | < 25      | < 625     | < 650     | 46           | 67           | 1        |  |
| sec-Butylbenzene  | 135988          | < 625    | < 25      | J 1,200   | < 650     | 625          | 1,200        |          |  |
| p-Isopropyltoluene  | 99876           | < 625    | < 25      | J 800     | < 650     | 525          | 800          |          |  |
| Methyl ethyl ketone   | 78933           | < 625    | 290       | < 625     | 1,300     | 710          | 1,300        |          |  |
| Toluene   | 108883          | J 67     | < 25      | < 625     | < 650     | 46           | 67           | 1        |  |
| 1,2,4-Trimethylbenzene  | 95636           | J 112    | < 25      | 2,100     | < 650     | 722          | 2,100        |          |  |
| o-Xylene  | 95476           | < 625    | < 25      | J 530     | < 650     | 278          | 530          | 1        |  |
| m,p-Xylenes   | 108383/106423   | J 136    | < 25      | 1,300     | < 650     | 528          | 1,300        |          |  |
| Naphthalene   | 91203           | < 625    | < 25      | J 1,100   | < 650     | 600          | 1,100        |          |  |
| TCLP Volatile Organics - Methods 1311 and 8260A µg/L                |                 |          |           |           |           |              |              |          |  |
|   | CAS No.         | R3-CA-01 | R15-CA-01 | R21-CA-01 | R23-CA-01 | Average Conc | Maximum Conc | Comments |  |
| Acetone   | 67641           | 1,500    | < 50      | 280       | B 1,100   | 733          | 1,500        |          |  |
| Toluene   | 108883          | JB 11    | < 50      | < 50      | < 50      | 11           | 11           | 1        |  |
| Methyl ethyl ketone   | 78933           | J 95     | < 50      | 210       | 250       | 151          | 250          |          |  |
| m,p-Xylene  | 108383 / 106423 | JB 10    | < 50      | < 50      | < 50      | 10           | 10           | 1        |  |
| Semivolatile Organics - Method 8270B µg/kg                          |                 |          |           |           |           |              |              |          |  |
|   | CAS No.         | R3-CA-01 | R15-CA-01 | R21-CA-01 | R23-CA-01 | Average Conc | Maximum Conc | Comments |  |
| Di-n-butyl phthalate  | 84742           | < 165    | < 165     | J 200     | < 165     | 174          | 200          |          |  |
| Phenanthrene  | 85018           | < 165    | J 160     | < 165     | < 165     | 160          | 160          | 1        |  |
| TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L            |                 |          |           |           |           |              |              |          |  |
|   | CAS No.         | R3-CA-01 | R15-CA-01 | R21-CA-01 | R23-CA-01 | Average Conc | Maximum Conc | Comments |  |
| Bis(2-ethylhexyl)phthalate  | 117817          | J 10     | < 50      | < 50      | < 50      | 10           | 10           | 1        |  |
| Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg |                 |          |           |           |           |              |              |          |  |
|   | CAS No.         | R3-CA-01 | R15-CA-01 | R21-CA-01 | R23-CA-01 | Average Conc | Maximum Conc | Comments |  |
| Aluminum  | 7429905         | 240,000  | 170,000   | 210,000   | 240,000   | 215,000      | 240,000      |          |  |
| Arsenic   | 7440382         | 26.0     | 13.0      | < 5.0     | < 5.0     | 12.3         | 26.0         |          |  |
| Beryllium   | 7440417         | 2.20     | 1.70      | 2.00      | 2.20      | 2.03         | 2.20         |          |  |
| Iron  | 7439896         | 23.0     | < 5.0     | < 5.0     | 52.0      | 21.3         | 52.0         |          |  |
| Manganese   | 7439965         | < 1.5    | 4.70      | 6.50      | 6.90      | 4.90         | 6.90         |          |  |
| Sodium  | 7440235         | 2,200    | 2,000     | 8,000     | 7,700     | 4,975        | 8,000        |          |  |
| Zinc  | 7440666         | 23.0     | 33.0      | 40.0      | 39.0      | 33.8         | 40.0         |          |  |

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**Table 3.6.4. Alkylation Treating Clay Characterization (continued)**

| TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L |         |          |           |           |           |              |              |          |
|---|---------|----------|-----------|-----------|-----------|--------------|--------------|----------|
|   | CAS No. | R3-CA-01 | R15-CA-01 | R21-CA-01 | R23-CA-01 | Average Conc | Maximum Conc | Comments |
| Aluminum  | 7429905 | 5,300    | 1,300     | 4,100     | 4,100     | 3,700        | 5,300        |          |
| Beryllium   | 7440417 | 0.05     | < 0.025   | < 0.025   | < 0.025   | 0.031        | 0.050        |          |
| Iron  | 7439896 | 1.60     | < 0.50    | 1.10      | 1.00      | 1.05         | 1.60         |          |
| Manganese   | 7439965 | < 0.08   | < 0.08    | 0.18      | 0.17      | 0.13         | 0.18         |          |
| Zinc  | 7440666 | B 1.10   | B 0.60    | B 0.82    | B 0.85    | 0.84         | 1.10         |          |
| Miscellaneous Characterization  |         |          |           |           |           |              |              |          |
|   |         | R3-CA-01 | R15-CA-01 | R21-CA-01 | R23-CA-01 | Average Conc | Maximum Conc | Comments |
| Total Fluorine (mg/kg)  |         | 39,000   | 4,500     | NA        | NA        | 21,750       | 39,000       |          |

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.

At the Ponca City refinery, Conoco uses activated alumina in one of the alkylation units to extract fluorides from propane and butane products. In the process, activated alumina is converted to aluminum fluoride. Activated alumina reaches the end of its useful life when 60-80% of the material is converted to aluminum fluoride. That is when it become an additive for aluminum manufacturers.

During EPA's site visits, one facility used distillation to dry its feed to the HF acid alkylation unit. Most facilities use a molecular sieve treating clay for this step, therefore this process configuration eliminates the need for molecular sieve infrequently generating an RC.

Some refineries are experimenting with additives to the HF acid catalyst. The purpose of these additives is to reduce the risk from an accidental leak of HF acid to the atmosphere. Although the technology is principally developed in reaction to safety concerns, it is likely that such additives would be present in some of the study residuals such as acid soluble oil. The identity of those additives were not reported (*Oil and Gas Journal*, August 22, 1994).

### **3.6.4 Catalyst from Hydrofluoric Acid Alkylation**

#### **3.6.4.1 Description**

The consent decree which identifies the residuals to be examined in this study specified "catalyst from HF alkylation". However, the analysis used to identify the residuals of concern in the consent decree contained some flaws and erroneously identified this alkylation catalyst as being generated in significant quantities. Upon further review of the data used to characterize this residual (derived from EPA's 1983 survey of the petroleum refining industry), it was determined that several large volume residuals were inappropriately identified as spent catalyst and instead should have been classified as acid soluble oil (ASO). After adjusting the data to remove these mischaracterized residuals, the remaining residuals classified as spent HF catalyst accounted for small volumes which are on the order of magnitude observed in the Agency's 1992 data.

A residual of high molecular-weight reaction by-products dissolves in the HF acid catalyst and lowers its effectiveness. To maintain catalyst activity, a slip stream of HF acid is sent to an acid regenerator where distillations separates the HF acid from by-product contaminants, called acid soluble oil. The HF acid from the regenerators is recycled back to the reactor. Fresh acid is added to replace acid losses at a rate of about 500 pounds per day depending on unit capacity.

ASO is charged to a decanting vessel where an aqueous phase settles out. The aqueous phase, an azeotropic mixture of HF acid and water, is referred to as constant boiling mixture (CBM). CBM is charged to the neutralization tank which neutralize effluent to the WWTP. The neutralization sludge was examined in the listing proposal and Background Document. The effluent from the neutralization tanks are reported to go to the WWTP. The Agency has no data suggesting that it can be handled in any other way.

As stated above, HF acid is an extremely corrosive and toxic chemical. Refineries go to great lengths to protect their personnel from coming into direct contact with HF acid.

### 3.6.4.2 Generation and Management

The refineries reported generating approximately 152 MT of HF alkylation catalyst in 1992. Residuals were assigned to be “HF alkylation catalyst” if they were assigned a residual identification code of “liquid catalyst” and was generated from a process identified as an HF acid alkylation unit. This corresponds to residual code 03-B in Section VII.2 of the questionnaire and process code 09-B in Section IV-1.C of the questionnaire. Table 3.6.5 provides a description of the quantity generated, number of streams reported, and number of unreported volumes. Catalyst from HF alkylation includes spills and removed acid from the HF alkylation process.

**Table 3.6.5. Generation Statistics for Catalyst from HF Alkylation, 1992**

| Final Management  | # of Streams | # of Streams w/ Unreported Volume | Total Volume (MT) | Average Volume (MT) |
|-------------------|--------------|-----------------------------------|-------------------|---------------------|
| Discharge to WWTP | 3            | 0                                 | 151.94            | 50.65               |

### 3.6.4.3 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 3.6.5. No data were available to the Agency suggesting any other management practices.

### 3.6.4.4 Characterization

Only one source of residual characterization is available from the industry study, reflecting the fact that this residual is not generated for management:

- Table 3.6.6 summarizes the physical properties of the HF catalyst as reported in Section VII.A of the §3007 survey.

Due to the rareness of the generation of this residual, no samples of this residual were available for collection and analysis during record sampling.

**Table 3.6.6. Catalyst from HF Alkylation: Physical Properties**

| Properties            | # of Values | # of Unreported Values | 10th % | 50th % | 90th % |
|-----------------------|-------------|------------------------|--------|--------|--------|
| pH                    | 2           | 1                      | 2.00   | 2.00   | 2.00   |
| Vapor Pressure, mm Hg | 1           | 2                      | 775.00 | 775.00 | 775.00 |
| Specific Gravity      | 1           | 2                      | 1.00   | 1.00   | 1.00   |
| Aqueous Liquid, %     | 2           | 1                      | 0.00   | 0.00   | 0.00   |
| Organic Liquid, %     | 2           | 1                      | 0.00   | 0.00   | 0.00   |
| Solid, %              | 2           | 1                      | 0.00   | 0.00   | 0.00   |
| Other, %              | 2           | 1                      | 100.00 | 100.00 | 100.00 |

#### 3.6.4.5 Source Reduction

As described in the spent treating clay alkylation in Section 3.6.3.5, several solid-acid catalysts used for alkylation are being tested in pilot plants. The reactor systems are different from the current liquid-acid systems, but for one system the other equipment is compatible. Three types of the new solid catalyst include aluminum chloride, alumina/zirconium halide, and antimony pentafluoride (a slurry system).

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

### **3.6.5 Acid Soluble Oil from Hydrofluoric Acid Alkylation**

#### 3.6.5.1 Description

A residual of high molecular-weight reaction by-products dissolves in the HF acid catalyst and lowers its effectiveness. To maintain the catalyst activity, a slip stream of catalyst is distilled, leaving the by-product, acid soluble oil (ASO), as a residue. The ASO is charged to a decanting vessel where an aqueous phase settles out. The ASO is scrubbed with potassium hydroxide (KOH) to remove trace amounts of HF and is either recycled, sold as product (e.g., residual fuel), or burned in the unit's boiler. In some cases, the ASO from the regenerator is sent directly to the neutralization tanks. Effluent from the neutralization tanks is sent to the WWTP. Neutralization tank sludges were examined under the listing proposal and Background Document.

ASO is generated exclusively from the HF process. The sulfuric acid alkylation process does not generate ASO.

Eight residuals of ASO, accounting for 25 percent of this category's volume, was reported as being managed as either D001, D002, or D008.<sup>8</sup>

#### 3.6.5.2 Generation and Management

The refineries reported generating approximately 33,493 MT of ASO in 1992. Residuals were assigned to be "ASO" if they were assigned a residual identification code of "alkylation acid regeneration tars" and were generated from a process identified as an HF acid alkylation unit. This corresponds to residual code 08 in Section VII.1 and process code 09-B in Section IV-1.C of the questionnaire. Note that sludges generated from neutralization of acid soluble oil were examined under the proposal and the Background Document and are not included here. Table 3.6.7 provides a description of the quantity generated, number of streams reported, and number of unreported volumes.

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<sup>8</sup>These 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, transfer as a fuel, offsite incineration, etc.).

**Table 3.6.7. Generation Statistics for Acid Soluble Oil, 1992**

| <b>Final Management</b>  | <b># of Streams</b> | <b># of Streams w/ Unreported Volume</b> | <b>Total Volume (MT)</b> | <b>Average Volume (MT)</b> |
|--|---------------------|--|--------------------------|----------------------------|
| Discharge to onsite wastewater treatment facility                                    | 6                   | 0  | 4,858.8                  | 809.8                      |
| Neutralization   | 15                  | 14                                       | 11,387.9                 | 759.2                      |
| Offsite incineration   | 2                   | 0  | 0.2                      | 0.1                        |
| Onsite boiler  | 3                   | 0  | 2,610.3                  | 870.1                      |
| Onsite industrial furnace  | 10                  | 1  | 3,274                    | 327.4                      |
| Other recovery onsite: alkylation or hydrotreating/ hydrorefining process or unknown | 3                   | 1  | 2,180                    | 726.7                      |
| Recovery onsite in a catalytic coker   | 5                   | 0  | 3,641.3                  | 728.3                      |
| Recovery onsite in a coker   | 1                   | 0  | 1,019                    | 1,019                      |
| Recovery onsite via distillation   | 2                   | 3  | 50                       | 25                         |
| Transfer for direct use as a fuel or to make a fuel                                  | 2                   | 0  | 740.6                    | 370.3                      |
| Transfer with coke product or other refinery product                                 | 4                   | 1  | 3,731                    | 932.8                      |
| <b>TOTAL</b>   | <b>53</b>           | <b>20</b>                                | <b>33,493</b>            | <b>631.9</b>               |

### 3.6.5.3 Plausible Management

EPA believes that most of the plausible management practices for this residual were reported in the 1992 RCRA §3007 Survey, as summarized in Table 3.6.7. The Agency gathered information suggesting that “disposal in industrial Subtitle D landfill” (1 MT) was used in other years. Upon closer examination of this residual, EPA determined that the facility neutralized its ASO and landfilled the sludge. This management practice is consistent with the practices reported above.

### 3.6.5.4 Characterization

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

- Table 3.6.8 summarizes the physical properties of the ASO as reported in Section VII.A of the §3007 survey.
- Four record samples of actual ASO were collected and analyzed by EPA. The ASO represent the various types of interim management practices typically used by the industry (i.e., with and without neutralization) and are summarized in Table 3.6.9.

The four record samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals, as well as ignitability. Three of the samples were found to exhibit the hazardous waste characteristic of ignitability. A summary of the results is presented in Table 3.6.10. Only constituents detected in at least one sample are shown in this table.

**Table 3.6.8. Acid Soluble Oil: Physical Properties**

| Properties                       | # of Values | # of Unreported Values <sup>1</sup> | 10th % | 50th %    | 90th %    |
|----------------------------------|-------------|-------------------------------------|--------|-----------|-----------|
| pH                               | 30          | 59                                  | 2.00   | 6.50      | 10.75     |
| Reactive CN, ppm                 | 12          | 77                                  | 0.00   | 0.13      | 50.00     |
| Reactive S, ppm                  | 14          | 75                                  | 0.00   | 5.00      | 200.00    |
| Flash Point, °C                  | 27          | 62                                  | 25.00  | 60.00     | 93.33     |
| Oil and Grease, vol%             | 26          | 63                                  | 15.00  | 90.00     | 100.00    |
| Total Organic Carbon, vol%       | 16          | 73                                  | 30.00  | 77.00     | 100.00    |
| Vapor Pressure, mm Hg            | 10          | 79                                  | 3.00   | 135.00    | 575.00    |
| Vapor Pressure Temperature, °C   | 9           | 80                                  | 20.00  | 25.00     | 38.00     |
| Viscosity, lb/ft-sec             | 11          | 78                                  | 0.00   | 0.01      | 0.40      |
| Viscosity Temperature, °C        | 6           | 83                                  | 15.00  | 17.50     | 37.80     |
| Specific Gravity                 | 34          | 55                                  | 0.80   | 0.90      | 1.00      |
| Specific Gravity Temperature, °C | 12          | 77                                  | 15.00  | 15.00     | 15.60     |
| BTU Content, BTU/lb              | 15          | 74                                  | 750.00 | 15,000.00 | 19,000.00 |
| Aqueous Liquid, %                | 47          | 42                                  | 0.00   | 10.00     | 75.00     |
| Organic Liquid, %                | 56          | 33                                  | 50.00  | 98.00     | 100.00    |
| Solid, %                         | 32          | 57                                  | 0.00   | 0.00      | 30.00     |
| Other, %                         | 27          | 62                                  | 0.00   | 0.00      | 0.05      |

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

**Table 3.6.9. Acid Soluble Oil Record Sampling Locations**

| Sample Number | Location                | Description                                       |
|---------------|-------------------------|---|
| R3-AS-01      | Exxon, Billings, MT     | Un-neutralized separator drum sample              |
| R5B-AS-01     | Marathon, Garyville, LA | Acid regenerator settler bottoms, not neutralized |
| R15-AS-01     | Total, Ardmore, OK      | Neutralized, skimmed from pit                     |
| R7C-AS-01     | BP, Belle Chasse, LA    | Neutralized from storage tank                     |

### 3.6.5.5 Source Reduction

As described in previous sections, several solid-acid catalysts used for alkylation are being tested in pilot plants. The reactor systems are different from the current liquid-acid systems, but for one system the other equipment is compatible. Three types of the new solid catalyst include aluminum chloride, alumina/zirconium halide, and antimony pentafluoride (a slurry system).

It is likely that ASO will not be generated in a solid catalyst system.

**Table 3.6.10. Acid Soluble Oil Characterization**

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| Volatile Organics - Method 8260A µg/L                |                 |           |           |           | (µg/kg)      |              | Average Conc | Maximum Conc | Comments |
|--|-----------------|-----------|-----------|-----------|--------------|--------------|--------------|--------------|----------|
| CAS No.  | R3-AS-01        | R5B-AS-01 | R7C-AS-01 | R15-AS-01 |              |              |              |              |          |
| Acetone  | 67641           | 49,000    | < 625     | B 40,000  | 3,000        | 23,156       | 49,000       |              |          |
| Acrolein   | 107028          | < 6250    | < 625     | 25,000    | < 1,250      | 8,281        | 25,000       |              |          |
| Benzene  | 71432           | < 6250    | < 625     | 30,000    | < 1,250      | 9,531        | 30,000       |              |          |
| n-Butylbenzene                                       | 104518          | < 6250    | < 625     | J 9,500   | < 1,250      | 4,406        | 9,500        |              |          |
| sec-Butylbenzene                                     | 135988          | < 6250    | < 625     | J 2,600   | J 488        | 1,238        | 2,600        | 1            |          |
| tert-Butylbenzene                                    | 98066           | < 6250    | < 625     | J 7,200   | J 1,350      | 3,856        | 7,200        |              |          |
| Carbon disulfide                                     | 75150           | < 6250    | < 625     | J 1,800   | < 1,250      | 1,225        | 1,800        | 1            |          |
| trans-1,3-Dichloropropene                            | 10061026        | < 6250    | < 625     | J 1,600   | < 1,250      | 1,158        | 1,600        | 1            |          |
| Ethylbenzene   | 100414          | < 6250    | < 625     | 37,000    | < 1,250      | 11,281       | 37,000       |              |          |
| Isopropylbenzene                                     | 98828           | < 6250    | < 625     | J 3,100   | < 1,250      | 1,658        | 3,100        | 1            |          |
| p-Isopropyltoluene                                   | 99876           | < 6250    | < 625     | J 6,600   | < 1,250      | 3,681        | 6,600        |              |          |
| Methyl ethyl ketone                                  | 78933           | < 6250    | < 625     | 27,000    | < 1,250      | 8,781        | 27,000       |              |          |
| 4-Methyl-2-pentanone                                 | 108101          | < 6250    | < 625     | 26,000    | < 1,250      | 8,531        | 26,000       |              |          |
| n-Propylbenzene                                      | 103651          | < 6250    | < 625     | J 8,200   | < 1,250      | 4,081        | 8,200        |              |          |
| Toluene  | 108883          | < 6250    | < 625     | 41,000    | < 1,250      | 12,281       | 41,000       |              |          |
| 1,2,4-Trimethylbenzene                               | 95636           | 18,000    | 7,400     | 110,000   | 3,300        | 34,675       | 110,000      |              |          |
| 1,3,5-Trimethylbenzene                               | 108678          | < 6250    | < 625     | 27,000    | J 1,260      | 8,784        | 27,000       |              |          |
| o-Xylene   | 95476           | < 6250    | < 625     | 20,000    | < 1,250      | 7,031        | 20,000       |              |          |
| m,p-Xylenes  | 108383 / 106423 | 16,000    | 2,100     | 55,000    | < 1,250      | 18,588       | 55,000       |              |          |
| Naphthalene  | 91203           | < 6250    | < 625     | 30,000    | < 1,250      | 9,531        | 30,000       |              |          |
| TCLP Volatile Organics - Methods 1311 and 8260A µg/L |                 |           |           |           |              |              |              |              |          |
| CAS No.  | R3-AS-01        | R5B-AS-01 | R7C-AS-01 | R15-AS-01 | Average Conc | Maximum Conc | Comments     |              |          |
| Acetone  | 67641           | NA        | NA        | B 350     | 350          | 350          |              |              |          |
| Isopropylbenzene                                     | 98828           | NA        | NA        | J 32      | 32           | 32           |              |              |          |
| Methyl ethyl ketone                                  | 78933           | NA        | NA        | J 80      | 80           | 80           |              |              |          |
| Semivolatile Organics - Method 8270B µg/L            |                 |           |           |           | (µg/kg)      |              | Average Conc | Maximum Conc | Comments |
| CAS No   | R3-AS-01        | R5B-AS-01 | R7C-AS-01 | R15-AS-01 |              |              |              |              |          |
| Methyl ethyl ketone                                  | 78933           | NA        | NA        | NA        | J 80         | 80           | 80           |              |          |
| 1-Methylnaphthalene                                  | 90120           | < 250,000 | < 46,000  | 100,000   | < 12,375     | 73,000       | 100,000      | 1            |          |
| 2-Methylnaphthalene                                  | 91576           | < 250,000 | < 46,000  | 180,000   | < 12,375     | 113,000      | 180,000      | 1            |          |
| Naphthalene  | 91203           | < 250,000 | < 46,000  | 79,000    | < 12,375     | 62,500       | 79,000       | 1            |          |
| 2-Methylnaphthalene                                  | 91576           | < 250,000 | < 46,000  | 180,000   | < 12,375     | 113,000      | 180,000      | 1            |          |
| Naphthalene  | 91203           | < 250,000 | < 46,000  | 79,000    | < 12,375     | 62,500       | 79,000       | 1            |          |

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**Table 3.6.10. Acid Soluble Oil Characterization (continued)**

| TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L                |         |          |           |           |             |              |              |          |
|---|---------|----------|-----------|-----------|-------------|--------------|--------------|----------|
|   | CAS No. | R3-AS-01 | R5B-AS-01 | R7C-AS-01 | R15-AS-01   | Average Conc | Maximum Conc | Comments |
| Aniline   | 62553   | NA       | NA        | NA        | J 20        | 20           | 20           |          |
| Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg     |         |          |           |           |             | (mg/kg)      |              |          |
|   | CAS No. | R3-AS-01 | R5B-AS-01 | R7C-AS-01 | R15-AS-01   | Average Conc | Maximum Conc | Comments |
| Aluminum  | 7429905 | < 0.10   | < 0.10    | < 0.10    | 290         | NA           | NA           |          |
| Calcium   | 7440702 | < 2.50   | < 2.50    | < 2.50    | 29,000      | NA           | NA           |          |
| Copper  | 7440508 | 1.00     | < 0.13    | < 0.13    | 37.0        | 0.42         | 1.00         |          |
| Iron  | 7439896 | < 0.50   | < 0.50    | < 0.50    | 120         | NA           | NA           |          |
| Lead  | 7439921 | 0.64     | < 0.015   | < 0.015   | < 0.30      | 0.22         | 0.64         |          |
| Manganese   | 7439965 | < 0.015  | < 0.015   | < 0.015   | 5.00        | NA           | NA           |          |
| Mercury   | 7439976 | < 0.01   | 0.022     | < 0.01    | < 0.05      | 0.014        | 0.022        |          |
| Nickel  | 7440020 | < 0.04   | < 0.04    | < 0.04    | 15.0        | NA           | NA           |          |
| Potassium   | 7440097 | < 2.50   | < 2.50    | < 2.50    | 5,900       | NA           | NA           |          |
| Sodium  | 7440235 | < 2.50   | < 2.50    | < 2.50    | 1,300       | NA           | NA           |          |
| Zinc  | 7440666 | 0.27     | < 0.10    | < 0.10    | < 2.00      | 0.16         | 0.27         |          |
| TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L |         |          |           |           |             |              |              |          |
|   | CAS No. | R3-AS-01 | R5B-AS-01 | R7C-AS-01 | R15-AS-01   | Average Conc | Maximum Conc | Comments |
| Potassium   | 7440097 | NA       | NA        | NA        | 140         | 140          | 140          |          |
| Zinc  | 7440666 | NA       | NA        | NA        | B 0.24      | 0.24         | 0.24         |          |
| Miscellaneous Characterization  |         |          |           |           |             |              |              |          |
|   |         | R3-AS-01 | R5B-AS-01 | R7C-AS-01 | R15-AS-01   | Average Conc | Maximum Conc | Comments |
| Total Fluorine (mg/L)   |         | 450      | 110       | 19.0      | 9,300 mg/kg | 193          | 450          |          |
| Ignitability (oF)   |         | 132      | 57        | 97        | > 158       | NA           | NA           |          |
| Corrosivity (pH)  |         | 3        | 5         | 7         | 10.8        | NA           | NA           |          |
| Heat of Combustion ( BTU/lb )   |         | 18,700   | 19,245    | 19,000    | 14,000      | 17,736       | 19,245       |          |

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.

## 3.7 POLYMERIZATION

Polymerization is a process utilized for the conversion of propane/propylene and/or butane/butene feeds from other operations into a low molecular weight, higher-octane, polymer product, referred to as dimate. Dimate is used as a high octane gasoline blending component of unleaded gasolines.

Almost 12 percent of the industry's polymerization catalyst (Dimersol and phosphoric acid) volume was reported to be managed as a hazardous waste ("as hazardous", D002 and D007).<sup>9</sup>

### 3.7.1 Process Descriptions

There are primarily two polymerization processes utilized by the petroleum refining industry: phosphoric acid polymerization and the Dimersol process, licensed by IFP (Institute Francais du Petrole, or the French Petroleum Institute). Process descriptions for each of these two processes are provided in the following sections.

#### 3.7.1.1 Phosphoric Acid Polymerization

Phosphoric acid polymerization units produce marginal octane gasoline from propylene feeds from other operating units (i.e., the FCC unit, coking, etc). Phosphoric acid polymerization is more widely used by industry than the Dimersol process, representing 80 percent of all polymerization units in the United States. Phosphoric acid polymerization unit capacities range from 400 to 8,000 barrels per stream day, with the majority of units ranging between 2,200 and 3,000 barrels per stream day (as reported in the §3007 survey).

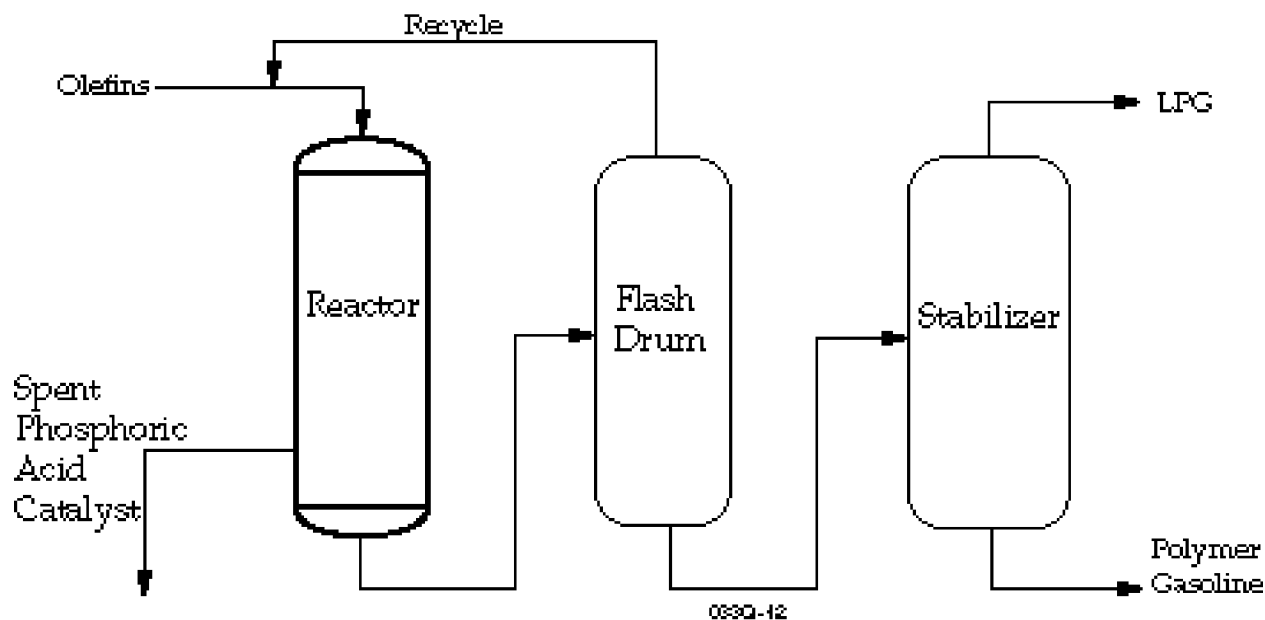
Phosphoric acid polymerization utilizes a catalyst consisting of an alumina substrate impregnated with phosphoric acid. A typical phosphoric acid polymerization unit contains one or more reactors consisting of a series of tubes coming off of a single header. The reactor feed is charged to the header and flows through the tubes. The tubes are packed with the phosphoric acid catalyst. The reaction conditions are controlled to stop the polymerization at the desired C6 or C9 product. The polymerization reaction is highly exothermic and boiler feed water is fed through the reactor (on the shell side of the tubes) to recover the heat for use as steam. Over time, the catalyst's acid sites become blocked and the catalyst is slated for change-out.

After leaving the reactor, the reactor effluent is fractionated to give the desired products. A simplified process flow diagram for a typical phosphoric acid polymerization unit is shown in Figure 3.7.1.

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<sup>9</sup>These 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, recovery in coker, etc.).

**Figure 3.7.1. Process Flow Diagram for Phosphoric Acid Polymerization Process**



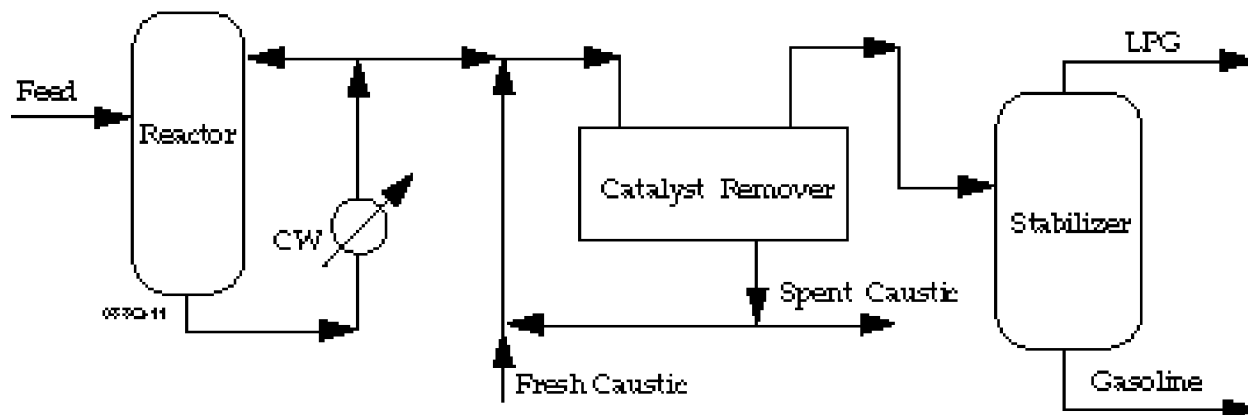
### 3.7.1.2 Dimersol Polymerization

As stated above, Dimersol polymerization units represent only 20 percent of the existing polymerization units in the United States. The capacity of Dimersol units range from 1,000 to 5,500 barrels per stream day, with an average capacity of approximately 3,200 barrels per stream day (as reported in the §3007 survey).

The Dimersol process is used to dimerize light olefins such as ethylene, propylene and butylene. The process typically begins with the pretreatment of the propane/propylene or butane/butene feed prior to entering the reactor section of the process. Pretreatment can include the use of molecular sieve dryers, sand filters, etc. to remove water and/or H<sub>2</sub>S. Water in the feed stream can deactivate the catalysts used in the Dimersol process. After drying the feed is combined with a liquid nickel carboxylate/ethyl aluminum dichloride (EADC) catalyst prior to entering the first of a series of three reactors. The first two are continuous stirred batch reactors and the third is a plug-flow tubular reactor. The reactor feed is converted to the process product, dimate, primarily in the first reactor, and additional conversion is achieved in the last two reactors. The final reactor effluent consists of dimate product, unreacted C<sub>3</sub>/C<sub>4</sub>s, and liquid catalyst. Immediately following the last reactor, the liquid catalyst is removed from the reactor effluent by treating the reactor effluent with caustic, subsequent water washing, and filtering to remove solids. Spent caustic residuals are typically reused or reclaimed on- or off-site, and as a result, do not constitute solid wastes. After filtering, the product stream enters a “Dimersol stabilizer,” a distillation unit that removes unreacted LPG from the dimate product. In some cases, the product stream is also further treated by drying. LPG from the stabilizer overhead is typically sent to another unit of the refinery for further processing. The dimate product from the bottom of the stabilizer is sent to storage or product blending.

A simplified process flow diagram for a typical Dimersol polymerization unit is shown in Figure 3.7.2.

**Figure 3.7.2. Dimersol Polymerization Process Flow Diagram**



### 3.7.2 Spent Phosphoric Acid Polymerization Catalyst

#### 3.7.2.1 Description

Spent phosphoric acid polymerization catalyst is generated after the solid catalyst active sites have become blocked and lost their reactivity.

#### 3.7.2.2 Generation and Management

During reactor change-outs, spent phosphoric acid catalysts are flushed or water drilled from the shell-and-tube reactors.

Twenty-two facilities reported generating a total quantity of 3,358 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be “spent phosphoric acid polymerization catalyst” if they were assigned a residual identification code of “spent solid catalyst” or “spent catalyst fines” and were generated from a process identified as a phosphoric acid polymerization unit. These correspond to residual codes 03-A and 03-B in Section VII.2 of the questionnaire and process code 11-A in Section IV-1.C of the questionnaire. Quality assurance was conducted by ensuring that all phosphoric acid polymerization catalysts previously identified in the questionnaire (i.e., in Section V.B) were assigned in Section VII.2.

Based on the results of the questionnaire, 25 facilities use phosphoric acid polymerization units and are thus likely to generate spent phosphoric acid polymerization catalyst. Due to the infrequent generation of this residual, not all of these 25 facilities generated spent catalyst 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 3.7.1 provides a description of the quantity generated, number of streams reported, number of streams not reporting volumes (data requested was unavailable and facilities were not required to generate it), total and average volumes.

**Table 3.7.1. Generation Statistics for Phosphoric Acid Catalyst from Polymerization, 1992**

| <b>Final Management</b>  | <b># of Streams</b> | <b># of Streams w/ Unreported Volume</b> | <b>Total Volume (MT)</b> | <b>Average Volume (MT)</b> |
|--|---------------------|--|--------------------------|----------------------------|
| Disposal in offsite Subtitle D landfill                          | 12                  | 0  | 1,429.5                  | 119                        |
| Disposal in offsite Subtitle C landfill                          | 3                   | 0  | 62                       | 20.7                       |
| Disposal in onsite Subtitle C landfill                           | 2                   | 0  | 349                      | 174.5                      |
| Disposal in onsite Subtitle D landfill                           | 6                   | 0  | 246.8                    | 41                         |
| Onsite land treatment  | 3                   | 0  | 728                      | 242.7                      |
| Transfer for use as an ingredient in products placed on the land | 7                   | 0  | 542.5                    | 77.5                       |
| <b>TOTAL</b>   | <b>33</b>           | <b>0</b>                                 | <b>3357.8</b>            | <b>101.7</b>               |

3.7.2.3 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 3.7.1. No data were available to the Agency suggesting any other management practices.

3.7.2.4 Characterization

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

- Table 3.7.2 summarizes the physical properties of the spent catalyst as reported in Section VII.A of the §3007 survey.
- One record sample of phosphoric acid polymerization catalyst was collected and analyzed by EPA. The sample is representative of typical phosphoric acid polymerization catalyst used by the industry and is summarized in Table 3.7.3.

The record sample was analyzed for total and TCLP levels of volatiles, semivolatiles, and metals, reactivity (pyrophoricity) and corrosivity. The sample was found to exhibit the hazardous waste characteristic of corrosivity. Dimersol and phosphoric acid catalysts were categorized together in the consent decree, therefore, a summary of the results for both residuals is presented in Table 3.7.7. Only constituents detected in at least one sample are shown in this table.

**Table 3.7.2. Phosphoric Acid Catalyst from Polymerization: Physical Properties**

| Properties                        | # of Values | # of Unreported Values <sup>1</sup> | 10th % | 50th % | 90th % |
|-----------------------------------|-------------|-------------------------------------|--------|--------|--------|
| pH                                | 21          | 21                                  | 1.4    | 4.7    | 7      |
| Reactive CN, ppm                  | 12          | 30                                  | 0.01   | 7      | 40     |
| Reactive S, ppm                   | 12          | 30                                  | 1      | 10     | 40     |
| Flash Point, °C                   | 14          | 28                                  | 60     | 93.3   | 200    |
| Oil and Grease, vol%              | 16          | 26                                  | 0      | 0      | 25.5   |
| Total Organic Carbon, vol%        | 15          | 27                                  | 0      | 0      | 16.6   |
| Specific Gravity                  | 20          | 22                                  | 0.85   | 0.96   | 1.4    |
| Aqueous Liquid, %                 | 29          | 13                                  | 0      | 0      | 50     |
| Organic Liquid, %                 | 28          | 14                                  | 0      | 0      | 1      |
| Solid, %                          | 35          | 7                                   | 50     | 100    | 100    |
| Particle >60 mm, %                | 16          | 26                                  | 0      | 0      | 0      |
| Particle 1-60 mm, %               | 17          | 25                                  | 0      | 95     | 95     |
| Particle 100 µm-1 mm, %           | 16          | 26                                  | 0      | 5      | 5      |
| Particle 10-100 µm, %             | 16          | 26                                  | 0      | 0      | 100    |
| Particle <10 µm, %                | 16          | 26                                  | 0      | 0      | 0      |
| Median Particle Diameter, microns | 10          | 31                                  | 5030   | 12,000 | 12,000 |

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

**Table 3.7.3. Phosphoric Acid Polymerization Catalyst Record Sampling Locations**

| Sample Number | Location           | Description              |
|---------------|--------------------|--------------------------|
| R16-PC-01     | Koch, St. Paul, MN | Phosphoric acid catalyst |

### 3.7.2.5 Source Reduction

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

### 3.7.3 Spent Dimersol Polymerization Catalyst

#### 3.7.3.1 Description

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

#### 3.7.3.2 Generation and Management

Dimersol catalysts are generated as solid wastes in the form of reactor sludges generated during reactor clean-outs and as spent nickel filters.

Four facilities reported generating a total quantity of 761.5 MT of this residual as a reactor sludge in 1992, according to the 1992 RCRA §3007 Survey. Residuals were assigned to be “spent dimersol catalyst” if they were assigned a residual identification code of “spent solid catalyst” or “spent catalyst fines” or “other process sludge” and were generated from a process identified as a Dimersol polymerization unit. These correspond to residual codes “03-A,” “03-B” and “02-D” in Section VII.2 and process code “11-B” in Section IV-1.C of the questionnaire. Quality assurance was conducted by ensuring that all dimersol catalysts previously identified in the questionnaire (i.e., in Section V.B) were assigned in Section VII.2.

Based on the results of the survey, 7 facilities use Dimersol polymerization units and may generate spent dimersol catalyst. Due to the continuous generation of this residual, 1992 is expected to be a typical year in regard to catalyst generation volume and management. There was no reason to expect that 1992 would not be a typical year with regard to this residual's generation and management. Table 3.7.4 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.

#### 3.7.3.3 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 3.7.4. No data were available to the Agency suggesting any other management practices. Unlike with phosphoric acid polymerization catalyst, EPA does not expect spent Dimersol catalyst to be land treated due to the physical nature of the filters.

**Table 3.7.4. Generation Statistics for Spent Dimersol Polymerization Catalyst, 1992**

| Final Management                     | # of Streams | # of Streams w/ Unreported Volume | Total Volume (MT) | Average Volume (MT) |
|--------------------------------------|--------------|-----------------------------------|-------------------|---------------------|
| Disposal Offsite Subtitle C Landfill | 1            | 0                                 | 3.4               | 3.4                 |
| Disposal Onsite Subtitle D Landfill  | 1            | 0                                 | 8.8               | 8.8                 |
| Offsite incineration                 | 1            | 1                                 | 0.3               | 0.3                 |
| Recover onsite in a coker            | 1            | 0                                 | 749               | 749                 |
| TOTAL                                | 4            | 1                                 | 761.5             | 190.4               |

#### 3.7.3.4 Characterization

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

- Table 3.7.5 summarizes the physical properties of the spent catalyst as reported in Section VII.A of the §3007 survey.
- Two record samples of Dimersol polymerization catalyst were collected and analyzed by EPA. The samples represent typical Dimersol polymerization catalyst used by the industry and are summarized in Table 3.7.6.

The two record samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals, and pyrophoricity and corrosivity. None of the samples were found to exhibit a hazardous waste characteristic. Dimersol and phosphoric acid catalysts were categorized together in the consent decree, therefore, a summary of the results for both residuals is presented in Table 3.7.7. Only constituents detected in at least one sample are shown in this table.

#### 3.7.3.5 Source Reduction

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



**Table 3.7.5. Spent Dimersol Polymerization Catalyst Physical Properties**

| Properties                 | # of Values | # of Unreported Values <sup>1</sup> | 10th % | Mean | 90th % |
|----------------------------|-------------|-------------------------------------|--------|------|--------|
| pH                         | 7           | 4                                   | 3.8    | 5.5  | 9      |
| Flash Point, C             | 4           | 7                                   | 93.3   | 93.3 | 100    |
| Oil and Grease, vol%       | 3           | 8                                   | 2.6    | 5.3  | 6.4    |
| Total Organic Carbon, vol% | 3           | 8                                   | 0.08   | 4.1  | 9.5    |
| Specific Gravity           | 6           | 5                                   | 0.7    | 1.2  | 1.4    |
| Aqueous Liquid, %          | 11          | 0                                   | 0      | 0    | 70     |
| Organic Liquid, %          | 11          | 0                                   | 0      | 0    | 60     |
| Solid, %                   | 11          | 0                                   | 20     | 100  | 100    |

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

**Table 3.7.6. Dimersol Polymerization Catalyst Record Sampling Locations**

| Sample Number | Location           | Description     |
|---------------|--------------------|-----------------|
| R6B-PC-01     | Shell, Norco, LA   | Dimersol filter |
| R16-PC-02     | Koch, St. Paul, MN | Dimersol filter |

**Table 3.7.7. Polymerization Catalyst Characterization**

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| Volatile Organics - Method 8260A µg/kg                   |                 |           |       |           |       |           |     |              |              |          |
|--|-----------------|-----------|-------|-----------|-------|-----------|-----|--------------|--------------|----------|
|  | CAS No.         | R6B-PC-01 |       | R16-PC-01 |       | R16-PC-02 |     | Average Conc | Maximum Conc | Comments |
| Ethylbenzene   | 100414          | <         | 25    | J         | 92    | <         | 625 | 59           | 92           | 1        |
| Isopropylbenzene   | 98828           | <         | 25    | J         | 350   | <         | 625 | 188          | 350          | 1        |
| Naphthalene  | 91203           |           | 58    | <         | 250   | <         | 625 | 58           | 58           | 1        |
| Toluene  | 108883          | <         | 25    | J         | 130   | <         | 625 | 78           | 130          | 1        |
| 1,2,4-Trimethylbenzene                                   | 95636           | <         | 25    | J         | 91    | <         | 625 | 58           | 91           | 1        |
| 1,3,5-Trimethylbenzene                                   | 108678          | <         | 25    | J         | 91    | <         | 625 | 58           | 91           | 1        |
| m,p-Xylenes  | 108383 / 106423 | <         | 25    | J         | 120   | <         | 625 | 73           | 120          | 1        |
| TCLP Volatile Organics - Methods 1311 and 8260A µg/L     |                 |           |       |           |       |           |     |              |              |          |
|  | CAS No.         | R6B-PC-01 |       | R16-PC-01 |       | R16-PC-02 |     | Average Conc | Maximum Conc | Comments |
| None Detected  | NA              |           | NA    |           | NA    |           | NA  |              | NA           |          |
| Semivolatile Organics - Method 8270B µg/kg               |                 |           |       |           |       |           |     |              |              |          |
|  | CAS No.         | R6B-PC-01 |       | R16-PC-01 |       | R16-PC-02 |     | Average Conc | Maximum Conc | Comments |
| Acenaphthene   | 83329           | <         | 2,063 | J         | 360   | <         | 165 | 263          | 360          | 1        |
| Anthracene   | 120127          | <         | 2,063 | J         | 300   | <         | 165 | 233          | 300          | 1        |
| Benz(a)anthracene  | 56553           | <         | 2,063 |           | 990   | <         | 165 | 578          | 990          | 1        |
| Bis(2-ethylhexyl) phthalate                              | 117817          | <         | 2,063 | <         | 413   |           | 630 | 521          | 630          | 1        |
| Di-n-butyl phthalate                                     | 84742           | <         | 2,063 | <         | 413   | J         | 77  | 77           | 77           | 1        |
| Chrysene   | 218019          | <         | 2,063 |           | 890   | <         | 165 | 528          | 890          | 1        |
| Dibenzofuran   | 132649          | <         | 2,063 | J         | 420   | <         | 165 | 293          | 420          | 1        |
| Fluoranthene   | 206440          | <         | 2,063 | J         | 210   | <         | 165 | 188          | 210          | 1        |
| Fluorene   | 86737           | <         | 2,063 |           | 1,300 | <         | 165 | 733          | 1,300        | 1        |
| 2-Methylchrysene   | 3351324         | <         | 4,125 | J         | 570   | <         | 330 | 450          | 570          | 1        |
| 1-Methylnaphthalene                                      | 90120           | <         | 4,125 |           | 1,800 | <         | 330 | 1,065        | 1,800        | 1        |
| 2-Methylnaphthalene                                      | 91576           | <         | 2,063 |           | 1,700 | <         | 165 | 933          | 1,700        | 1        |
| Phenanthrene   | 85018           | <         | 2,063 |           | 3,100 | <         | 165 | 1,776        | 3,100        | 1        |
| Pyrene   | 129000          | <         | 2,063 |           | 3,400 | <         | 165 | 1,876        | 3,400        | 1        |
| TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L |                 |           |       |           |       |           |     |              |              |          |
|  | CAS No.         | R6B-PC-01 |       | R16-PC-01 |       | R16-PC-02 |     | Average Conc | Maximum Conc | Comments |
| None Detected  | NA              |           | NA    |           | NA    |           | NA  |              | NA           |          |

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**Table 3.7.7. Polymerization Catalyst Characterization (continued)**

| Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg     |         |           |           |           |              |              |          |
|---|---------|-----------|-----------|-----------|--------------|--------------|----------|
|   | CAS No. | R6B-PC-01 | R16-PC-01 | R16-PC-02 | Average Conc | Maximum Conc | Comments |
| Aluminum  | 7429905 | 6,500     | 3,400     | 19,000    | 9,633        | 19,000       |          |
| Arsenic   | 7440382 | 210       | < 1.00    | 5.30      | 72.1         | 210          |          |
| Barium  | 7440393 | 2,600     | < 20.0    | 4,200     | 2,273        | 4,200        |          |
| Calcium   | 7440702 | 1,200     | 3,500     | < 500     | 1,733        | 3,500        |          |
| Chromium  | 7440473 | 2.70      | 33.0      | < 1.00    | 12.2         | 33.0         |          |
| Cobalt  | 7440484 | 15.0      | < 5.00    | < 5.00    | 8.33         | 15.0         |          |
| Copper  | 7440508 | 7.40      | 21.0      | 28.0      | 18.8         | 28.0         |          |
| Iron  | 7439896 | 1,300     | 4,200     | 500       | 2,000        | 4,200        |          |
| Lead  | 7439921 | 3.50      | 9.70      | 2.20      | 5.13         | 9.70         |          |
| Magnesium   | 7439954 | < 500     | 1,200     | < 500     | 733          | 1,200        |          |
| Manganese   | 7439965 | 13.0      | 57.0      | 15.0      | 28.3         | 57.0         |          |
| Mercury   | 7439976 | 0.10      | < 0.05    | < 0.05    | 0.07         | 0.10         |          |
| Nickel  | 7440020 | 9,600     | 52.0      | 75,000    | 28,217       | 75,000       |          |
| Potassium   | 7440097 | 1,100     | < 500     | < 500     | 700          | 1,100        |          |
| Sodium  | 7440235 | 13,000    | < 500     | 8,000     | 7,167        | 13,000       |          |
| Vanadium  | 7440622 | < 5.00    | 21.0      | < 5.00    | 10.3         | 21.0         |          |
| Zinc  | 7440666 | 1,700     | 1,400     | 3,000     | 2,033        | 3,000        |          |
| TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L |         |           |           |           |              |              |          |
|   | CAS No. | R6B-PC-01 | R16-PC-01 | R16-PC-02 | Average Conc | Maximum Conc | Comments |
| Arsenic   | 7440382 | 0.19      | NA        | < 0.05    | 0.12         | 0.19         |          |
| Barium  | 7440393 | < 1.00    | NA        | 36.0      | 18.5         | 36.0         |          |
| Nickel  | 7440020 | 160       | NA        | 67.0      | 114          | 160          |          |
| Zinc  | 7440666 | B 1.40    | NA        | B 4.90    | 3.15         | 4.90         |          |
| Miscellaneous Characterization  |         |           |           |           |              |              |          |
|   |         | R6B-PC-01 | R16-PC-01 | R16-PC-02 |              |              |          |
| Corrosivity (pH)  |         | NA        | < 1.0     | 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.