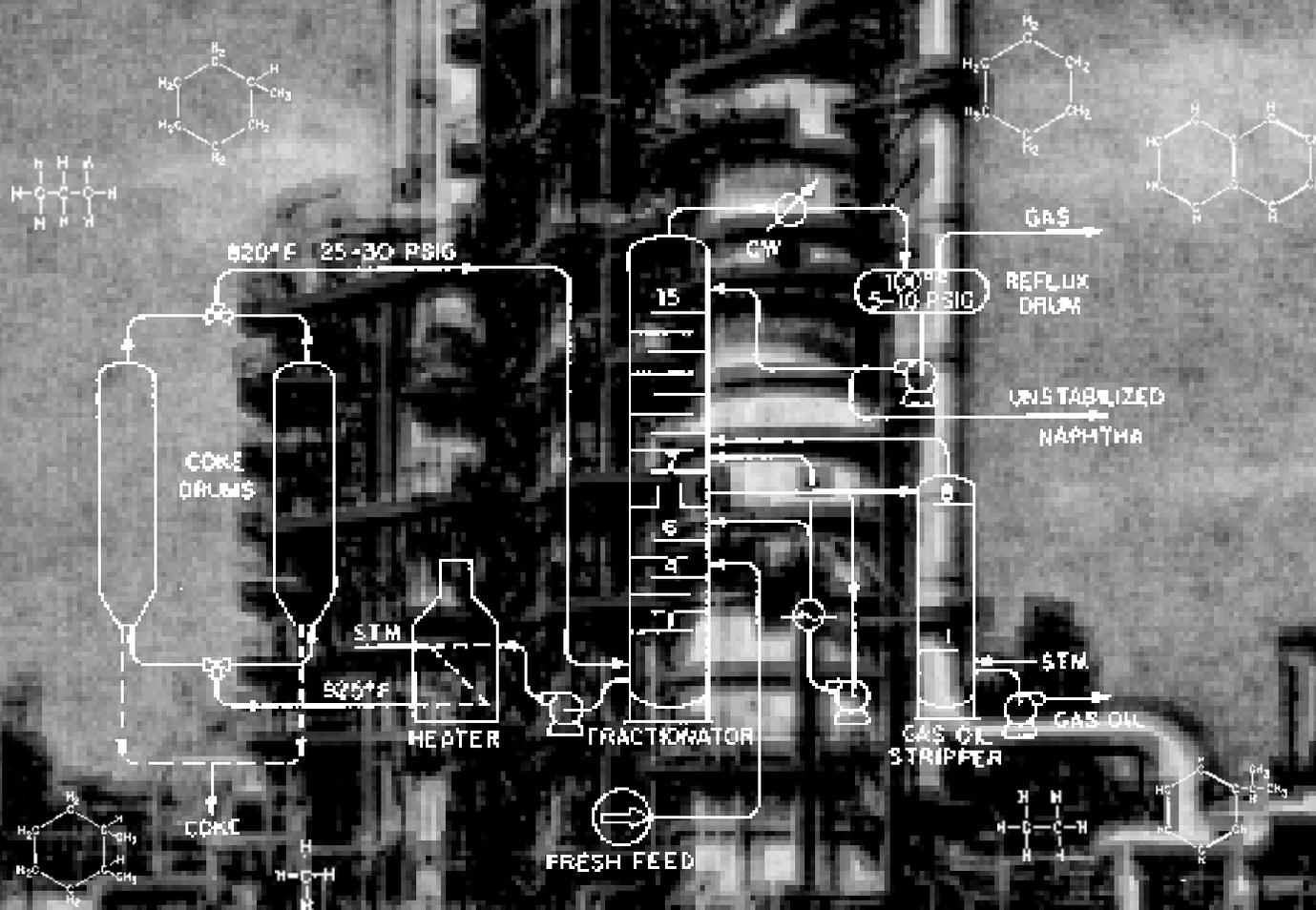




ASSESSMENT OF THE PETROLEUM INDUSTRY HAZARDOUS WASTE SOURCE REDUCTION PLANNING EFFORTS



Pete Wilson, Governor
State of California

James M. Strock, Secretary
California Environmental Protection Agency

Jesse R. Huff, Director
Department of Toxic Substances Control

California Environmental Protection Agency
Department of Toxic Substances Control

Office of Pollution Prevention and
Technology Development

June 1997

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Prepared by Arvind Shah

**California Environmental Protection Agency
Department of Toxic Substances Control
Office of Pollution Prevention and Technology Development**

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This report was prepared by Arvind Shah under the direction of Alan Ingham and Kim Wilhelm, Source Reduction Unit, Office of Pollution Prevention and Technology Development.

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DISCLAIMER

The mention of any products, companies or source reduction technologies, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products, companies or technologies.

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REPORT OVERVIEW

This report summarizes the results of the Department of Toxic Substances Control's (DTSC) second assessment of the California petroleum industry source reduction planning efforts. These efforts are mandated by the California Hazardous Waste Source Reduction and Management Review Act of 1989 (the Act or SB 14). The petroleum industry was previously evaluated following its response to the initial 1990-1994 source reduction planning cycle under the Act. During the review, DTSC examined a total of eighteen sets of petroleum industry 1991 source reduction planning documents and released the first "Assessment Of The Petroleum Industry Facility Planning Efforts" in December 1993.

This second assessment is based upon a review of 1995 documents prepared by twenty-four facilities. Many of the eighteen facilities participating in the initial 1991 industry review are among the twenty four 1995 documents reviewed. The source reduction documents prepared under the Act include information on the sources and types of hazardous waste generated and describe the source reduction steps taken to reduce the quantities or hazardous characteristics of generated waste. These documents also provide information on the progress made by 1) implementation of previously selected source reduction measures in 1991, and 2) any reduction achieved through recycling and treatment actions taken during the period 1991-1995. Three case studies are featured as practical examples showing how source reduction practices benefitting particular facilities can be implemented at other similar facilities.

The Act requires DTSC to select at least two categories of generators by the Standard Industrial Classification (SIC) code every two years for evaluation. This evaluation consists of reviewing documents prepared by facilities which are subject to the Act because of the quantity of hazardous waste generated at their sites (i.e. annual hazardous waste generation exceeding 12,000 kg. or 12 kg. of extremely hazardous waste). The Act requires hazardous waste generators to evaluate options for decreasing the quantity or the hazardous characteristics of hazardous waste routinely generated in their operations every four years.

The primary SIC code represented in this report is 2911 which generally represents all small and large petroleum refineries. To a lesser extent, other SIC codes presented in the report include 1311 and 1381, representing oil exploration facilities and storage and blending facilities.

A total of 73 facilities were requested to submit source reduction planning documents for evaluation. Twenty-four submitted their documents and reviews were completed for this report. Of the 49 companies not completing documents, one had closed its operations, one had sold part of its refinery to an other entity, and 47 were deemed not to be subject to the Act. In addition to reviewing 24 sets of source reduction planning documents, the DTSC staff visited some of these facilities to verify common source reduction process implementation details.

In 1994, the largest hazardous waste streams generated by the petroleum industry were: 1) hazardous aqueous waste streams entering the onsite waste water treatment plant; 2) oil/water separator sludge; 3) tank bottom waste; and 4) spent catalyst waste.

Section III of this "second assessment" report provides a comparison of 1990 versus 1994 waste generation and reduction data and discussion of hazardous waste streams and waste reduction measures. Section IV provides a concise summary of selected waste stream-specific source reduction measures identified by the twenty-four facilities for implementation by 1998. Section V presents three case studies which describe in detail the technical and cost benefits associated with implementing a variety of source reduction measures.

DTSC's second focus on petroleum industry documents provides an excellent opportunity to track waste reduction progress of California's largest hazardous waste generating industry. The Department's first focus in 1993 was based on the review of eighteen sets of 1991 source reduction documents. This review enabled the Department to project that the petroleum industry as a whole would reduce twenty percent of its hazardous waste by implementing more than 80 source reduction measures during the 1990-1994 SB 14 planning cycle. Actual data based on the twenty-four facilities participating in the second review based on 1995 Performance Reports, the petroleum industry indicates a 32% percent reduction of hazardous waste generation during the 1990-1994 period. This amounted to more than 61,000 tons annually. The above data reflect all hazardous wastes except aqueous hazardous waste treated in the onsite aqueous waste treatment plants. Aqueous hazardous waste quantity data and select aqueous waste source reduction measures detail are provided else where in this report.

With current hazardous waste disposal costs for petroleum waste ranging from \$125 to \$750 per ton, these reductions are estimated to have saved the petroleum industry \$7.6 to \$45.7 million annually. Based on our review of the latest documents (1995) produced under the Act DTSC projects that the industry will implement 122 measures during the 1994-1998 SB 14 planning cycle. Based on this review of the 1995 planning efforts, it is projected that the industry nonaqueous hazardous waste reduction can achieve an additional 31% (equivalent to more than 53,500 tons annually over the 61,000 tons reduced over the first 1990-1994 planning cycle) of hazardous waste reduction over the next several years. This projection amounts 53,500 additional tons annually reduced over the 61,000 tons annual reduction achieved during the initial SB 14 planning cycle (1990-1994). If fully achieved, this results in a total annual savings of \$6.7 to \$40.1 million.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

REPORT OVERVIEW

I.	BACKGROUND	5
II.	OVERVIEW OF REFINERY PROCESSES	9
III.	FINDINGS	11
IV.	SOURCE REDUCTION MEASURES	26
V.	CASE STUDIES	46
VI.	SUMMARY	61

APPENDICES

A.	Refinery Operation Description	63
B.	Selected Source Reduction Measures List	69
C.	Applicable California Waste Code (CWC) List	76
D.	Rejected Source Reduction Measures List	77
E.	Selected Source Reduction Measure Abstract - Examples	82

TABLES

1.	California Petroleum Industry's Nonaqueous Waste Reduction Efforts [1990 vs. 1994]	16
2.	California Petroleum Industry Four Year Hazardous Waste (Nonaqueous) Reduction Goal [1994 - 1998]	18
3.	California Petroleum Industry 1994 Source Reduction Measures For Nonaqueous Waste	20
4.	California Petroleum Industry 1994 Nonaqueous Hazardous Waste Streams	22
5.	California Petroleum Industry 1994 Aqueous Hazardous Waste Quantities And Projected Waste Reduction	24

I. BACKGROUND

The Hazardous Waste Source Reduction and Management Review Act of 1989 (the Act or SB 14) is codified in Health and Safety Code sections 25244.12 to 25244.24. This law applies to businesses that generated over 12,000 kilograms (13.2 tons) of hazardous waste, or 12 kilograms (26 pounds) of extremely hazardous waste, in 1990 and every four years thereafter. The law requires generators to prepare documents which reflect their efforts to identify, and then implement feasible methods for reducing the quantity and/or the hazardous characteristics of hazardous waste routinely generated in their operations. The first set of source reduction documents was due September 1, 1991. Documents are to be completed every four years thereafter, provided that the above threshold is exceeded in the "reporting year". The reporting year is the year which immediately precedes the year in which the documents are required to be completed. For example, the most recent SB 14 documents should have been completed by September 1, 1995, for waste generated in 1994 (the most recent reporting year).

To comply with SB 14, generators must prepare a Source Reduction Plan (Plan), a Management Performance Report (Report), summaries of the Plan and the Report, and a Progress Report. The Plan must include information about the facility's operations and provide waste generation data for the reporting year. The Plan must also include a list of potential source reduction measures for "major" waste streams that are routinely generated and describe the company's evaluation of the measures. Major waste streams are defined to be those waste streams that exceed five percent of the total weight of routinely-generated hazardous wastes.

Using specific criteria to evaluate a source reduction measure's feasibility, such as amount of reduction, technical feasibility, economic viability, and effect on workplace health and safety; the Plan must describe the rationale for selecting successful measures for implementation. The generator must then specify a timetable for implementing feasible source reduction options. Finally, the Plan must contain technical and financial certifications to ensure that the documents were prepared by a qualified person, and reviewed by an owner or operator who has the authority to commit financial resources necessary to implement the Plan.

The Management Performance Report (Report) discusses waste stream generation and management, and describes source reduction measures and other changes in waste management practices that have been made since the baseline year. As with the Plan, the Report must also contain technical and financial certification statements.

The purpose of the Progress Report is to track, on a biennial basis, the percentage of waste reduction achieved for the site's major waste streams, normalized to account for changes in throughput (or other relevant factor(s)). Companies subject to SB 14 satisfy the Progress Report requirement by using Form GM from their U.S. Environmental Protection Agency Biennial Hazardous Waste Report.

SB 14 requires DTSC to select at least two categories of generators by SIC code every two years and request that selected generators submit documents for review. The review process involves sending request letters to generators via certified mail. Upon receipt of the letter, generators have 30 days to send copies of their documents to DTSC. Once the documents are received, they are reviewed for completeness using checklists found in DTSC's "Hazardous Waste Source Reduction Guidance Manual". Following the completeness review, a comment letter is prepared and sent to the generator to inform of any revisions necessary to comply with the provisions of the Act. In cases where there are significant deficiencies or omissions, DTSC asks generators to revise and resubmit the documents.

In addition to monitoring compliance, a primary purpose of DTSC's review is to obtain and share information regarding successful source reduction measures. Information collected from the reviewed documents is disseminated through factsheets, presentations, and reports (such as this one) to generators having similar operations, and other interested parties.

DTSC selected the petroleum industry (primarily represented by SIC code 2911) as one of the targeted industrial categories for review during 1995. DTSC also selected the petroleum industry as one of the targeted industries during 1991 as well. The petroleum industry was chosen because it is one of the largest hazardous waste producers in the state. An initial list of companies within this classification was assembled during 1995 using a list provided by the Western States Petroleum Association (WSPA) and the American Petroleum Institute (API). DTSC's manifest tracking database was also used to check the records of petroleum companies listed in the California Manufacturers Register. The twenty-four facilities reviewed for this report represent most if not all of the petroleum facilities that are subject to SB 14.

Source reduction is given the highest preference in the hierarchy of preferred approaches in hazardous waste management. The purpose of planning and implementing a source reduction strategy is to minimize the generation of hazardous waste and thereby minimize the need to control it after generation. California's Health and Safety Code defines source reduction as:

- Any action which causes a net reduction in the generation of hazardous waste; or
- Any action taken before the hazardous waste is generated that results in lessening of the properties which cause it to be classified as hazardous.

Furthermore, the Act clearly states that source reduction does not include any actions taken after a hazardous waste is generated:

- Actions that merely concentrate the constituents of the waste to reduce its volume or that dilute the waste to reduce its hazardous characteristics.
- Actions that merely shift hazardous wastes from one environmental medium to another environmental medium.
- Treatment.

The primary purpose of this assessment report is to provide information regarding hazardous waste source reduction progress by petroleum industry facilities (sites). Due to the unique nature of the petroleum industry, where recycling can play a key waste reduction role, several effective waste minimization recycling measures have also been included in this report.

Finally, this report includes consideration of aqueous hazardous waste streams processed in a waste water treatment plant. For the initial documents prepared during the first cycle (September 1991), many of the petroleum industry generators did not address aqueous waste streams in their source reduction evaluation which were included in their current 1995 documents. SB 1133 was enacted September 5, 1991 and clarified the requirements for evaluating both aqueous and non aqueous waste streams. For 1995 documents, due September 1, 1995, generators are required to determine the total quantity of waste water generated, then conduct an additional calculation excluding the consideration of waste waters to determine the major non aqueous waste streams. The separate evaluation enables the source reduction review of non aqueous waste streams that would otherwise have been missed as "major" due to a large

quantity of aqueous wastes being present. Thus, SB 1133, 1991, enabled source reduction consideration of both aqueous and nonaqueous waste streams.

A major hazardous waste stream is further defined in Health and Safety Code Section 25244.19 (b) (3) as a hazardous waste which is routinely generated on an ongoing basis, exceeds five percent of the total yearly volume of hazardous waste, and may be either an aqueous waste stream as defined in (A) or a non aqueous waste stream as defined in (B) below.

- (A) It is a hazardous waste stream processed in a waste water treatment unit which discharges to a publicly owned treatment works or under a National Pollutant Discharge Elimination System (NPDES) permit as specified in the Federal Water Pollution Control Act, as amended (33 U.S.C. Section 1251 and following), and its weight before treatment exceeds five percent of the weight of the total yearly volume at the site.
- (B) It is hazardous waste stream which is not processed in a waste water treatment unit and its weight exceeds five percent of the weight of the total yearly volume at the site, less the weight of any hazardous waste stream identified in subparagraph (A).

II. OVERVIEW OF REFINERY PROCESSES

The petroleum industry is basically comprised of oil exploration and production, crude oil transportation, refineries, distribution terminals and marketing or retail outlets. The latter are typically small quantity generators and are not captured by SB 14.

Petroleum refinery operations are complex. Appendix A contains a more detailed description of some of the major refinery operations. These descriptions are taken from refinery source reduction documents. Refinery operations can be divided into four general categories:

- 1) Fuel production
- 2) By-product processing
- 3) Ancillary operations
- 4) Waste treatment

- 1) Fuel production encompasses those operations which manufacture petroleum products such as gasoline, jet fuel, diesel fuels, and petroleum coke. The following key processes are generally used to produce saleable petroleum products:
 - i) distillation
 - ii) hydrotreating,
 - iii) catalytic reforming and
 - iv) hydrocarbon cracking.
- 2) By-product processing covers refinery operations that process used materials and/or undesirable petroleum constituents into saleable or reusable end products. The following main processes are used for by-product processing:
 - i) sour water/gas processing,
 - ii) acid production and
 - iii) caustic production.
- 3) Ancillary operations are those activities which support refinery functions such as:
 - i) cogeneration of electricity and steam and
 - ii) water treatment to demineralize and soften municipal water before use in refinery operations.
- 4) Waste management activities include:
 - i) waste water treatment,
 - ii) oil recovery and
 - iii) solid and hazardous waste disposal.

The processes and operations of oil exploration and production companies are directed toward finding, producing, and selling crude oil and natural gas. The following are key activities:

- a) Drilling to find oil and natural gas;
- b) Lifting production fluids from subsurface reservoirs to the surface;
- c) Collecting the production fluids at central collection facilities;
- d) Cleaning and separating the crude oil and natural gas from most of the water, formation solids and other contaminants; and
- e) Transporting crude oil and natural gas through pipeline systems, by marine tanks or by trucks.

III. FINDINGS

This report's findings are presented in Table 1 through Table 5. The following discussion focuses on the findings displayed in each consecutive table.

Nonaqueous Waste Reduction Results 1990 versus 1994:

- This is the second source reduction assessment report for the petroleum industry. During first cycle, this industry - comprised of twenty-four sites - generated more than 192,000 tons of SB 14 applicable nonaqueous hazardous waste. These quantities are based on 1990 calendar year data determined from a review of the industry's 1995 Waste Management Performance Reports. Observed individual nonaqueous waste quantities ranged from 38 to 49,000 tons annually. During the 1994 calendar year (second cycle) the industry generated approximately 169,000 tons (see Table 2) of SB 14 applicable nonaqueous hazardous waste. This information was obtained from the 1995 Source Reduction Plans representing the industry's twenty-four sites affected by SB 14. Four out of the twenty-four sites increased their hazardous waste generation ranging from 28 to 283 tons (5 to 131 percent) from the 1990 calendar year to the 1994 calendar year. Unocal San Francisco attributed the increase in waste generation to an increase in the quantity of crude distillation; a normalization of data by production indicates that Unocal actually reduced its waste per unit of product.
- The comparison does not include the Chevron El Segundo site (among three other sites) because Chevron only reported waste disposal quantities for 1990 as opposed to waste generated quantities. The amount of disposal of major waste streams for this site decreased by approximately 45 percent from 1990 to 1994.
- In 1995, that portion of the petroleum industry affected by SB 14 projected its ultimate hazardous waste reduction to be 32 percent of that quantity generated by this industry in 1990. This reduction quantity will amount to more than 60,000 tons annually. These estimates do not include aqueous hazardous wastes treated onsite in waste water treatment plants. Aqueous hazardous waste quantity data detailed by those facilities generating aqueous waste are presented separately in this report.

Nonaqueous Waste Reduction Goal:

- Table 2 outlines nonaqueous hazardous waste data generated during calendar year 1994. It also shows individual site hazardous waste reduction goals for reducing wastes under optimal conditions for the four year period 1994-1998 and beyond.
- Hazardous waste generation during 1994 ranged individually from 66 tons to 41,000 tons, with an average generation of approximately 7,000 tons per site. The average hazardous waste reduction goal is 31 percent per site and accounts for a total of more than 2,200 tons for each of the twenty-four SB 14 sites annually.
- Eighteen out of the twenty-four sites reported their hazardous waste reduction goals ranged from 1 to 100 percent amounting from 7 to 17,000 tons for the next four years beginning in 1995. Powerine oil was in the process of dismantling its plant prior to selling it overseas; therefore this facility could not provide a hazardous waste reduction goal information.
- Twenty-four of the California petroleum sites collectively generated more than 169,000 tons of nonaqueous, SB 14 applicable hazardous waste. Based on the estimated goal specified by these facilities in their Plans, we project the industry collectively is capable, under ideal conditions, of reducing approximately 31 percent of its present nonaqueous hazardous waste generation amounting to more than 53,000 tons annually during 1994 - 1998 and beyond.

Source Reduction Measures For 1994 Nonaqueous Waste:

- Table 3 identifies the number of major waste streams and source reduction measures considered, selected and rejected by the petroleum industry based on 1994 data.
- The number of major waste streams varies from 1 to 6 among the individual twenty-four sites, with an average of 3 major waste streams identified per site. The breakdown is as follows:

<u>Percentage of Sites</u>	<u>No. Major Wastes Streams</u>
13	1
38	2
25	3
17	4
4	5
4	6

- The industry considered a total of 217 measures for reducing hazardous waste; more than half (56 percent) were selected and the remaining 44 percent were rejected. Listings of selected and rejected measures are contained in Appendix B and D.
- The number of measures considered ranged for each site from 1 to 32 with an average of 9 measures considered per site. More than 2/3 of the sites considered approximately 10 measures.
- The number of measures selected ranged for each site from 1 to 21 with an average of 5 measures selected per site. One site selected 21 measures out of 27 considered (78 percent). Another site selected 14 measures out of 21 considered (67 percent).
- The number of measures rejected varied from 0 to 24 with an average of 4 rejected per site. One site rejected 24 measures out of 32 considered (75 percent). Nearly 40 percent of the sites did not reject any of the measures considered.

Nonaqueous Hazardous Waste Streams:

- Table 4 displays the number of major nonaqueous hazardous waste streams and the total nonaqueous hazardous waste streams identified in 1994. The total number of nonaqueous hazardous waste streams ranged from 1 to 13 with an average of between 8 to 9 per site. Three quarter of the industry declared more than 5 total nonaqueous waste streams; half declared more than 10 total nonaqueous waste streams in 1994.
- Collectively, the industry identified more than 32 percent of all 205 nonaqueous waste streams as major SB 14 waste streams generated during 1994.

Aqueous Hazardous Waste Streams And Projected Reduction:

Unlike nonaqueous hazardous waste, aqueous hazardous waste quantities comparison between 1990 and 1994 is not applicable. For the initial documents prepared during the first cycle (September 1991), many of the petroleum industry generators did not address aqueous waste streams in their source reduction evaluation which are now included in their current 1995 documents. SB 1133 was enacted September 5, 1991 and clarified the requirements for evaluating both aqueous and nonaqueous waste streams. For 1995 documents, due September 1, 1995, generators are required to determine the total quantity of waste water

generated, then conduct an additional calculation excluding the consideration of waste waters to determine the major non aqueous waste streams.

- Table 5 summarizes aqueous hazardous waste generation data analyzed during calendar year 1994 along with appropriate waste reduction information and applicable measures.
- The applicable SB 14/SB 1133 individual site aqueous hazardous waste generation in 1994 ranges from 620 tons to 7.2 million tons. Aqueous waste is defined as the hazardous waste stream processed in a waste water treatment unit which discharges to a publicly owned treatment works or under a National Pollutant Discharge Elimination System (NPDES) permit as specified in the Federal Water Pollution Control Act, as amended (33 U.S.C. Sec. 1251 and following). [Reference: Health and Safety Code 25244.19(b) (3) (A) and (B)]. Twelve sites indicated that they did not generate SB 14/SB 1133 applicable waste during 1994; one site was not able to provide aqueous waste generation data by the time of report publishing.
- Collectively, in 1994, the industry generated 16.78 million tons of aqueous waste. Approximately 46 percent of sites reported their aqueous wastes generation data for 1994. Most of the remainder did not generate hazardous aqueous wastes. The eleven sites reporting aqueous waste collectively selected 12 source reduction measures.
- The number of source reduction measures selected by each site ranged from 0 to 5, with an average of between 1 to 2 measures per site. DTSC noticed at least 3 sites that were proactive in reducing aqueous waste stream generation and implemented several measures that were successful in annually reducing several thousands of tons of aqueous waste prior to 1995.
- Only 3 sites individually targeted reduction of generated aqueous waste(s) which ranged from 13 percent (9402 tons) to 25 percent (0.33 million tons) annually. Six sites were unable to provide a specific aqueous waste reduction goal or reduction tonnage.
- It is estimated that collectively, the petroleum industry will reduce approximately 2.0 percent or 0.34 million tons annually of hazardous aqueous waste during 1994 - 1998 and beyond.

- The petroleum industry generated a total of 16,949,931 tons of **aqueous and nonaqueous SB 14/SB 1133 applicable** hazardous waste in 1994, and projected to reduce 393,030 tons annually after 1994 (Refer to Tables 2 and Table 5). The nonaqueous hazardous waste generation in 1994, and estimated reduction of nonaqueous waste after 1994 amounted to be 1.1 and 0.4 percent of the total aqueous and nonaqueous wastes generated in 1994.
- When all of the selected measures are implemented, the industry will be saving between \$6.7 to \$40.1 million annually by reducing projected nonaqueous waste alone. This figure will be even greater considering the large quantity of aqueous waste that will be reduced. Due to complexity of petroleum refinery processes it is difficult to figure dollar savings merited to the reduction of aqueous waste.

TABLE - 1
CALIFORNIA PETROLEUM INDUSTRY'S NONAQUEOUS WASTE⁽¹⁾ REDUCTION
RESULTS [1990 vs. 1994, WASTE GENERATION]

<u>Site</u>	<u>1990</u> <u>Quantity</u> <u>(Tons)</u>	<u>1994</u> <u>Quantity</u> <u>(Tons)</u>	<u>Amount</u> <u>Reduced</u> <u>(Tons)</u>	<u>Amount</u> <u>Reduced</u> <u>(%)</u>
ARCO, Los Angeles	12,110	4,963	7,147	59
CAL RESOURCES/(SHELL WESTERN), Bakersfield	1,248	446	802	64
CHEVRON, Richmond	7,300	6,967	333	5
CHEVRON, Bakersfield	3,152	2,577	575	18
CHEVRON, El Segundo	7,467 ⁽²⁾	34,569 ⁽³⁾	N/A ⁽³⁾	N/A ⁽³⁾
EXXON, Benicia	49,171	41,674	7,497	15
GATX TANK STORAGE, Carson	N/A	3,654	N/A ⁽⁴⁾	N/A ⁽⁴⁾
HUNTWAY, Benicia/Wilmington	345	277	68	20
MOBIL, Torrance	7,400 ⁽⁵⁾	1,163	6,237	84
PACIFIC REFINERY, Hercules	178	412	(234)	(131)
PARAMOUNT PETROLEUM, Paramount	868	640	228	26
POWERINE OIL, Santa Fe Springs	970	272	698	72
SHELL, Carson	N/A	197	N/A ⁽⁶⁾	N/A ⁽⁶⁾
SHELL, Martinez	24,490	15,110	9,380	38
TEXACO (Area 1&2), Bakersfield	6,968	723	6,245	90
TEXACO (Area 3), Bakersfield	38	66	(28)	(74)
TEXACO, Wilmington	28,015	16,100	11,915	43
TOSCO, Martinez	2,539	2,015	524	21
ULTRAMAR, INC., Wilmington	4,835	1,660	3,175	66
UNOCAL, Santa Maria	1,325	1,563	(238)	(18)
UNOCAL, Carson	12,125	9,290	2,835	23
UNOCAL, Wilmington	22,130	18,600	3,530	16
UNOCAL, San Francisco	5,800	6,083	(283)	(5)
WITCO CORP. OILDALE REFINERY, Oildale	1,288	610	678	53
TOTAL	192,295 ⁽²⁾	131,408 ⁽⁷⁾	61,084	32

Footnotes on page 17.

TABLE 1 - FOOTNOTES

(1) The waste data in Table 1 represents only nonaqueous, SB 14 applicable, hazardous waste generated as reported in each site's SB 14 Hazardous Waste Performance Report. Nonaqueous waste for SB 14 applicable hazardous waste can be defined as: "the hazardous waste stream which is not processed in a waste water treatment unit". The definition of aqueous waste stream is outlined on page 8.

(2) Hazardous Waste "disposed" quantity. Not included in the Total. Disposed quantities [major waste streams] for 1990 and 1994 are 7,476 and 3,880 tons respectively.

(3) Since the 1990 quantity is disposed vs. 1994 quantity is generated the "Amount Reduced (Tons)" and "Amount Reduced (%)" can not be determined.

(4) GATX mentioned that it was not captured during 1990 due to lower threshold SB 14 applicable hazardous waste generation quantity. Therefore its baseline and reporting years are same i.e. 1994. Hence "Amount Reduced (Tons) and Amount Reduced (%)" are not determined.

(5) Revised figure - In 1990 the hazardous waste generation quantity was erroneously reported.

(6) The Shell Carson plant is the result of a significant reduction in overall facility size and operation of what formerly was the Wilmington Manufacturing Complex. In December 1991 a portion of the refinery was sold. The refinery wrote their first SB 14 documents in 1994. Therefore the baseline and reporting years are same i.e., 1994. Hence "Amount Reduced (Tons) and Amount Reduced (%)" are not determined.

(7) The 1994 total does not include the GATX quantity (3,654 tons) because 1990 data are not available. The total also does not include Chevron El Segundo quantity (34,569 tons).

Amounts noted in () indicate an increase in hazardous waste generation.

TABLE - 2⁽¹⁾
CALIFORNIA PETROLEUM INDUSTRY FOUR YEAR HAZARDOUS WASTE
(NONAQUEOUS) REDUCTION GOAL [1994 - 1998]

<u>Site</u>	<u>1994 Hazardous Waste Generation (Tons)</u>	<u>Goal Reduction Percentage (%)⁽²⁾</u>	<u>Goal Quantity (Tons)</u>
ARCO, Los Angeles	4,963	20	992
CAL RESOURCES/(SHELL WESTERN), Bakersfield	446	100	446
CHEVRON, Richmond	6,967	18	1,254
CHEVRON, Bakersfield	2,577	20	515
CHEVRON, El Segundo	34,569	60	21,040
EXXON, Benicia	41,674	5	2,000
GATX TANK STORAGE, Carson	3,654	29	1,060
HUNTWAY, Benicia/Wilmington	277	17	46
MOBIL, Torrance	1,163	43	507
PACIFIC REFINERY, Hercules	412	19	78
PARAMOUNT PETROLEUM, Paramount	640	16	102
POWERINE OIL, Santa Fe Springs	272	N/A ⁽³⁾	N/A
SHELL, Carson	197	80	158
SHELL, Martinez	15,110	10	1,493
TEXACO (Area 1&2), Bakersfield	723	10	72
TEXACO (Area 3), Bakersfield	66	10	7
TEXACO, Wilmington	16,100	1	200
TOSCO, Martinez	2,015	20	403
ULTRAMAR, INC., Wilmington	1,660	5	80
UNOCAL, Santa Maria	1,563	57	890
UNOCAL, Carson	9,290	29	2,694
UNOCAL, Wilmington	18,600	92	17,112
UNOCAL, San Francisco	6,083	29	1,764
WITCO CORP. OILDALE	610	95	580
TOTAL	169,359⁽⁴⁾	31	53,493⁽⁵⁾

Footnotes on page 19.

TABLE 2 - FOOTNOTES

(1) The waste data in Table 2 represents only nonaqueous, SB 14 applicable, hazardous waste generated as reported in each site's 1995 SB 14 Hazardous Waste Source Reduction Plan. Nonaqueous waste for SB 14 applicable hazardous waste can be defined as: "the hazardous waste stream which is not processed in a waste water treatment unit". The definition of aqueous waste stream is outlined on page 8. The aqueous waste data are contained in Table 5, page 24.

(2) In most cases, the percent goal for each site was taken from its 1995 Plan. In few cases, when the goal was not specified in site's Plan, DTSC projected the goal based on the planned waste reduction information provided in the Plan.

(3) Not applicable - Powerine indicated that it was planning to sell the business and equipment to an entity overseas.

(4) The "Total" quantity differs from Table 1 because
a) Powerine waste quantity is not included in Table 2 and
b) Chevron El Segundo, and GATX, 1994 waste generation quantities are included in the Table 2 Total, but are not included in the Table 1 Total.

(5) The overall waste reduction goal for the petroleum industry was derived by using "total goal quantity" and "total 1994 nonaqueous hazardous waste generation" quantity.

TABLE - 3
CALIFORNIA PETROLEUM INDUSTRY 1994 SOURCE REDUCTION MEASURES
FOR NONAQUEOUS WASTE⁽¹⁾

<u>Site</u>	<u>Number of Major Wastes</u>	<u>Number of Measures Considered</u>	<u>Number of Measures Selected</u>	<u>Number of Measures Rejected</u>
ARCO, Los Angeles	2	2	2	0
CAL RESOURCES/(SHELL WESTERN), Bakersfield	1	1	1	0
CHEVRON, Richmond	2	32	8	24
CHEVRON, Bakersfield	3	12	9	3
CHEVRON, El Segundo	3	12	6	6
EXXON, Benicia	1	7	3	4
GATX TANK STORAGE, Carson	2	9	5	4
HUNTWAY, Benicia/Wilmington	1	7	4	3
MOBIL, Torrance	3	14	8	6
PACIFIC REFINERY, Hercules	4	7	4	3
PARAMOUNT PETROLEUM, Paramount	4	4	4	0
POWERINE OIL, Santa Fe Springs	3	N/A	N/A	N/A
SHELL, Carson	2	21	14	7
SHELL, Martinez	2	8	8	0
TEXACO (Area 1&2), Bakersfield	3	2	2	0
TEXACO (Area 3), Bakersfield	4	2	2	0
TEXACO, Wilmington	2	12	4	8
TOSCO, Martinez	4	6	5	1
ULTRAMAR, INC., Wilmington	6	1	1	0
UNOCAL, Santa Maria	3	1	1	0
UNOCAL, Carson	2	15	4	11
UNOCAL, Wilmington	2	14	5	9
UNOCAL, San Francisco	5	27	21	6
WITCO CORP. OILDALE REFINERY, Oildale	2	1	1	0
TOTAL	66⁽²⁾	217⁽³⁾	122⁽³⁾	95⁽³⁾

Footnotes on page 21.

TABLE 3 - FOOTNOTES

(1) Based on 1994, SB 14 applicable hazardous waste generation quantities.

(2) The total of 66 waste streams are comprised of 16 California waste codes outlined in Appendix C.

(3) Total of measures columns will reflect multiple counts of the same measure considered by other sites.

TABLE - 4
CALIFORNIA PETROLEUM INDUSTRY
1994 NONAQUEOUS HAZARDOUS WASTE STREAMS

<u>Site</u>	<u>Number of Hazardous Waste Streams</u>	<u>Number of Major Waste Streams</u>
ARCO, Los Angeles	9	2
CAL RESOURCES/(SHELL WESTERN), Bakersfield	1	1
CHEVRON, Richmond	10	2
CHEVRON, Bakersfield	10	3
CHEVRON, El Segundo	10	3
EXXON, Benicia	13	1
GATX TANK STORAGE, Carson	4	2
HUNTWAY, Benicia/Wilmington	2	1
MOBIL, Torrance	7	3
PACIFIC REFINERY, Hercules	5	4
PARAMOUNT PETROLEUM, Paramount	4	4
POWERINE OIL, Santa Fe Springs	10	3
SHELL, Carson	5	2
SHELL, Martinez	12	2
TEXACO, (Area 1 and 2), Bakersfield	13	3
TEXACO, (Area 3), Bakersfield	10	4
TEXACO, Wilmington	9	2
TOSCO, Martinez	12	4
ULTRAMAR, INC., Wilmington	12	6
UNOCAL, Santa Maria	8	3
UNOCAL, Carson	9	2
UNOCAL, Wilmington	11	2
UNOCAL, San Francisco	11	5
WITCO CORPORATION OILDALE REFINERY, Oildale	8	2
TOTAL	205⁽¹⁾	66⁽¹⁾

Footnotes on page 23.

TABLE 4 - FOOTNOTES

(1) Total of Waste Streams Columns will reflect multiple counts of the same waste stream appropriate to "different sites". The total is comprised of the 16 California Waste Codes (CWC) outlined in Appendix C.

TABLE - 5
CALIFORNIA PETROLEUM INDUSTRY 1994 AQUEOUS⁽¹⁾ HAZARDOUS WASTE QUANTITIES
PROJECTED REDUCTION

<u>Site</u>	<u>1994 Quantity Generated (Thousand Tons)</u>	<u>No. of Selected Source Reduction Measures</u>	<u>Projected Amt. to be Reduced 1994-1998 (Thousand Tons)</u>	<u>Percent Reduction Projected (%)</u>
ARCO, Los Angeles	1331.900	4	329.750	25
CAL RESOURCES (SHELL WESTERN), Bakersfield	0	N/A	N/A	N/A
CHEVRON, Richmond	0	N/A	N/A	N/A
CHEVRON, Bakersfield	0	N/A	N/A	N/A
CHEVRON, El Segundo	0.620	N/A	N/A	N/A
EXXON, Benicia	243.352	0	0	0
GATX TANK STORAGE, Carson	2.030	5	0.385	19
HUNTWAY, Benicia/Wilmington	72.100	1	9.402	13
MOBIL, Torrance	5245.000	1	N/AV	N/AV
PACIFIC REFINERY, Hercules	0	N/A	N/A	N/A
PARAMOUNT PETROLEUM, Paramount	0	N/A	N/A	N/A
POWERINE OIL, Santa Fe Springs	N/A	N/A	N/A	N/A
SHELL, Carson	0	N/A	N/A	N/A
SHELL, Martinez	7200.000	0	N/AV	N/AV
TEXACO (Area 1&2), Bakersfield	0	N/A	N/A	N/A
TEXACO (Area 3), Bakersfield	0	N/A	N/A	N/A
TEXACO, Wilmington	0	N/A	N/A	N/A
TOSCO, Martinez	1100.000	0	0	0
ULTRAMAR, INC., Wilmington	1170.000	N/A	N/A	N/A
UNOCAL, Santa Maria	N/AV	N/AV	N/AV	N/AV
UNOCAL, Carson	0	N/A	N/A	N/A
UNOCAL, Wilmington	58.970	0	0	0
UNOCAL, San Francisco	356.600	1	N/AV	N/AV
WITCO CORP. OILDALE REFINERY, Oildale	0	N/A	N/A	N/A
TOTAL	16780.572	12	339.537	2.0

Footnotes on page 25.

TABLE 5 - FOOTNOTES

(1) Aqueous Hazardous Waste stream is defined as a hazardous waste stream processed in a waste water treatment unit which discharges to a publicly owned treatment works or under a National Pollutant Discharge Elimination System (NPDES) permit as specified in the Federal Water Pollution Control Act, as amended (33 U.S.C. Section 1251 and following). [Reference: SB 1133, 1991, Health and Safety Code 25244.19(b)(3)(A) and (B)].

- N/A - Not Applicable
- N/AV - Not Available

IV. SOURCE REDUCTION MEASURES

DTSC has reviewed Source Reduction documents prepared by the 24 California petroleum facilities affected by SB 14. These 24 sites collectively generated a total of 66 nonaqueous and several aqueous major hazardous waste streams, considered 217 measures for nonaqueous wastes and of these selected 122 measures (12 additional measures were selected for aqueous wastes) to reduce hazardous waste during 1998 and beyond. A detailed breakdown of these selected measures by site is presented in Table 3 and Table 5, and a listings of selected and rejected measures are outlined in Appendix B and D. The following discussion describe key source reduction example(s) taken from each of the 24 sites. These examples represent the cost effective approaches that are generally applicable throughout the industry.

ARCO, Los Angeles Refinery:

Waste Water Reduction: ARCO refinery waste water is a combination of process water and stormwater, since it does not have a separate stormwater sewer. The refinery reduced its discharge of waste water, which is hazardous waste, by an estimated 85 percent from 1990 to 1994. ARCO's process waste waters originate from tank draws, desalters, refinery operating units and cooling tower blowdown. Waste water is processed to meet specification and then it is discharged to a POTW. Benzene concentrations of 0.5 ppm or greater (as benzene) results in this waste water being classified as a RCRA hazardous waste due to toxicity. Potential source reduction options for refinery waste water include both 1) reducing the total volume requiring discharge to the POTW; and 2) lowering the benzene concentration so that the water may be classified as nonhazardous.

The volume of waste water generated by ARCO depends primarily on the refinery's water consumption, and the quantity of rainfall. ARCO has a long history of water conservation efforts and has consistently reduced considerable waste water volume over the last three years. This has been done due, at least in part, to a variety of water reuse projects.

During the last ten years, wherever possible, the refinery has segregated the stormwater drainage from process waste water. Segregation prevents storm water from becoming contaminated with process hydrocarbons. Segregation also prevents oil/water sludge formation.

The refinery implemented several source reduction projects to reduce benzene concentration in waste water to below 0.5 ppm. These projects were completed by 1992. In 1994, the benzene level of the final effluent was below 0.5 ppm 80 percent of the time. The following key projects were implemented in the last four years, which contributed to the benzene reduction: 1) Installation of closed loop sampling system 2) Segregation and recycling of high benzene concentration waters and 3) Benzene waste water stripping.

ARCO is committed to further reduce, benzene concentration in refinery waste water. In order to achieve this result, the refinery will continue promoting an increased awareness by plant personnel of the importance of restricting hydrocarbons from entering the sewer. ARCO intends to accomplish this increased awareness by all refinery personnel by publishing articles in the refinery newspaper and conducting frequent training sessions for operation and maintenance personnel.

Agricultural Use Of Spent Polymerization Catalyst: The Catalytic Polymerization Unit converts propylene from the Fluid Catalytic Cracking (FCC) unit into gasoline blending stock and commodity chemicals. This reaction occurs in ten vertical reactors and is activated by the action of phosphoric acid on extruded silica-alumina pellets. This material is a cationic polymer catalyst. Spent catalyst is removed from the reactors approximately eighty times per year. This spent catalyst is a non-RCRA hazardous waste due to its corrosivity which is due to its phosphoric acid content.

Phosphoric acid is widely use for producing fertilizer to be used in agricultural and horticultural applications. A project is underway to divert this material from the landfill to applications in the agricultural industry.

**CAL RESOURCES (Formerly Known as SHELL WESTERN E & P INC.),
Bakersfield:**

Refractory Waste As A Non-Routine Waste: Refractory brick is used to construct the furnace box of steam generators and may be used to construct or line other high temperature process units. With prolonged use, the refractory becomes impregnated with nickel and vanadium introduced by the crude oil fuel. The concentrations of nickel and vanadium are sufficient to cause this refractory to be classified as hazardous. Hazardous refractory waste is generated when the process unit is demolished or when damaged refractory is repaired during routine maintenance operations. Cal Resources is switching from crude oil to

gas fuel. By using gas, the damaged refractory will not be classified as hazardous because fuel gas does not contain nickel or vanadium. Although not an SB 14 waste stream due to its non-routine generation, Cal Resources' elimination of this waste stream reduces their hazardous waste management costs and future liability.

CHEVRON, Bakersfield:

Reduce Sand Blast Grit: Sand blast grit is generated during the surface stripping/cleaning of equipment, platforms and storage tanks. Sand blast grit is potentially a hazardous waste due to contamination by metal-containing paints and primers stripped from the equipment. Occasionally metals contamination can appear in the sand blast grit due to the base metal content of the equipment itself. Chevron selected two measures for implementation and plans to modify its current decision-making procedure that is used to determine painting/sand blasting operation frequently. It will also determine which paints and primers are best for use. Painting/sand blasting frequency and the paint type selected will depend on site specific factors including economic and compliance issues present at the time of repainting.

Survey/Audit to Reduce Crude Tank Bottoms: Tank bottoms are the result of solids such as sand, dirt, etc. settling out of produced crude oil and onto the bottom of tanks, vessels, and other processing equipment. In the past, certain tank bottoms have been determined to be a hazardous waste due to toxicity. This toxicity may be associated with crude oil metals that adhere to the settled solids. Chevron's present tank cleaning methods include water washing of these solids from the tanks and vessels.

Chevron has decided to conduct the following three survey/audit measures: 1) improve tank cleaning procedures 2) improve the chemical and mechanical processes to remove water, and solids from process streams and 3) examine sand control processes to find ways to reduce sand carryover. The procedures and approach of these three measures involve establishing the scope and detail of the project and then conducting the audit/survey. The survey/audit approach may be conducted by either an outside consultant or by Chevron personnel. Upon completion of the survey/audit, identified procedural improvements will be evaluated to determine specific applicability and implementation feasibility.

CHEVRON, El Segundo Refinery:

Oily Sludge Source Reduction through Inspection and Repair of Drainage Systems: The Chevron El Segundo refinery generated 20,700 tons of this waste during 1994. The waste is generated during passive and active separation of oil and solids from waste water streams. This measure would reduce the formation of oil/water separation sludge generation by minimizing the amount of sand originally entering the drainage system. Capital and O & M costs are estimated at more than ten million dollars. Due to the high capital costs, Chevron mentioned that the project could extend beyond the present SB 14 four-year cycle.

CHEVRON, Richmond Refinery:

Eliminate the Use of Sandbags for Plugging Sewers: The Chevron Richmond Refinery generated 5,832,000 pounds per year API separator and other sludges. API separator sludge is generated during the gravitational separation of waste solids from refinery process waste waters in its API separators. This waste stream is made up of tank water draw solids, rust, scale, and other process equipment contaminants and soil runoff. Much of these solids originate from sandbags used to plug stormwater drains during maintenance activity. Deterioration of the sandbags, spillage of sand and gravitational separation of solids from waste water flows are key contributors to this waste stream.

Chevron will use alternate methods for plugging process drains, using commercial products such as Insert-A-Seals or Duck ponds. Economic review and feasibility studies were scheduled to be performed during 1996. Approximately 560,000 pounds per year of this waste is estimated to be reduced upon implementation of this measure.

Screen Out Inert Ceramic Support Spheres from Spent Catalyst and Reuse Spheres: Spent catalyst is generated from processes that treat, crack, or reform hydrocarbon streams by passing these streams over a metal impregnated catalyst. These catalysts are manufactured with nickel, molybdenum or other non-RCRA metal contaminants that typically cause them to be classified as hazardous when spent. These metals are required to achieve the necessary reaction to process hydrocarbons through operations such as catalytic hydrocracking, hydrotreating, and hydrogen manufacturing. These catalysts become worn out over time. The Chevron refinery generated more than five million pounds of total spent catalyst in the reporting year 1994.

Chevron will screen the spent catalyst to remove support spheres for reuse as fresh catalyst support in the reactors. Operating cost, analytical cost and return on investment are estimated at \$100,000 per year, \$2,000 per year and more than 100% respectively. Chevron estimated that nearly 500,000 pounds/year will be reduced.

EXXON, Benicia:

Improved Handling of Electrostatic Precipitator (ESP) Fines: Exxon uses an electronic precipitator to collect Fluid Catalytic Cracking Unit (FCCU) catalyst particles (fines) that pass through two furnaces. The ESP fines are collected by baghouses and deposited into rolloff boxes which are then taken to another part of the refinery for transfer onto bulk transport trucks suitable for this material. Although this material is not regulated as hazardous waste in California, fugitive emissions and spills/leakage from handling may enter the refinery sewer system where they can cause up to a ten-fold increase in sewer sludge.

Exxon has proposed a direct transfer of ESP fines into a transport vehicle compared to the current practices of moving a rolloff box to another part of the refinery where it can then be loaded to a transport vehicle. This current practice causes increased leakage or spillage of this material. It appears that 5 to 10 pounds of ESP fines are lost for each ton handled. Based on the 1994 quantity handled, ESP fines loss would be approximately 2.6 to 5.2 tons. Since each pound of solids entering into sewer can generate 10 pounds of oil/water separation solids, eliminating the loss of ESP fines may reduce the waste water treatment solids by 25 to 50 tons per year. It is estimated that implementing this source reduction measure will cost \$350,000. However, inplant management costs of about \$150,000 per year will be significantly reduced and will result in a 35 percent discounted cash flow rate of return. This potential source reduction measure is attractive because it will reduce generation of oil/water separation solids by removing dust particles at the source, prior to entering the sewer.

Improve Operation of the Desalter: Crude oil must be desalted before it can be processed in the refinery. Removing salt reduces the corrosion on refinery process equipment. Salt removal is done in a desalter vessel which uses electric current, chemical additives, and water to transfer the salts into a water phase that is then discharged to the waste water treatment plant. The desalted oil phase then enters the crude preheat and distillation

equipment. Any oil that is inadvertently removed with the water (known as oil under carry) would increase the sludges generated at the waste water treatment plant by combining with solids in the sewer. When certain crudes are processed, there may be as much as a 10 percent oil under carry in the brine water leaving the desalter. Exxon selected the following two mechanisms for improving desalter operations to reduce oil under carry:

- Changing the desalter internals to a Petreco BIELECTRIC design from the current Petreco Low-Velocity design; and
- Optimization of chemical usage at the desalters to reduce oil/water emulsions.

Oil/water separation sludges are created when oils and solids particles in the sewer agglomerate. Reducing either of the precursors (solids or oils) will reduce the oil/water separation sludges generated at the waste water treatment plant. The crude desalter operation has been previously identified as the single largest source of oil to the oily sewer system. Changing the desalter internals to a Petreco BIELECTRIC design from the current Petreco Low-Velocity design can reduce the oil under carry to a maximum of 2 percent. This modification also requires that the desalter mudwash or solids removal system be improved for separation of oil/water/solids separation in the desalter operation itself.

Assuming a wash water rate of 6 percent, average oil under carry of five percent, and a 10 percent reduction in resulting sludges provides an estimated reduction of about 2,500 tons per year of oil/water separation sludges. Exxon contacted several other refineries that have installed similar desalters. In all cases, impacts of the suggested BIELECTRIC desalter were positive including improved salt removal and decreased under carry. It is estimated that conversion to the Petreco BIELECTRIC desalter design and improving the desalter mudwash system will cost \$800,000 and provide a 30 percent discounted cash flow rate of return.

GATX TANK STORAGE, Carson:

Repair Tank Roofs to Reduce Oily Water Waste: During 1994, GATX generated 2,600, 2765 and 292 tons of oily water at its Carson, Harbor, and Marine Terminals facilities respectively. One primary source of oily water generation at these facilities is water that collects at the bottom of petroleum product storage tanks. This water is routinely removed from the tanks and the water stream thus removed is

referred to as "water draw". The water draw contains a high portion of petroleum product due to the desire to remove as much water as possible from products. During 1994, oily water generated from water draws at the Carson and Harbor Terminal was either diverted to slop tanks for subsequent transport to an off-site hazardous waste treatment facility for recycling and disposal, or pre-treated at the Carson onsite waste water treatment plant for subsequent discharge to a POTW.

The Carson facility has several storage tanks; two of these tanks have damaged roofs that allow accumulation of rain water in the tanks. GATX is planning to repair the two damaged petroleum tank roofs at the Carson terminal facility. Implementation of this measure would result in a reduction of storm water infiltration into the two petroleum product storage tanks. It is estimated that all of these facilities combined can reduce at least 750 tons per year of oily waste water once the tank roofs are repaired. GATX believes that this measure is technically feasible and the final product quality will improve by completely excluding rainwater infiltration. The capital cost of repairing the two tank roofs is approximately \$550,000.

Install Additional Sumps and Sloping Tank Bottoms:
There are several factors such as water draw described above that contribute to generating oily waste water at GATX's three facilities. On occasion, the contents of a tank and its associated pipelines are emptied for cleaning purposes. During a typical tank cleaning, fresh water is sprayed on inner tank surfaces laden with petroleum residuals. The amount of water used in tank cleaning operations is directly proportional to the amount of residual tank bottoms product present. Additionally, sumps and sloped bottoms will facilitate draining residual product and help minimize the amount of product that contacts and contaminates wash water. Cleaning only a thin residual film reduces the amount of water necessary for tank cleaning operations and helps minimize product/water contamination.

In the past few years, GATX has been installing sumps and sloping bottoms when constructing new tanks, which may require frequent product changes. The capital costs associated with retrofitting all existing tanks with sloping bottoms and sumps is estimated to be \$12,000,000. Under this option, GATX will continue future installation of sloping bottoms if these measures can be economically justified on a case by case basis.

HUNTWAY REFINING COMPANY, Wilmington:

Isolate Water/Oil Recycling Treatment (WORT) System: Oil/water separation sludge solids are generated as the result of recycling oily process water and storm waters in the refinery's WORT system. The WORT system includes a series of oil/water separator tanks for the separation of oil and solids from the waste water stream. Oil recovered from this system is recycled back to the process. The California waste code for this waste is CWC 222 oil/water separator sludge.

Huntway will isolate the drains from storm water inflow and hence reduce both the solids quantity and storm water entering the WORT system. This method will be implemented by berming the selected sections of the process area. Huntway will spend a considerable amount of attention to employee health and safety by eliminating tripping hazards as it conducts its berming activity. It is estimated that approximately 90 tons of waste will be reduced. The capital cost and annual maintenance cost have been estimated at \$10,000 and \$1,000 respectively. The payback period is estimated at 2.5 years.

Segregate Boiler Blowdown: Huntway selected this measure for further study. Hard water from boiler blowdown may contribute to waste water sludge accumulation. It is assumed that the hardness in boiler blowdown precipitates and accumulates in the WORT system as sludge. Huntway will analyze accumulated sludge to determine what percentage consists of boiler blowdown solids. Huntway will then evaluate the feasibility of segregating boiler blowdown from the waste water stream.

MOBIL OIL, Torrance Refinery:

Reduction of Aqueous Solutions with Organic Residues < 10%: Mobil generated more than 5 million tons of this waste in 1994. Process waste water enters into the industrial waste water treatment plant (IWW) at many different places in the refinery. The sewer system which brings process waste waters into the IWW is commonly referred to as the "oily water sewer" or the "process sewer". The process sewer system is segregated from storm water sewer system. The following are typical process sewer waste water sources:

- 1) Drains in the process unit - All process units in the refinery are constructed on concrete pads, these pads drain to the process sewer. This is done so that drips, leaks, or spills of hydrocarbon material do not

contaminate adjacent soil. The concrete pads are washed with steam, water and cleaning agent on a periodic basis. The water and any hydrocarbons on the surface of the pad are drained to the process sewer.

- 2) Drains on pump pads and compressor pads - Rotating equipment such as pumps and compressors are common sources of hydrocarbon material leaks. When leaks occur, this material is allowed to drain to the oily water sewer.
- 3) Drains at sample points - The operation of the refinery requires frequent sampling of intermediate and final products. At many sample points, sample ports are flushed into the sewer for sufficient time to ensure that the line from the process is purged so that the sample taken is representative. Where practical, the refinery has installed a closed loop sampling system which avoids draining into process sewer.
- 4) Vacuum truck wash out area and heat exchanger bundle cleaning pad - In the case of vacuum truck operation, water and hydrocarbons from the vacuum truck cleaning area enter the process sewer. In the case of the heat exchanger bundle cleaning pad the material entering the sewer consists of water and hydrocarbons from the hydroblasting and steam cleaning of process equipment, mainly heat exchanger tube bundles.
- 5) Drains inside tank dikes - Inside the tank dike there is often a process drain. Material spilled from tanks is often drained to the process sewer for recovery.
- 6) Oil water separation vessels - In vessels where water is separated from hydrocarbons the water fraction is often drawn off and sent to the process sewer.
- 7) Boiler blow down - Steam boiler blowdown water is sent to the process sewer.
- 8) Water draws on storage tanks - Certain product or intermediate product storage tanks will over time accumulate water. This water is drawn off and sent to the process sewer.

In the IWW hydrocarbons are separated and the water is discharged to a POTW. Oil separated by gravity is called "recovered oil" and it is not regulated. Recovered oil is returned to the refining process by addition to the crude feed unit. Oily sludges generated in the IWW are returned to the coker to recover the hydrocarbon content. A small

quantity of contaminated debris and certain pieces of replaced equipment are generated in the IWW and disposed of in a landfill.

The refinery implemented one key process sewer measure: exclude hazardous substances from the process sewer. For example, the refinery now covers process sewer drains during maintenance periods to avoid dust and debris from catalyst change outs from entering the sewer. This prohibits formation of large amount of sludge and reduces sludge recycling costs.

The refinery manufactures "clean fuels" (CARB gasoline). This has a positive effect on the total amount of benzene present in the refinery process waste waters. The more stringent CARB gasoline formulation allows only about half the amount of benzene in gasoline. The refinery made major process changes and decommissioned a process unit which was contributing high levels of benzene and other aromatic blending stock in their gasoline products. These changes were scheduled during the 1995-96 period and the CARB gasoline production was commenced during the first quarter of 1996.

PACIFIC REFINING COMPANY, Hercules:

Install Close Loop Sampling Ports: Pacific Refining Company will install closed loop sampling ports at all process units throughout the plant. This measure will reduce the amount of oil entering into their waste water treatment plant, hence minimizing oily sludge generation. Pacific estimated a 10 tons per year reduction of the sludge. Capital cost is approximately \$30,000 with a payback period of approximately 2.3 years.

PARAMOUNT PETROLEUM COMPANY, Paramount:

Tank Bottom Waste Reduction using a Filter Press: Tank bottom sludge occurs due to water and sediment settling out of the stored product in the tank and accumulating on the bottom. The use of a filter press results in recovering and separating as much oil and water as possible. Oil is then reprocessed through the refinery's processes and the water directed to the refinery waste water system and discharged to a POTW. If the filter cake's heating value is more than 5,000 BTU per pound, the material can be used as fuel for permitted cement kilns.

POWERINE OIL COMPANY, Santa Fe Springs:

No Key Measures: Powerine was unable to prepare source reduction measures for 1994 since the company ceased operation in July 1995. Powerine signed a contract transferring ownership of the Refinery's assets (equipment) to a third party who plans to dismantle the refinery and reassemble the plant overseas. Therefore, Powerine will no longer routinely generate hazardous waste. Powerine's 1994, Source Reduction Plan will be updated in the future, if necessary.

SHELL OIL, Carson:

Reduce Hydrocarbon Spills and Leaks in the Pump Pad Area: Under normal operating conditions, Shell has experienced seal leaks and lubricating oil drippings as the major sources of waste hydrocarbons in their pump pad area. Pump bases serve as collector pans and are usually provided with a drain hole. These pans must be kept clean of solids for waste hydrocarbons to adequately drain. Shell will administer special efforts to drain the equipment and lines prior to repairs, and hence avoid hydrocarbon spillage. This will help Shell reduce filter cake. Shell believes that the change in the hazardous waste generation could be significant through implementation of this selected measure.

Note: The Shell Carson plant is the result of a significant reduction in an overall facility size and operations of what was formerly the Wilmington Manufacturing Complex, a refinery which sold the majority of its operation to another oil company.

SHELL OIL, Martinez:

Segregate High Salt Waters directly to the Biotreater: Stripped sour water and boiler blowdown are two of the many precursors to oil/water separator sludge generated by suspended and precipitated solids which form sludges in the presence of oil. Contaminants in these streams are primarily inorganic, and could be managed downstream of the API and dissolved air flotation units. Shell has an existing pipeline that could be used for the purpose of routing stripped sour water and boiler blowdown streams directly to the biotreater. The only costs associated with implementation might be the effort required to modify one or two operational procedures. Shell expects to reduce oil/water separation sludge by 25 tons per year by implementing this measure.

Reduce High Solids Input Streams: Shell identified the following three measures to reduce equipment clean out waste. 1) Identify and implement source reduction of high solids input streams, 2) Identify and segregate or return to processing, low-solids input streams, and 3) Identify non-hazardous input streams which could be managed as designated waste. Several input streams contribute solids to equipment clean-out waste. They are primarily recovered oil streams from various refinery sources, and include the brine deoiler unit, the recovered oil tank at the effluent treating unit, vacuum truck discharges, samples from the laboratory and skim oils from oil/water separators. As feedstock materials are transferred from a tank for processing, representative samples could be drawn and tested for base sediment and water. This information would then be used to separate high solids from low solids streams. Returning the low solids streams directly to a process unit would save unnecessary double handling and reduce formation of oil/solids sludges. Further identification of the type of solids present in each high solid stream would lead to the development of source reduction projects for each one.

Shell believes that some of its equipment clean-out input streams are as high as 35 percent solids. A conservative estimate, assuming limited source reduction opportunities and success, would be to reduce equipment clean-out by 100 tons per year by reducing high solids input streams. Shell selected two other measures (mentioned above) to reduce this waste. The study is expected to take approximately one year to complete at an estimated cost of \$60,000. The study will comprise sampling, testing and data tracking. This will provide information for Shell to consider when considering all three measures for implementation to reduce equipment clean-out waste.

TEXACO, Bakersfield (AREA 1, 2 AND 3):

Oil Emulsions Injection into Delayed Coker Unit: Several hazardous waste streams contributed to the organic solid waste stream from Texaco's Plant 1 and 2. These hazardous waste streams included hydrocarbon solids, heat exchanger bundle sludge, filter cake from tank cleaning, primary treatment sludge, slop oil emulsion solids and lab waste. In 1991 Texaco initiated a process change that allowed a small stream of oil emulsions to be processed in the Plant 3 delayed coking unit. Injecting the oil emulsion into the delayed coker unit recovered the lighter hydrocarbons while the remainder of the emulsion mixture was incorporated into the coke product. According to Texaco, this process change does not adversely affect the quality of the petroleum coke product.

Due to the success of this source reduction measure during the last SB 14 cycle, Texaco engineers have designed a new hydrocarbon recovery system intended to increase the amount of oil emulsion sludge which can be injected into the delayed coker. This hydrocarbon recovery system has been designed to use existing plant equipment to the greatest extent possible. This will help reduce capital expenditure. Once operational, Texaco expects a large reduction in the petroleum sludge waste streams sent offsite for disposal. The new hydrocarbon recovery system is scheduled to be completed by December 1997. Although the estimated implementation costs for this measure were not known at the time of the preparation of SB 14 documents, Texaco estimated waste management savings of approximately \$248,000 per year. Texaco believes that by implementing this measure on large scale, the organic wastes (filter cake - 450,000 lbs., primary treatment sludge - 80,000 lbs., slop oil emulsion solids - 6,600 lbs., and heat exchanger bundle sludge - 7,320 lbs.) will be nearly eliminated except for large solids screened from the tank sludge.

Installation of Automatic Self Cleaning Filters:
Texaco's waste waters generated in Area 1 and 2 are combined and handled in a common waste water treatment plant prior to disposal by deep well injection. In order to prevent subsurface plugging of the injection well aquifer, cartridge type filtration units are used to remove solids greater than 5 microns in size from the injection waste water stream. The installation of the automatic self cleaning filters was identified in the 1991 Plan as a source reduction measure to reduce filter cartridge waste. The automatic self cleaning prefilters, which will remove particulates larger than 15 microns will reduce the downstream loading on the filter cartridges. Only particulates in the 5 to 15 micron size range will be removed by the filter cartridges resulting in a decreased disposal frequency for the filter cartridges. When the automatic self cleaning filters accumulate solids to a predetermined point, captured particulate matter is removed by backwashing.

Texaco conducted several pilot studies using automatic self cleaning filters from various suppliers. Although one pilot study was successful, most did not perform satisfactorily. In 1993, Texaco decided to defer this measure's implementation, due to high capital costs and low return on investment. Texaco's process engineers are continuing their evaluation of the automatic self cleaning filters, including additional economic feasibility of this measure. Texaco has set December 1998 as their goal to complete the oil/emulsions/solids study and make the associated feasible upgrades identified by the study.

TEXACO, Wilmington:

Waste Water Sludge Reduction Using Circulating Sample Points and Installation of Cyclonic Separator: Sewer sludge is chiefly a result of unit pads wash down activity. Other activities and contaminants which contribute to sewer sludge include heat exchanger bundle cleaning, pipe cleaning, boiler blowdown, waste lime slurry and coke fines. The residuals from washing unit pads and other washdown activities, flow to the sewer system where sewer sludge accumulates over time. Texaco selected four source reduction measures. The following two are focused on reducing sewer sludge.

Texaco started using circulating sample points instead of traditional sampling bibs to reduce the amount of flushing time and product loss needed before obtaining a representative sample. This decreases the amount of product drained onto the unit pads and reduces the overall toxicity of the sewer sludge. Texaco spent \$87,500 in capital cost to install circulating sample points at thirty five different places throughout the plant. This allows for more timely and accurate sampling but offers poor payback in terms of waste management costs (less than \$10,000 per year).

Texaco used upstream cyclonic separators to assist gravity separators. This measure will reduce the amount of fines that contribute to sewer sludge. Texaco estimated 3,000 to 10,000 pounds reduction of sewer sludge handled by the waste water treatment plant. The use of upstream separation enabled reuse of specific solid side streams within their process thus eliminating the combined waste sludge generated by the waste water treatment plant gravity separator.

TOSCO REFINING COMPANY, Martinez:

Replace Sand with Absorbent: A key source of generation of oil/water sludge is absorptive cleanup of oily surfaces using sand. Sand remaining after physical removal using a broom and shovel is washed down the sewer. Sand entering the sewer contributes to oil/water separation sludge solids. Tosco will replace sand with an absorbent more easily swept from hard surfaces thus eliminating the need for water cleanup. Diatomaceous earth and vermiculite are two alternatives under consideration. Tosco will reduce sludge by approximately 10 tons per year. There is no capital cost involved. The cost savings of \$31,850 per year will be realized with implementation of this measure. A recurring cost of \$1,000/year is estimated for purchase of

fresh absorbent and disposal of contaminated absorbent as hazardous waste. This recurring cost is currently spent using the traditional sand absorbent.

Use of Lead Blankets For Covering Sewers: Another source of oil/water separation sludge is the use of a burlap cover topped with sand to close sewer openings during maintenance activities. Sand lost to the sewer when covers are removed contributes to the formation of oil/water separation sludge solids. Tosco is planning to cover sewer openings with lead blankets rather than burlap and sand. This is estimated to reduce sludge by 5.6 tons per year. Capital cost and payback period are estimated at \$15,625 based on the purchase of 125 lead blankets at \$125 per blanket, and 1.2 years respectively.

ULTRAMAR, Wilmington Refinery:

Evaluate Potential Alkylation Waste Recycle Options: In recent years, Ultramar has attempted to establish a recycling program for the reduction of alkylation sludges. One alternative being considered is the potential use of alkylation sludges as a fluxing substitute in metal refining or as a raw material in the manufacturing of hydrofluoric acid. Ultramar will continue to evaluate this and other recycling alternatives in the hopes of developing a viable alkylation waste recycle program.

UNOCAL, Santa Maria Facility:

API Separator Sludge Reduction using the Delayed Coker: Unocal's demonstrated current practice is to direct API sludge to the delayed coking process and hence recover oil product. Unocal mentioned that the delayed coking process has eliminated the need for the disposal of sludge and currently delayed coking is the best technical and economical method for handling this waste.

UNOCAL, Los Angeles Refinery, Carson Plant:

Evaluate Potential Spent Catalyst Recycle Options: Unocal uses six different types of catalysts throughout its refinery. One spent catalyst type is produced in the hydrotreating process. The remaining five spent catalysts are generated in the hydrogen plant. Unocal has two hydrotreaters. They remove metals, sulfur compounds, and some nitrogen from gas oil feedstocks. Hydrotreating must be completed to remove sulfur from gas oil and to help prevent deactivation of the catalyst used in other

downstream processes. Metals removed during the hydrotreating process deposit on the catalyst. The hydrogen plant uses a sulfur conversion catalyst, typically a cobalt molybdenum catalyst. This is to convert all sulfur compounds in the light gas feed streams to hydrogen sulfide.

Unocal will evaluate the sale/use of spent hydrotreating and spent steam reforming catalysts as a raw material feed to an abrasive manufacturing facility. It will also evaluate sale/use of hydrogen plant spent catalyst as a raw material feed to a primary smelting facility. There are no capital, operating or maintenance costs involved. Estimated source reduction benefit is expected to be reduction of approximately 290,000 pounds of spent hydrotreating catalyst and 100,000 pounds of spent hydrogen plant catalyst annually.

Although not an SB 14 major waste stream but because significant source reduction opportunities exist for the spent catalysts, Unocal actively pursued source reduction evaluation of this minor waste stream.

Tank Inventory Optimization Study: Tank bottom wastes are generated at Unocal throughout the various tanks used by the refinery for storage of raw crude and various crude oil intermediate streams. Unocal generated approximately 2,500 tons of tank bottom wastes in 1994. This waste stream accounted for twenty seven percent of the total hazardous waste generated at the site. Tank bottom wastes are generated when solids or semi-solid materials in the raw crude or intermediate stream settle to the bottom of the storage tanks. The material that accumulates in the tank bottoms is a combination of various heavy constituents. These heavy constituents include solids in the raw crude oil or intermediate stream, rust or scale from tanks, pipes, and other equipment, and heavy wax like paraffin hydrocarbons.

The above material accumulates over time since the concentration of the solids in the stored materials is very low. Many years pass before a tank is taken out of service. Tanks are taken out of service when the tank requires repairs or for routine inspection. Unocal recycles essentially all refinery tank bottom wastes to the on site coker unit where the oil is recovered to produce hydrocarbon fuels and the solids are recovered as saleable coke. Residual water in the sludges serves as quench water, replacing some of the quench steam.

Unocal believes that its tank bottom waste could potentially be reduced or eliminated through two measures: 1) reduce tank inventory at the refinery and 2) manage sludges as an excluded recyclable material. Feasibility

studies for both options indicate further evaluation is essential to determine viability. Unocal will conduct a tank inventory optimization study to determine the optimum tank needs for the refinery. It may also be possible to reduce tank sludges by using dedicated tanks to store specific product types. Capital, operating and maintenance costs are estimated to be zero; estimated source reduction benefit is unknown at this point. Unocal mentioned that the only barrier to implement this measure would be that it should not affect existing processing capabilities or product quality.

UNOCAL, Los Angeles Plant, Wilmington Plant:

Evaluate/Implement Process Modification to Reduce Stretford Sulfur Waste: Stretford waste is generated in the tail gas unit. Unocal uses a Beavon Stretford (Stretford) process. The Stretford Plant processes the sulfur recovery plant off gases to recover residual sulfur compound. The sulfur cake removed by the Stretford process contains residual vanadium. This sulfur cake is not saleable as elemental sulfur due to its undesired structure as well as its vanadium impurities. The vanadium content classifies the sulfur cake as a non-RCRA hazardous waste. This material, according to the regulations, cannot currently be sold for use in the fertilizer industry. Therefore, Unocal is currently sending it to a landfill for disposal.

Unocal is examining process modifications that will add heat exchange and evaporation capacity to the tail gas unit thus allowing additional cake washing to remove vanadium. This modification will make sulfur cake a saleable product to the fertilizer industry. The resultant sulfur will no longer be classified as a hazardous waste due to vanadium content. Capital, operating and maintenance costs per year for this project are \$400,000, \$100,000 and \$4,000 respectively. More than 1,500 tons per year of this waste will be reduced.

Implement Tank Block Modifications: The refinery's oily process waters and oily stormwaters are treated initially at the waste water treatment plant by the API separator. The separator uses gravity and retention time to separate and recover bulk amounts of oil from the process water and stormwater collected in the refinery sewer system. Heavier solids contained in these waters are removed as a sludge from the bottom of the separator. The waste water then flows to Unocal's three dissolved air flotation units, where emulsified oil and some solids are removed through the addition of flotation air and treatment chemicals. The key to reducing the quantity of sludge and float is minimization

of solids entering the refinery sewer system. Solids sources to the refinery sewer system originate from solids present in the raw crude, solids from raw water, solids from unpaved plant areas, solids entering the sewers during turnaround activities, unit maintenance washdowns, and residual solids on the unit pads from routine operations.

These source of solids to the oily process sewers will be reduced by placing chad rock on the earthen tank block floors to impede solids entrainment to sewers. This approach also includes installing paving and small berms around sewer openings in the tank blocks to impede solids from entering the sewer. Unocal also plans to implement stormwater impoundment cleaning. Again, the source of solids to the oily process sewers will be reduced by cleaning dirt and debris from stormwater surface impoundments prior to the rainy season. These solids could potentially enter the sewer when the stormwater is managed in the unsegregated sewer system. While capital and operating costs of both these projects are zero, the maintenance cost is estimated at \$30,000 per project per year. Source reduction of the waste is estimated at 200 tons annually per project.

UNOCAL, San Francisco Refinery:

Substitute Nickel-Based Catalyst for the Current Copper-Based Catalyst: Numerous refinery processes units use catalysts, including the hydrocracker unit and its associated catalytic reformer and unisar units, the isom units, and the steam power plant. Spent catalysts are periodically removed from these process units during unit turnarounds and replaced with new or regenerated catalysts.

Unocal's sulfur sorber reactor currently uses a copper-based catalyst. A nickel-based catalyst has been identified as having the potential to approximately double service life for the unit from approximately 22 months to 46 months. If successful, this catalyst substitution would achieve approximately 50% source reduction of the spent catalyst waste stream originating at this particular reactor. Approximately 28 tons of spent catalyst is currently generated from this reactor during turnaround.

Unocal has already determined that this alternative is technically feasible. Although the cost of the nickel-based catalyst is almost double the cost of copper-based catalyst, installation of the nickel-based catalyst would reduce the total catalyst replacement cost by 5 percent due to its longer life.

Repair Heat Exchanger Leak: The low temperature shift reactor currently uses copper- and zinc-based catalyst and has historically achieved runtimes lasting approximately four years. However, over the last four to six years, runtimes lasting only one to two years have been achieved. An operational problem has been identified that appears to be the cause of these shortened runtimes; specifically a heat exchanger leak was found that, when combined with a changed chemical treatment of boiler water, may have resulted in the preliminary deactivation of the catalyst. The heat exchanger leak was repaired at the most recent unit turnaround and should enable the reactor to again achieve four year runtimes.

Approximately 70 tons of spent catalyst is currently generated from this particular reactor during turnaround. The reactor can again achieve four year runtimes, thereby 50 percent to 75 percent source reduction of the portion of the spent catalyst waste stream originating from this particular reactor can be expected. Unocal engineers already determined that this alternative was technically feasible.

WITCO CORPORATION, Oildale Refinery:

The Witco's oildale refinery, processes selected local crude oils to produce a variety of hydrocarbon products such as refined lubricating oil base stocks, finished lubricating oils, asphalt, specialty oils and diesel fuel. Witco's 1994 SB 14 documents declared only one major hazardous waste stream: Tank bottoms. Approximately 500 tons of this waste were generated in 1994. This waste stream contains only asphalt and lime. This tank bottom waste was generated through the use of lime slurry to neutralize acids present in the refinery crude oil feedstock. Acids must be neutralized to produce neutral or near neutral distillates that meet manufacturing specifications. An excess lime is the traditional neutralizing treatment, and this creates the tank bottom waste stream.

Witco has developed a plan to reduce the excess lime usage, which in turn, reduces the quantity of asphalt tank bottom generated. The long range plan calls for not allowing unreacted lime to reach the distillation unit. This plan will use saturated lime water to react with the acid in the crude. The water will be separated from the crude prior to crude entering the distillation unit and, after cleanup, is recycled back to be saturated with lime makeup and consequently redirected back to neutralize the crude feedstock. The refinery's conservative estimate suggests that at least 95 percent reduction of this waste

can be achieved after 1994. This projection is based on the refinery's laboratory and limited pilot plant experiments. Further pilot studies are needed to select proper equipment for full scale operation. An Economic evaluation indicated that the costs of designing and installation of the new full size equipment will be recovered in three to four years.

V. CASE STUDIES

The following section presents three case studies. Each was selected to describe in detail its past achievements and future projections for hazardous waste reduction. These are beneficial measures that can be employed generally at most refineries.

1. Unocal San Francisco Refinery

The Unocal San Francisco Refinery is located in Rodeo, Contra Costa County and has operated at the same location for the last 100 years. Unocal's production at this facility includes butane, various grades of gasolines, diesel fuel, jet fuel, lubricating oils, fuel oils, waxes, sulfur, and petroleum coke. In order to produce these specific products, the refinery is designed to process two specific types of crude oil: San Joaquin Valley Heavy crude and Alaskan Cook Inlet Crude oil.

Unocal has several process units at its present location. More than half of the currently operating process units have been constructed since the early 1970s. A new coking unit and a new crude distillation unit were constructed in the 1980s, and the addition of sludge coking facilities to the coking unit were completed in the early 1990s. Unocal started its reformulated gasolines (CARB gasoline) construction project during early 1995, and were planning to complete in fall 1995.

Unocal's 1995 Plan identified the following major waste streams:

- Stretford solution
- Tank bottoms
- Spent catalyst
- Stretford solids and
- Oily trash

Unocal generated 6,080 tons and 5,800 tons of SB 14 applicable nonaqueous hazardous waste during reporting year (1994) and baseline year (1990) respectively. Although it appears that Unocal increased its waste generation by approximately 5 percent in the reporting year compared to the baseline year, the refinery estimates that it has actually achieved a source reduction of approximately 18.4 percent between 1990 and 1994. This reduction is measured by the ratio of the total quantity of major hazardous waste generated to total raw material throughput (i.e. total quantity of major hazardous waste streams generated normalized to production).

Unocal generated 420,000 tons and 355,000 tons of SB 14/SB 1133 applicable aqueous waste during 1990 and 1994 respectively, a reduction of 15 percent or 65,000 tons. The percent reduction would be greater if a normalization factor was considered in this particular reduction calculation.

The following table provides a comparison of Unocal's major hazardous waste generation totals in 1990 and 1994:

Hazardous Waste Reduction Percentage

<u>Nonaqueous</u>	<u>CWC</u>	<u>Generation</u> <u>1990</u>	<u>Tons</u> <u>1994</u>	<u>Change</u> <u>Percent</u>
Stretford solution	132	3,842	3,620	5.8
Stretford solids	181	58	358	(517)
Spent catalyst	162	716	527	26.4
Oil/water sludges	222	616	5	99.2
Oily trash	223	56	333	(495)
Tank bottoms	241	30	997	(3223)
TOTAL (Major & Minor Waste Streams)		5,800	6,080	(5)

Aqueous

Phenolic sour water	132	241,100	236,600	2.1
Unicracker water	132	120,000	60,000	50.0
Steam pwr, plnt. water	132	60,000	60,000	0.0
TOTAL		421,100	356,600	15.0

Past Achievement - 1990 - 1994

Unocal identified six major waste streams for the 1990 baseline year: Stretford solution, spent catalyst, oil/water separator sludge, phenolic stripped sour water, unicracker demineralizer regeneration water, and steam power plant demineralizer regeneration water. All were identified as major streams for the 1994 reporting year, except for oil/water separator sludge. Three additional major hazardous waste streams were added in the 1994 reporting year: Stretford solids, oily trash, and tank bottoms.

The following section discusses the evaluation of progress made from 1990 to 1994 for reducing the nine waste streams identified in the Unocal 1994 Hazardous Waste Management Performance Report:

Stretford solution/Stretford solids (CWC 132/CWC 181)

These waste streams represent 65 percentage of the total hazardous waste streams generated in the current reporting year. These are the most significant of Unocal 1994 hazardous waste streams. Therefore, they have been the focus of numerous source reduction and waste minimization efforts over the last four years as discussed below:

- Startup of Verti-Press filters - Unocal observed that the heating of Stretford solution in autoclaves was contributing to an accelerated rate of thiosulfate by-product formation, which in turn was necessitating more frequent purges of the Stretford solution than was desirable. In 1991, Unocal installed two Verti-Press filter units to replace Beavon-Stretford plant autoclaves. Although the filter presses have had minor operational problems, in general, Unocal felt that the presses have led to a significant net reduction in the generation of Stretford solution.
- Reslurry sulfur from filter presses to autoclaves - After startup of the ventri-press filters in 1991, Unocal attempted to reslurry sulfur from the verti-press filters cake with condensate and then return the slurry to the autoclaves in order to melt the recovered sulfur. Sulfur purified by melting has a much greater value on the open market than sulfur filter cake, which, due to low demand is usually disposed in the landfill. However, Unocal discontinued these attempts due to multiple operational problems, including getting the slurry into the sulfur pit, corrosion problems, and line plugging problems.
- Door sheets installation in the baffle of the oxidizer tanks - Unocal installed doorsheets on two of the three internal baffle plates found in each of the three Stretford oxidizer tanks. Implementation of this alternative facilitated the removal of Stretford solids from the tanks during changeouts and had the net effect of increasing the quantity of Stretford solids generated. However, it facilitated the cleaning of the oxidizer tanks, and therefore, resulted in a decrease in the quantity of Stretford-contaminated wash water generated, to an extent that more than offset the increase in generated solids.

- Change from continuous batch purging - Unocal's standard practice was to purge Stratford solution on a continuous basis. Up to 20,000 gallons of spent Stretford solution per week (equivalent to a million pounds per year) was continuously purged. Following the first 1993 quarter changeout, Unocal discontinued continuous purging due to operational considerations. The units ran from first quarter of 1993 changeout until the October 1994 changeout without any purges, a 16 month batch run. During the October 1994 changeout, Unocal purged the entire inventory of Stratford units. This resulted in the generation of approximately 350,000 gallons of spent Stretford solution. The net effect of this change was to decrease the yearly generation rate of spent Stretford from a maximum of approximately one million gallons to a maximum of about 262,000 gallons, i.e. 350,000 gallons over 16 months.
- Regeneration of Stretford solution using the Global Sulfur Systems, Inc. Process - The Global process is a portable treatment process designed to extend the life of a given charge of Stretford solution by removing contaminants such as thiosulfates from the Stretford solution prior to the contaminants' accumulation to concentrations that would render the solution spent. The Global process accomplishes this removal by converting thiosulfates to sodium sulfates and then removing the sodium sulfates from solution. Implementation of the Global process alternative would theoretically result in reduced hazardous waste generation rates by 50% or more, due to the extended run times that would be made possible for a given charge of Stretford solution.

Unocal made an attempt during 1992 to implement the Global source reduction alternative. Unocal experienced numerous operational difficulties and implementation was stopped for reasons of technical performance and cost. Although the attempt to implement the Global process in 1992 was unsuccessful, Unocal will evaluate this approach again, since the process has a potential to significantly source reduce Unocal's largest hazardous waste stream.

In summary, the Stretford solution/Stretford solids generation for 1990 and 1994 were 3,900 tons and 3,978 tons respectively, a two percent increase. Among other factors discussed above, the greatest single factor influencing Unocal's Stretford solution/solids waste generation rates between 1990 and 1994 was the timing and scale of solution changeouts. The lowest quantity of Stretford was generated

during 1992 (2,750 tons), when the attempts at using the Global process took place, and before the major solution changeout occurred in the first quarter 1993. Total raw material and total undiluted crude throughputs were also increased by 12.2 percent and 10.6 percent respectively from 1990 to 1994.

Spent Catalyst (CWC 162)

Numerous refinery process units use catalysts, including the hydrocracker unit, and its associated catalytic reformer and unisar units, the isom unit, etc. Spent catalysts are periodically removed from these process units during unit turnarounds and replaced with new or regenerated catalysts. During 1990, Unocal generated spent cobalt/molybdenum, nickel/molybdenum, palladium, chromium/nickel, and copper/zinc based catalysts. Unocal manifested all spent catalysts offsite as hazardous waste to metal recycling/reclamation facilities. The offsite facilities either regenerated the spent catalysts or used leaching/chemical precipitation processes in order to reclaim metals from the spent catalysts. The following discusses the two source reduction measures used to manage this waste stream:

- Maximize process unit run length - The run length of some catalysts were increased during the 1991-1994 period, resulting in the net effect of reducing the quantities of spent catalyst generated. The midbarrel unifier catalysts formerly had been changed out every nine months, but sufficient capacity was available to extend the run length to 24 months from 1993 to 1995.

Unocal generated 715 tons, 162 tons, 527 tons of spent catalysts during 1990, 1991, and 1994 respectively. The overall trend in spent catalyst generation is generally one of decrease.

Oil/Water separator sludges (CWC 222)

Implementation of one source reduction alternative, the sludge coking facilities, had the net effect of reducing the amount of oil/water separator sludge manifested offsite for disposal by more than 99%-as cited by Unocal. Unocal treatment/disposal data as offsite management of this waste indicates that they managed 617 tons vs. only 5 tons of this particular waste in the 1990 baseline vs. the 1994 reporting year. In 1994, 1,836 tons of oil/water sludges were used as feedstock for the coker.

Unocal also implemented several programs during this reporting period to prevent solids from entering the waste water collection system which were cost effective and resulted in reducing the formation of sludges and the need to manage these sludges.

- Construction of sludge coking facilities at the delayed coker - Test runs for the sludge coking facilities at Unocal were conducted in December 1990 and March 1991; the permanent facilities were placed into service on July 10, 1992. The sludge coking facilities enabled Unocal to process oil-bearing material concurrently with normal process streams in order to produce refined petroleum products. Previously these sludges were discarded as wastes and included as tank bottoms and oil/water separator sludges.

The following is a listing of the projects Unocal successfully implemented to prevent solids entering their waste water collection system: 1) street sweeping, 2) construction of sediment catch basins/runoff trench systems for solids collection, 3) erosion control program, and 4) unit sweeping.

Unocal documented solids collection over the four year reporting period which ranged from 19,700 pounds (in 1991) to 91,400 (in 1993) and averaged approximately 50,000 pounds annually. The actual amount of solids prevented from entering the waste water collection system was greater, due to non-documented solids collection efforts and to the unquantifiable effect of an erosion control program implemented on an adjacent hillside and embankments. This effort has likely captured solids at quantities at least double the rate attributed to the documented efforts. Assuming each pound of solids entering the waste water collection system gives rise to eight pounds of oil/water separator sludge, these solids control programs in their aggregate likely prevented, on an annual basis, the formation of 800,000 pounds of oil/water separator sludge.

Tank Bottoms (CWC 241)

Unocal did not have any routinely scheduled tank cleaning activities in 1990. They cleaned only two tanks in 1990 to perform repairs. Like oily trash, tank bottoms were not a "SB 14 significant" waste stream during 1990 baseline year. In order to comply with a new regulatory program starting in 1992, Unocal cleaned a total of 15 tanks annually compared to the two cleaned in 1990. This had a net effect of increasing this waste category by more than 3000 percent between 1990 and 1994.

- Construction of sludge coking facilities using tank bottoms - The sludge coking facilities can be used to process many oil-bearing materials, including tank bottoms. After successful test runs and securing a permit to operate, Unocal successfully processed more than 95 percent of their tank bottoms as coker feedstock during 1994.

Phenolic stripped sour water (CWC 132)

Phenolic stripped sour water is classifiable as hazardous due to its selenium concentration of 5 mg/l. Unocal made attempts to implement the following three measures resulting in the reduction of 4,500 tons from baseline to reporting year: 1) Selenium source control study - several recycling measures were implemented to control the volume of selenium laden waste water and to reduce water usage during the drought period in early 1990's. Approximately 10 gallons per minute (gpm) of the phenolic stripped sour water from the coking unit was being recycled as heater coil injection water. The phenolic stripped sour water was identified as having the highest selenium mass load at Unocal. All non-phenolic-stripped sour water was being recycled as either process wash water or cooling tower make-up water. The reuse as cooling tower make-up resulted in a 10% to 20% removal of selenium across the cooling tower system. 2) Treatment approaches using unit #100 - in 1993, a temporary connection was installed at Unit 100 that allowed the phenolic stripped sour water to be introduced upstream of the DAF unit, as opposed to downstream. The objective of the temporary connection was to facilitate the evaluation of: a) potential selenium removal across the DAF unit, b) potential solids removal across the DAF unit, and c) to test if the phenolic stripped sour water stream would assist in killing coliform bacteria within the DAF unit. The temporary connection had only been used to facilitate waste water treatment evaluations and was used only for one month at a time. and 3) Pilot study to evaluate new treatment processes - During 1995, Unocal started a pilot study to evaluate the use of ion exchange resins for treating selenium-containing waste water. The initial results of the pilot study were being evaluated at the time. Unocal planned to scale-up to full-scale plant, if the results were promising.

Unicracker demineralizer regeneration water (CWC 132)

Between the 1990 baseline and 1994 reporting years, Unocal reduced this waste stream by 60,000 tons (50 percent). In the years following the 1994 reporting year,

Unocal expects to reduce this waste stream by more than 95 percent. The success can be attributed to the installation of a reverse osmosis unit placed upstream of ion exchange units and an elementary neutralization tank located at the unicracker.

Some of the above measures are noteworthy in spite of being treatment or recycling and not source reduction. SB 14 encourages generators to include in their 1995 Reports, all types of measures including treatment and recycling, implemented during 1990-1994 for their hazardous waste reduction efforts.

Plan to Reduce Hazardous Waste During 1994-1998 and Beyond

The hazardous waste streams generated at Unocal in 1994 were divided into two categories for the purpose of determining the major hazardous waste streams: hazardous process (nonaqueous) waste, and hazardous industrial waste waters (aqueous waste). A hazardous process waste defined as any solid, sludge, or liquid that was shipped (manifested) offsite for recycling, treatment, and/or disposal or any solid or sludge that was managed onsite through recycling, treatment, or disposal. A hazardous industrial waste water or aqueous waste is defined as any hazardous liquid waste arising from a refining or other industrial process that was treated in Unocal's industrial waste water treatment plant and subsequently discharged to San Pablo Bay under the conditions stated in Unocal's NPDES Permit No. CA0005053.

Unocal generated a total of 6080 tons of nonaqueous, SB 14 applicable waste during 1994. This was comprised of five major SB 14 hazardous waste streams each constituted more than 5 percent of the total nonaqueous hazardous waste generated: Stretford solution (comprising 59.5 percent of the total hazardous process waste generated; Tank bottoms (16.4 percent); Spent catalyst (8.7 percent); Stretford solids (5.9 percent); and Oily trash (5.5 percent). In addition, three aqueous hazardous waste streams, the phenolic stripped sour water, unicracker demineralizer regeneration water, and steam power plant demineralizer water. Each of these wastes comprised more than 5 percent of the total hazardous waste generated at Unocal during 1994 (including both hazardous process wastes and industrial waste waters) and thus were defined to be major waste streams under SB 14. Aqueous and nonaqueous waste create a total of eight major hazardous waste streams generated at Unocal during 1994.

Unocal identified and evaluated source reduction alternatives for these eight major waste streams and one nonmajor waste stream - oil/water separator sludges in 1994. The refinery identified 27 source reduction measures. Two waste minimization alternatives were identified for the nine waste streams using the following three SB 14 source reduction approaches: 1) operational improvements, 2) production process changes, and 3) administrative steps. Six of these alternatives were rejected as infeasible. The remaining 21 source reduction measures were selected and given high and low priorities. Ten priority measures were identified, and an implementation strategy for these higher ranking measures was developed. Discussion of each selected measure is beyond the scope of this assessment report, however, we encourage those who are interested, to review Unocal's 1994 SB 14 documents. A listing of all twenty one source reduction measures is contained in Appendix B. and examples of source reduction selected measures' abstracts are contained in Appendix E.

Unocal's goals for reducing its major waste streams is very ambitious. If the modified Global process source reduction alternative for Stretford waste streams can be successfully implemented, Unocal's overall source reduction goal for hazardous nonaqueous waste for the 1994 to 1998 reporting period will be 43 percent. If the Global process implementation proves either technically or economically infeasible, Unocal's overall source reduction goal for the period will be revised downwards to 15 percent. In terms of weight reduction, 43 percent reduction amounts to an annual reduction of more than 2,600 tons of nonaqueous waste.

The total raw material throughput at Unocal increased by 12.2 percent between 1990 and 1994. Due to new regulations Unocal implemented its aboveground tank cleaning and inspection program. If tank cleaning had not occurred, the major waste stream generation rate would have decreased by approximately 8.2 percent between baseline and reporting year. Combining the two factors, Unocal achieved source reduction of approximately 20.4 percent for its major waste streams between 1990 and 1994.

2. ARCO Products Company

The ARCO Products Company is located in Los Angeles area and was originally constructed as a part of the Pan American Oil company. Currently, it has a crude oil processing capacity of 245,000 barrels per day. Major process units include three crude oil distillation units, two vacuum distillation units, a fluid catalytic cracking (FCC) unit, three reformers, two delayed cokers, a

hydrocracker, a hydrotreater, an alkylation plant, an MTBE unit and a sulfur tailgas recovery unit. The waste water treatment plant operated at the refinery includes API separators and induced gas flotation units.

The products produced by ARCO include gasoline, jet fuel, diesel, sulfur, coke, propane, butane, fuel oil and carbon dioxide.

The refinery generated nine SB 14 waste streams by CWC code during 1994 totalling 1.337 million tons. One out of nine wastes was a major aqueous waste stream and two were major nonaqueous wastes. They were: 1) waste water (CWC 135) - 1.332 million tons 2) waste water sludges (CWC 222) - 3,190 tons and 3) polymerization catalyst (CWC 161) - 413 tons.

The refinery generated thirteen SB 14 nonaqueous waste streams by CWC code during 1990 totaling 12,100 tons. Three out of thirteen waste streams were major waste streams. They were: 1) Oil/water separator sludge - 9,626 tons (79.5 percent) 2) Oil containing waste (CWC 223) - 1,327 tons (11 percent) and 3) Sand blast media (CWC 181) - 667 tons (5.5 percent).

Comparison of major hazardous waste streams are as follows:

Nonaqueous:

<u>Waste</u>	<u>CWC</u>	<u>1990</u> <u>tons</u>	<u>1994</u> <u>tons</u>	<u>Reduction</u> <u>Percentage</u>
Polymerization* catalyst	161	290	413	(42)
Sandblast sand	181	667	20	97
Waste water sludge	222	9,626	3,189	67
Oil-containing waste	223	1,327	218	84
TOTAL (Major and Minor)		12,110	4,963	59
* not a major waste stream				

Aqueous:

<u>Waste</u>	<u>CWC</u>	<u>1990</u> <u>tons</u>	<u>1994</u> <u>tons</u>	<u>Reduction</u> <u>Percentage</u>
Waste water discharged to POTW	135	9.158x10 ⁶	1.332x10 ⁶	85

The following section describes the evaluation of progress made from 1990 to 1994 for the reduction achieved for the four waste streams identified in the 1995 Hazardous Waste Management Performance Report:

Polymerization catalyst (CWC 161) Generated quantities of this hazardous waste increased by 43 percent from 1990 to 1994. The increase was attributed to a change in the method of spent catalyst removal from the reactors. In the past, spent catalyst was water blasted but at present it is dry-drilled and chipped from reactor walls. The wet method resulted in losses of solids to the sewer becoming hazardous waste water sludges.

Sandblast sand (CWC 181) The generation of hazardous waste sandblast sand has been reduced by 97 percent. This has resulted from the use of alternative abrasive that did not have high metal content. In addition, successful efforts were undertaken to reduce the actual use of some sands. In 1995, Dewayne Reeher of maintenance department won a \$2,000 corporate stamp out waste award for his successful efforts to reduce the use of hydrohone sand-a grit high in hazardous metals content.

Waste water sludges (CWC 222) Hazardous waste water sludges accounted for less than 7 million pounds generated in 1994. This is a 67 percent reduction from the waste water sludge generation rate in the 1990 baseline year. These sludges are formed from oil and solids that enter the refinery waste water system and are then removed during the treatment of the waste water to meet POTW discharge standards. This waste is comprised of 1) API separator sludge 2) DAF float and 3) primary sludges. The refinery has characterized these sludges and have identified the following four major sources:

- Dirt from the refinery that enters the oily water sewer.
- Calcium salts from the refinery water supply that precipitates in the refinery waste water system.
- Dirt from the producing formation that enters the refinery with the crude oil.
- Heavy oil that becomes attached to the dirt and precipitates in the oily water sewer.

In 1993 ARCO spent more than \$100,000 to study source reduction options for waste water sludges. Due to this study, several projects were implemented. Many projects were also implemented from the selected measures selected in

the 1990 SB 14 Plan. The following is a partial list of successful projects implemented to reduce sludges:

- Increase street cleaning frequency.
- Application of asphalt to unpaved areas.
- Modify FCC catalytic polymerization dumping procedure.
- Reduce FCC catalyst fine losses.
- Plantwide closed loop sampling system.
- Modify tank basins for stormwater bypass.
- Common cooling tower blowdown header.

ARCO selected six source reduction measures for their three major waste streams in 1994. The refinery's numerical goal for reducing the amount of hazardous waste generated is 20 percent. The following summarizes each selected measure's detail to reduce hazardous waste during 1994-1998 and beyond.

Polymerization catalyst (CWC 161):

Measure: Begin Agricultural use of spent catalytic polymerization catalyst.

The catalytic polymerization unit converts propylene from the FCC unit into gasoline blending stock and commodity chemicals. This reaction occurs in ten vertical reactors and is activated by a catalyst consisting of phosphoric acid on extruded silica-alumina pellets. This material is called cat poly catalyst. Spent catalyst is removed from the reactors approximately eighty times per year. This spent catalyst is non-RCRA hazardous waste due to its corrosivity. This corrosivity is due to its phosphoric acid content.

Phosphoric acid is widely used in agricultural and horticultural applications. A project is underway to divert this material from the landfill to useful product in the agricultural industry.

Oil/water separation sludge (CWC 222):

Measure: Divert Cogeneration cooling tower blowdown to the cooling tower header.

Calcium salts in the refinery water supply causes an increase in the generation of waste water sludges. When cooling tower blowdown enters the refinery waste water system the sludge formation increases due to the high concentration of calcium salts resulting from evaporation. In 1991, the refinery installed a separate system which segregates refinery cooling tower blowdown from the process sewers. At the time of installation, the cooling tower operated by the Watson Cogeneration Company was not included in the project. The cooling tower blowdown diverted from the oily water sewers is combined with treated process waste water in Tank 95 prior to discharge to the local POTW.

While the majority of the calcium precipitation in the refinery was eliminated by segregation, precipitation of calcium salt occurs in Tank 95, generating sludge. This precipitation will be reduced when the Watson cooling tower system is installed.

3. Ultramar

The Ultramar Refinery processes 100,000 barrels per day (BPD) at its Wilmington facility, southern California and produces gasoline, low sulfur diesel, jet fuel, fuel oil, fuel-oil blending components, sulfur, propane, and fuel gas. Their Report was prepared for the 1994 reporting year, with 1990 cited as the baseline year.

Ultramar's 1995 Plan identified the following major waste streams:

- Stretford solution (CWC 135)
- Alkylation sludge (CWC 181)
- Oily Sewer and API sludges (CWC 222)
- Spent Alumina catalyst (CWC 162)
- Tank Bottom Sludge (CWC 241)
- Fluid Catalytic Cracking (FCC) fines (CWC 161)

This refinery is equipped with two conventional crude oil distillation units, a vacuum fractionator unit, two delayed cokers, a fluid catalytic cracking (FCC) unit, reformer, hydrotreater, hydrorefiner, hydrogen fluoride (HF) alkylation unit, and a sulfur tail gas recovery unit. The refinery also operates a waste water treatment process using an oil/water separator and a dissolved air flotation/induced air flotation (DAF/IAF) unit.

Ultramar's primary product, finished gasoline, production in 1994 was approximately same as in 1990. However, the refinery's overall hazardous waste generation decreased to 1,660 tons during the reporting year 1994 compared to 4,835 tons in the baseline year 1990. These totals represent 66 percent reduction in the refinery's hazardous waste generation. In addition, approximately 61 percent of the Ultramar's 1994 hazardous waste generation was recycled.

The following table provides a comparison of Ultramar's major hazardous waste generation totals from 1990 to 1994:

<u>Hazardous Waste</u>	<u>CWC</u>	<u>Generation</u> <u>1990</u>	<u>Tons</u> <u>1994</u>	<u>Reduction</u> <u>Percentage</u>
Stretford solution	135	2,378	108	95
FCC fines	161	557	588	(5)
Spent alumina catalyst	162	325	155	52
Alkylation sludge	181	671	411	39
Oily sewer and API sludge	222	463	269	42
Tank bottom sludge	241	168	108	36
TOTAL (Major and Minor) (Waste streams)		4,835	1,660	66

Past Achievements - 1900-1994

Overall four year hazardous waste reduction:
3,175 tons.

Stretford solution reduction (CWC 135) Crude oil processed by the refinery contains contaminants such as sulfur which must be removed prior to processing. Sulfur removed from the crude is carried by the main refinery amine system to the sulfur plant. The sulfur plant processes the sulfur compounds to elemental sulfur using a Stretford process. Consequently, the residual gaseous sulfur from the sulfur plant is removed by the tail gas treating unit (TGTU) to meet stringent environmental regulations. The circulating tail gas solvent is "Stretford Solution" which contains vanadium. Over time, the Stretford solution accumulates thiosulfates which in effect reduces the solution effectiveness. Spent Stretford solution is a hazardous waste due to vanadium contamination from vanadium catalyst and from high alkalinity (pH > 12.5).

The installation of the new TGTU resulted in the reduction of Stretford solution by > 95 percent. In 1992, Ultramar completed the construction of a new TGTU which replaced the refinery combined amine tail gas treater and Stretford unit, and at the same time it upgraded the refinery main amine system to process 180 tons per day of sulfur. The new TGTU and Stretford unit allow for increased high sulfur crude processing while maintaining strict compliance with sulfur emissions limitations. The old Stretford unit was retained as a backup allowing the refinery to continue operation (albeit at a reduced sulfur crude feed) while the TGTU is out of service.

Alkylation sludge reduction (CWC 181) Ultramar reduced alkylation sludge by 40 percent starting in 1994. Byproducts of the alkylation unit process are two highly acidic streams that are neutralized with potassium hydroxide (KOH). KOH is spent to potassium fluoride (KF) which is reconverted to KOH using lime. The residual (alkylation sludge) is a precipitate, composed principally of calcium fluoride, which is managed as a hazardous waste.

Oil/Water separation sludge (CWC 222) A number of refinery oil-bearing sludges are separated at the waste water treatment plant. These waste streams originate primarily from process sewers and the tank cleaning operations. Ultramar recycles these sludges back into its delayed coking operation under license using the patented Mobil oily sludge coking (MOSC) process. The MOSC process uses process water mixed with oily sludges as a partial substitute for quench water in the final stage of the coking cycle. Oily sewer and API sludges have been recycled in Ultramar's MOSC unit since November 1987. Implementation of this process has practically eliminated generated waste water sludge by an annual amount of 460 tons.

Spent alumina catalyst (CWC 162) The refinery reduced spent catalyst by 52 percent, from a 1990 generation of 325 tons to a 1994 quantity of 155 tons. In 1993, Ultramar entered into an agreement with suppliers to take the refinery spent catalysts from the Alkylation unit for reuse in the production of fresh alumina catalyst. The suppliers could not handle spent catalyst high volume and packaging. Therefore Ultramar's recycling effort was only partially successful. Ultramar investigated the feasibility of using all the spent catalysts as process feed to cement production. Since 1994, spent alumina catalysts have been recycled as process feed in cement kiln foundries.

VI. SUMMARY

1. Actual data based on the twenty four facilities covered in the second review based on 1995 Performance Reports, the petroleum industry indicates that 32 percent of its annual hazardous waste generation was reduced during the 1990-1994 period. This amounted to more than 61,000 tons annually. The above data reflect all hazardous wastes except aqueous hazardous waste treated in the onsite aqueous waste treatment plants. With current hazardous waste disposal costs for petroleum waste ranging from \$125 to \$750 per ton, these reductions are estimated to have saved the petroleum industry \$7.6 to \$45.7 million annually.

For the initial documents prepared during the first cycle (September 1991), many of the petroleum industry generators did not address aqueous waste streams in their source reduction evaluation which were included in their current 1995 documents. SB 1133 was enacted September 5, 1991 and clarified the requirements for evaluating both aqueous and non aqueous waste streams. Therefore, comparison of 1990 and 1994 aqueous waste reduction is not feasible.

2. Based on our review of the latest documents (1995) produced under the Act the industry projects that it will implement 122 measures during the 1994-1998 cycle. Based on review of the 1995 planning efforts, it is projected that the industry nonaqueous hazardous waste reduction can achieve an additional 31 percent of hazardous waste reduction over the next several years. This projection amounts 53,500 additional tons annually reduced over the 61,000 tons annual reduction achieved during the initial SB 14 planning cycle (1990-1994). If fully achieved, this can result in an additional annual savings of \$6.7 to \$40.1 million.
3. In 1994, the petroleum industry generated 16.7 million tons of aqueous waste. It is estimated that collectively, the petroleum industry will reduce approximately 2.0 percent or 0.34 million tons annually of hazardous aqueous waste during 1994 - 1998 and beyond.
4. Oil/Water separator sludge was number one waste stream during 1994 and it may remain number one in the future too. In the previous cycle the industry selected 33 measures to reduce this waste stream and in this second cycle it selected 44 measures.

5. No extremely hazardous waste was generated during 1994. During first cycle two sites mentioned extremely hazardous waste generation in 1991. Both eliminated these waste streams between 1991 and 1995.

APPENDIX - A

Refinery Operation Description

Refinery Operations

For the purpose of simplifying the presentation this discussion on refinery operations has been divided into four basic categories: Fuel Production; By-Product Processing; Ancillary Operations and Waste Water Management. Fuel Production encompasses those operations which manufacture petroleum products such as gasoline and coke. By-Product Processing covers refinery operations that convert used materials and/or undesirable petroleum constituents into salable or reusable end products. Ancillary Operations include those activities that support refinery functions and recover energy. Finally, Waste Water Management deals with the treatment of refinery waste waters including the recovery of usable oil products from refinery waste water streams.

Petroleum Product Production

There are three basic raw materials used in the crude oil refining process : crude oil; catalysts; and process chemicals. Heat, the final component in this process, is used to accelerate reactions, separate components, and reduce viscosity. Crude oil arrives at the refinery by ship or pipeline and is stored in tankage prior to processing. Initial separation of crude components occurs in distillation columns. Subsequently, materials recovered by distillation are used as a fuel source in the refinery, or sent to other processes to generate useful products. The processes used to produce salable petroleum products are discussed in further details in the following sections.

Distillation

Distillation is the first process a barrel of crude oil encounters after it leaves the crude oil storage tanks in the refinery. Crude oil consists of many miscible substances all with different boiling points. While it is virtually impossible to separate each compound in crude oil individually, the distillation process uses temperature and pressure control to effectively separate groups of compounds with similar boiling points into unique mixtures.

Crude oil is initially heated and salts are removed prior to distillation. The first material to separate out from the crude oil mixture during distillation is the sour (hydrogen sulfide containing) gases. Sour gases are routed to refinery plants so that hydrogen sulfide can be separated from fuel gases. Hydrogen sulfide does not have value as a fuel source but is an important source of sulfur which can be recovered for use in the refinery or for resale to other industries. The next fraction removed during distillation are propane and butane. These materials can be processed further and sold as liquefied petroleum gas (LPG), used as an in-plant fuel source or used to produce hydrogen or other chemicals.

Continued fractionation in the distillation columns yields gasoline, jet and diesel fuels. The lower boiling materials, gas oil and reduced crude, are the last materials to separate and require additional processing to reach desired endpoints. Reduced crude is used as feed material in vacuum distillation columns (distillation under vacuum lowers the boiling point of the materials and eases separation).

Hydrotreating

Hydrotreating is a catalytic process which uses hydrogen to improve the stability of and remove impurities from distillation products. Impurities in crude oil such as sulfur, nitrogen and metals must be removed to meet product specifications and to prevent poisoning of catalysts used in some down stream processes. A potential negative side effect of hydrotreating is hydrocracking. During hydrocracking desirable hydrocarbons are broken up into potentially unusable by-products.

Catalytic Reforming

Catalytic reforming employs catalysts to mediate reactions that boost the octane level of distillation products. During the process of catalytic reforming, hydrogen is produced for use in hydrotreating. Catalytic reforming encompasses four types of reactions:

- 1) Dehydrogenation of naphthene to produce aromatics.
- 2) Dehydrocyclization of paraffins to naphthenes and aromatics.
- 3) Isomerization of naphthenes and paraffins to more highly branched isomers.
- 4) Cracking of naphthenes and paraffins to shorter hydrocarbon chains.

The fourth reaction listed above is undesirable because it reduces yields, lowers hydrogen purity and consumes hydrogen.

Hydrocarbon Cracking

Hydrocarbon cracking is a process in which large molecules are cleaved into smaller ones. This process can be accomplished either thermally or catalytically resulting in maximization of salable products from crude oil.

During catalytic cracking of hydrocarbons, the catalysts act to increase the yield of desirable products and minimize the production of less useful materials, or allow cracking to occur at more favorable temperatures and pressures.

Thermal cracking, which occurs in the coker, is a process that is typically used to crack the heaviest hydrocarbons, the residuum. Coke, a hydrogen poor (carbon rich) by-product of thermal cracking is left over after heating, is also sold as a fuel source.

By-Product Processing

During the petroleum product refining process, by-products are produced that have resale value or they may be reused directly in refinery processes thus displacing normal feed stocks. Some of these by-products, such as hydrogen sulfide which is used in sulfur production, are natural constituents in crude oil that are removed to make the products cleaner. By-product processing at the refinery is discussed in more detail below.

Sour Water/Gas Processing

One of the principal by-products of petroleum refining is sour off-gases. Sour gases contain hydrogen sulfide, a noxious volatile compound, that is easily stripped from crude oil or partially refined products containing hydrogen sulfide and may be transported to hydrogen sulfide (H_2S) plants. The hydrogen sulfide plants effectively separate sour off-gases into "sweet" and "sour" fractions. "Sweet" gases containing low hydrogen sulfide levels are then transported to the refinery fuel gas system while sour gases are routed to Claus sulfur units for sulfur recovery (sometimes referred to as the Stretford Process). The Claus units produce elemental sulfur.

Sour waters are also generated by many processes at the refinery. In addition to hydrogen sulfide, ammonia is also present in sour waters. Sour water is first concentrated in stripping towers and subsequently delivered to facilities capable of recovering the ammonia. During ammonia recovery, hydrogen sulfide is separated out and returned to the sulfur recovery process.

Caustic and Acid

A critical chemical used in the oil refining process is caustic soda. After being used in the production of jet fuel and light gasoline, the caustic soda, with entrained cresols or naphthenes, is sold as a product. After leaving the refinery, these materials are processed to create fresh caustic soda and to recover the cresols and naphthene. Spent sulfuric acid, used in alkylation and also to treat jet fuels, remains sufficiently concentrated, and it is sold typically for off-site remanufacture as commercial acid.

Ancillary Operations

Ancillary refinery operations include power production and process water purification. These operations do not directly result in a salable product; however, they are desirable operations because they reduce costs, recover energy (power production), and provide softened water for refinery processes.

Cogeneration

In the Cogeneration (Cogen) Plant refinery fuel gas, natural gas, and LPG are used to generate electricity from turbines located on site and to fire boilers that produce steam. Steam is a critical in many refining processes and for the generation of electricity.

Water Treatment

The water treatment system consists of the demineralizing and softening municipal drinking water prior to use in refinery operations. Inorganic ions such as sodium, calcium, magnesium, and chloride are removed from drinking water using exchange resins. The purified water created in this process extends the life of refinery equipment by reducing scale and eliminating compounds which interfere with the refinery processes.

Waste Water Management

Waste water treatment includes the physical and biological purification of aqueous wastes. Part of this process involves oil/water separation. This leads directly to the recovery of oil and oil products from the refinery effluent system. Waste water treatment facilities consist of both passive and active oil/solids separation, oil recovery, biological waste water treatment, and biological sludge digestion. The collection of waste water is accomplished using a parallel system of pipes designed to carry different waste water materials as discussed below. This two tiered waste water collection system is referred to as the segregated and unsegregated drain system.

The segregated drainage system collects discharges from refinery operations producing process waste waters. The unsegregated system is used to convey non-process waste waters, such as cooling tower blow down, and rainwater runoff. The parallel systems join after passing through their respective treatment facilities and ultimately discharges to a POTW operating under the National Pollutant Discharge Elimination System permit program and its strict pollution control limits.

Passive oil/solids separation is a process common to both the segregated and unsegregated systems. Separation is accomplished by transmitting waste waters through an oil/solids separator where materials are removed from the water based on their differing densities. Oils, which float on water, are recovered from this process and the settleable solids are periodically removed from the separator bottom.

Active oil separation processes are also employed on both the segregated and unsegregated systems. These processes include dissolved and induced air flotation (DAF and IAF respectively) units. Oil removal by the DAF unit occurs down stream of passive oil separation in the segregated system. An IAF is used to polish unsegregated system flow, including runoff.

The biological waste water treatment plant takes all waste water flow from the segregated drainage system. This facility consists of an activated sludge process for the removal of dissolved organic material. Subsequent to biological processing, solids generated during biological treatment are removed by settling in clarifiers. The majority of the settled material, which consists of biological matter, is recirculated to the process to maintain aerobic (oxygenated) biological treatment activity. The balance of this separated biological solid is processed in the sludge digester.

Sludge digestion is an anaerobic process (biological treatment occurs without oxygen) that reduces the mass of biological solids. Digested sludge is ultimately disposed of to the sanitary sewer or sent for dewatering and disposal to drying beds or by other means.

Throughout the waste water treatment process, oil recovery is a preference to extract usable crude oil and refined or partially refined petroleum products from liquid and solid materials. Using a two-tiered approach, liquid materials are transported to tanks and allowed to passively separate. Recoverable oil is removed after passive separation and returned to the refining process. Solid and semi-solid secondary materials generated in the waste water treatment process are processed to recover trapped oil via MOSC or another alternative such as mechanical separation.

APPENDIX - B

List of Selected Source Reduction Measures

The following is a summary listing of source reduction measures selected by the petroleum industry. Many of the measures have been discussed in detail in the "Source Reduction Measures" section of this report. Some non source reduction measures have been also included in the following, if their implementation have broadly applicable beneficial environment effect.

Measure	CWC
ARCO, Los Angeles	
1. Divert stormwater to Dominguez Channel	135
2. Divert cooling tower blowdown to Channel	135
3. Train Personnel to avoid discharging benzene to the sewer	135
4. ARCO's Stamp Out Waste program	135
5. Divert Cogen cooling tower blowdown to the cooling tower header	222
6. Send cat poly acid for agricultural use	161
CalResources, Bakersfield	
1. Request DTSC not to consider refractory waste as non-routine waste and hence exempt from SB 14	181
Chevron, Richmond	
1. Screen out the inert ceramic support spheres from the spent catalyst and reuse the spheres	162
2. Install vegetative cover to hills and barren areas to reduce erosion	222
3. Eliminate use of sand bags to avoid particulates	222
4. Improve the sludge removal process	222
5. Regenerate bauxite filter media off-site	222
6. Modify recovered oil system procedures to minimize solids to the crude unit	222
7. Use a street sweeper to remove soils from streets and process areas	222
8. Cover bare soil areas in pipeways	222

Measure**CWC****Chevron, Bakersfield**

1.	Modify existing decision-making process	181
2.	Phase out use of cellar boards	223
3.	Waste segregation	223
4.	Personnel training	223
5.	Survey/Audit improved tank cleaning procedures	241
6.	Survey/Audit chemical products and mechanical processes for improved oil, water, and solids separation	241
7.	Survey improved sand control procedures	241
8.	Use of environmental friendly paints	181
9.	Decrease frequency of painting	181

Chevron, El Segundo

1.	Continue using MOSC system and lobby U.S. EPA to prove system's legitimacy	222
2.	Institute routine drain line inspection and maintenance program	222
3.	Install a heat exchanger on rec. oil system	222
4.	Coat tanks for longer service life	241
5.	Lobby for legal asphalt incorp. of non-RCRA tank bottoms	241
6.	Recycle metals catalyst (not a source reduction)	162

Exxon, Benicia

1.	Improved handling of ESP fines	222
2.	Modify desalter	222
3.	Optimize chemical usage at desalter	222

GATX Tank Storage, Carson

1.	Repair tank roofs	221
2.	Improve housekeeping and maintenance practices at loading racks	223
3.	Additional employee training	221
4.	Install additional sumps and sloping tank bottoms	223
5.	Manage oil from pressure relief valves as a non-waste material	221

Measure**CWC****Huntway, Benicia/Wilmington**

1.	Pave the tank farm access road	222
2.	Reduce the sludge volume through centrifugation	343
3.	Isolate WORT conveyances from storm water run-on	222
4.	Install closed loop water recycling units on Vacuum and Seifer Mill water cooling system	343

Mobil Oil, Torrance

1.	Reduce particulates into vacuum truck washout sump	222
2.	Reduce truck wash out frequency	222
3.	Segregate hazardous and non-hazardous truck services	222
4.	Eliminate vacuum truck washout sump	222
5.	Improved tracking of vacuum truck washout area usage	222
6.	Addition of bio-filtration unit	352
7.	Segregate hazardous and non-hazardous waste	352
8.	Analyze and re-categorize other wastes contributing to the total generation of CWC	352
9.	Improve CARB gasoline production process	134

Pacific Refinery, Hercules

1.	Convert API to CPI oil separator to enhance oil/water separation	222
2.	Install close loop sampling ports throughout process units	222
3.	Establish new procedures for tank filling flange maintenance and sump level measurement	611
4.	Implement new spill prevention procedures	352

Paramount Petroleum, Paramount

1.	Use filter press to recover oil	222
2.	Participate in EPA Merit source reduction program	222
3.	Recharter in-house Hazardous Waste Committee	222
4.	Employee awareness training	222

Powerine Oil, Santa Fe Springs

None (Facility closing)

Measure

CWC

Shell, Carson

1. Improve maintenance of roof drains	352
2. Optimize cleaning water temperature	181
3. Reuse liquid for water conservation and to reduce waste water	181
4. Train plant and contractor employees	181
5. Maintain records of contractors waste source reduction performance	
6. Provide incentives to employees	
7. Remove dry solids from surfaces draining into separator	181
8. Reduce product loss during tank water draws	
9. Reduce hydrocarbon spills and leaks in pump pad area	181
10. Reduce product loss in truck loading area	181
11. Improve equipment maintenance	
12. Improve separator maintenance	
13. Use separator standing water to conserve fresh water	
14. Keep records of truck loading area spills	

Shell, Martinez

1. Coat, gunite and curb to reduce sludge formation	222
2. Reduce oil entry into sewer system at sample stations	222
3. Segregate high salts waters to biotreater	222
4. Institute street sweeping program	222
5. Relocate sand pile to avoid particulate contamination	222
6. Reduce high solids input streams	223
7. Return low solids streams to processes	223
8. Segregate hazardous waste and nonhazardous waste	

Texaco, Bakersfield Plant, 1 and 2

1. Install automatic self cleaning filters	223
2. Install hydrocarbon recovery unit	352

Texaco Bakersfield, Plant 3

Same as Texaco Plant, 1 and 2

Measure	CWC
Texaco, Los Angeles	
1. Improve unit housekeeping and pave areas around the sewers	222
2. Implement local/Internal waste reduction program	
3. Change sample bibs at circulating sample points	222
4. Use cyclonic precipitators to replace gravity separation	222
Tosco, Martinez	
1. Improve segregation of catalyst support materials from spent catalyst	162
2. Reclaim spent catalyst	162
3. Recycle oily solids using the coker	222
4. Segregate nonhazardous from hazardous oily waste	
5. Use recyclable/reusable absorbent	
6. Replace demineralizer system with reverse osmosis system	222
Ultramar, Wilmington	
1. Offsite recycling of spent catalysts and FCC fines	162
Unocal, Santa Maria	
1. Recover oil through delayed coking	
Unocal, Carson	
1. Evaluate spent hydrogen plant catalyst use as feed to primary smelting facility	162
2. Implement tank inventory optimization study	241
3. Tank bottom waste management as excluded recyclable material	241
4. Evaluate spent hydrotreating catalyst sale/use as feed to abrasive manufacturing process	162
Unocal, Wilmington	
1. Implement tank farm modifications	222
2. Implement stormwater impoundment and maintenance program	222
3. Evaluate sale/use of spent catalyst to an abrasive manufacturing facility	162
4. Evaluate spent hydrogen plant catalyst use as feed to a primary smelting facility	162
5. Evaluate Stretford sulfur washing	441

Measure**CWC****Unocal, San Francisco**

1.	Substitute a nickel-based catalyst for current zinc-based catalyst in the sulfur sorber reactor	162
2.	Improve operations of the two Verti-Press filters	181
3.	Implement modified Global Sulfur Systems Process	181
4.	Increase evaporative capacity in mini cooling tower	132
5.	Increase conversion of H ₂ S into elemental sulfur in the upstream Claus units	132
6.	Substitute Unisulf (thiocyanate process) for existing Stretford process	181
7.	Investigate Dow process for recovering anthraquinone disulfonic acid (ADA) and vanadium from Stretford solution	132
8.	Substitute other liquid redox processes such as Sulferox, Locat, Sulfolin, or Hiperion processes for the Stretford process	181
9.	Investigate RUST process for removing vanadium from Stretford solution and/or dilute Stretford contaminated washwaters (Waste Minimization)	132
10.	Ship Stretford solution to Cri-Met facility in Louisiana for vanadium recycling/reclamation instead of to Dupont facility in New Jersey for treatment/disposal (Waste Minimization)	181
11.	Fix heat exchanger leak at low temperature shift reactor	162
12.	Improve mixing operations for tanks #F101 and/or #F501	132
13.	Lengthen unit runtime of one of the hydrocracking reactors	162
14.	Evaluate economic feasibility of solids control by evaluating each of the following and subsequently implement those methodologies found feasible: A) connecting roof drains to sewer basins, B) construct sediment traps around tank block drains, C) construct risers/weirs around tank block drains, D) Install sediment traps within tank block drains, and E) Pave or oil tank block sediments	222

	Measure	CWC
15.	Evaluate economic feasibility of solids control in the non-tank areas of the refinery using the following five existing Unocal methodologies. Optimize the existing programs by implementing the economically feasible modifications, and develop a system for documenting the quantities of solids collected/prevented from entering the washwater collection system a) construction of additional sediment catch basins and/or runoff trenches b) maintenance of sediment catch basins, pipe trenches, and other drainage structures c) street sweeping program d) unit vacuuming program e) erosion control program (pave surfaces, oil surfaces, plant vegetation control)	222
16.	Repair bottom rakes on coke oil separator	222
17.	Evaluate tank filling and cleaning procedures to determine if discharge of oil to waste water treatment system can be reduced, for instance, by using detectors to reduce oil drainage during tank draws	222
18.	Discharge non-hazardous cooling tower blowdowns to salt water discharge system instead of to waste water treatment system	222
19.	Optimize handling and management of oily trash compounds at unit 220 equipment pad	223
20.	Evaluate administrative measures to segregate non-hazardous compounds from oily trash waste system	223
21.	Redirect employee hazardous waste training to address specific components of the oily trash waste stream that offers source reduction opportunities	223
22.	Evaluate methods for reducing the quantities of iron scale found with the tank bottoms	223
23.	Coordinate the tank cleaning planning process with the "Sludge Injection Committee" planning process	223

Witco, Oildale Refinery, Oildale

1. Reduce tank bottoms by reducing amount of excess lime

APPENDIX - C

California Waste Code (CWC)

132	Aqueous solution with metals
134	Aqueous solution with total organic residues less than ten percent
135	Unspecified aqueous solution
161	Fluid Catalytic Cracker (FCC) waste
162	Other spent catalyst
181	Other inorganic solid waste
221	Waste oil and mixed oil
222	Oil/water separation sludge
223	Unspecified oil-containing waste
241	Tank bottom waste
321	Sewage sludge
352	Other organic solids
343	Unspecified organic liquid mixture
441	Sulfur sludge
611	Contaminated soil from site clean-ups
791	Liquids with pH < or = 2

APPENDIX - D

List of Rejected Source Reduction Measures

	Measure	CWC
ARCO, Los Angeles		
	None	
CalResources, Bakersfield		
	None	
Chevron, Richmond		
1.	Reformulate catalyst with less metals to reduce toxicity	162
2.	Redesign process for in-situ regeneration of spent catalyst	162
3.	Develop catalysts that have longer run lives	162
4.	Limit crude rate	222
5.	Filter crude oil to remove particulates	222
6.	Buy crude with lower solids content	222
7.	Enclose bauxite conveyor belts	222
8.	Improve recovered oil quality	222
9.	Reduce oil to process water system	222
10.	Convert all process drains to be insert-A-seal compatible	222
11.	Install diesel flash tower	222
12.	Use a diesel drying salt that would not form solids in API separator	222
13.	Coat/Gunite bare areas	222
14.	Optimize addition of precipitation reagents	222
15.	Change process plant metallurgy	222
Chevron, Bakersfield		
1.	Segregate and test each waste bin	181
2.	Reuse grit	181
3.	Alter tank cleaning frequency	241

	Measure	CWC
Chevron, El Segundo		
1.	Replace centrifugal pumps at No. 2, 3, and 4 separators with low shear pumps	222
2.	Upgrade No. 4 separator	222
3.	Use street sweeper to clean roads	222
4.	Reduce inventory of oil and products resulting in reduction of the number of storage tanks in service	241
5.	Use different catalyst	162
6.	Control feed quality to catalyst reactors	162
Exxon, Benicia		
1.	Reduce solids in crude feed to the refinery	222
2.	Pave tank farm diked areas	222
3.	Remove biological oxidation solids	222
4.	Minimize water content of sludges	222
GATX Tank Storage, Carson		
1.	Treat, store and reuse pipeline hydrotest water	221
2.	Cover loading racks	221
3.	Cover manifold drains	221
4.	Recover product and reuse wash water	221
Huntway, Benicia/Wilmington		
1.	Install screens at WORT conveyance system's opening and entrances	222
2.	Use treated water for irrigation purposes	343
3.	Install new crude oil suction lines on crude oil storage tanks	222
4.	Install automatic shut-off valves on crude oil and product storage tanks	222
5.	Install a tank and pumpback system to recover oily wastes from laboratory sinks	222
Mobil Oil, Torrance		
1.	Change pipe and equipment composition to control corrosion for scale and solids reduction	352
2.	Change fluid composition in pipe to reduce scale	352
3.	Use corrosion inhibitors and anti fouling agents	352
4.	Stop or reduce water flow to groundwater carbon bed	352
5.	Run carbon bed to avoid generation of spent carbon	352
6.	Stop input of hazardous material to process sewer	134

Measure

CWC

Pacific Refinery, Hercules

- | | | |
|----|---|-----|
| 1. | Replace crude oil feed with lower solid content | 222 |
| 2. | Develop procedures to reduce solids from heat exchanger bundle and catalyst fines | 222 |
| 3. | Use street sweeper to remove dust and dirt | 222 |

Paramount Petroleum, Paramount

None

Powerine Oil, Santa Fe Springs

None

Shell, Carson

- | | | |
|----|--|-----|
| 1. | Improve filtration of incoming product | 181 |
| 2. | Optimize concentration of stored-product additives | 181 |
| 3. | Recirculate tank bottoms | 181 |
| 4. | Install sloping, secondary bottom in product tanks | 181 |
| 5. | Use steam and detergent to clean tanks | 181 |
| 6. | Optimize cleaning water temperature | 181 |
| 7. | Optimize cleaning water pressure | 181 |

Shell, Martinez

None

Texaco, Bakersfield Plant, 1 and 2

None

Texaco Bakersfield, Plant 3

None

Measure**CWC****Texaco, Los Angeles**

1.	Pave entire refinery	321
2.	Use sandbags around sewer entrances	321
3.	Implement wipe out waste (WOW) program	321
4.	Reduce cooling tower blowdown frequency	222
5.	Reduce boiler blowdown by using demineralized boiler feedwater	222
6.	Soften cooling water make-up	222
7.	Use reverse osmosis process for boiler feedwater	222

Tosco, Martinez

1.	Pave refinery pipeways	222
----	------------------------	-----

Ultramar, Wilmington

None

Unocal, Santa Maria

None

Unocal, Carson

1.	Change refinery crude feed to lower sulfur content	162
2.	Redesign fresh catalyst	162
3.	Install partial oxidation hydrogen plant	162
4.	Reduce crude supply solids	222
5.	Pave additional areas	222
6.	Provide groundcover	222
7.	Install process sewer opening filtration system	222
8.	Install desalter filtration system	222
9.	Reduce crude supply solids	241
10.	Implement crude polymer injection	241
11.	Implement tank sludge polymer injection	241

Measure**CWC****Unocal, Wilmington**

1.	Change refinery crude feed to lower sulfur content	162
2.	Redesign fresh catalyst	162
3.	Reduce crude supply solids	222
4.	Segregate storm and sewer system	222
5.	Change refinery crude feed to lower sulfur content	441
6.	Install sulfur de-entrainment device	441
7.	Change acid plant feed structure to reduce weak acid waste quantity	791
8.	Reduce excess oxygen to prevent formation of sulfur trioxide	791

Unocal, San Francisco

1.	Remelt sulfur solids and market this waste stream as a raw material for sulfuric acid production	132
2.	Evaluate installation of a partially or totally segregated sewer system from storm water system	222
3.	Enclose coke pit with a curtain to minimize the loss of coke fines	222
4.	Control hardness in cooling tower and boiler feed wastes	222
5.	Discharge non-hazardous boiler blowdown to salt water discharge system instead of to waste water treatment system	222
6.	Use low temperature dryer to dry filter cake	222

Witco, Oildale Refinery, Oildale

None

APPENDIX - E

Selected Source Reduction Measure Abstract - Examples

The following three abstracts are taken from Unocal, San Francisco refinery 1994 Source Reduction Plan. They all are comprehensive, providing detail of three selected source reduction measures seven criteria such as technical feasibility, effect on product quality, economic evaluation (feasibility), to name a few. They also detail other pertinent information such as waste stream ID by CWC code, quantities generated in reporting year, process or activity generating the waste, measure description, type of alternative, and expected change in hazardous waste generation. They provide cost savings and net benefit derive by implementing the measures.

Selected Source Reduction Measure Abstract - 1

Waste Stream ID: CWC:	Oil/Water Separator Sludge 222
Quantity of Waste Generated, 1994	5 tons were manifested off site for treatment/disposal. (1,836 tons were reused on site at the sludge coking unit)
Process or Activity Generating the Waste:	Oil/Water separator sludges are generated at Unit 100, the Unocal waste water treatment plant.
Measure Description:	Evaluate the economic feasibility of installing solids control measures in the non-tank block areas using any or all of the following five existing Unocal methodologies listed below; optimize existing programs by implementing those measures found economically feasible, and develop a system for documenting the reduced quantities of solids entering the waste water collection system: 1. Construction of additional sediment catch basins and/or runoff trenches;

2. Maintain sediment catch basins, pipe trenches, and other drainage structures;
3. Implement a street sweeping program;
4. Implement a unit vacuuming program; and
5. Implement an erosion control program (pave surfaces, oil surfaces, and plant vegetation).

During the 1990 to 1994 reporting period, all of the above five solids control methodologies were used at Unocal: a street sweeping program was implemented beginning in 1990, a unit vacuuming program was implemented in 1992, catch basins and/or runoff trenches were constructed at 16 separate locations. Sediments were collected from these locations, and an aggressive erosion control program was implemented beginning in 1992. This alternative will assess which solids control programs are economically viable based on the current sludge management techniques, and result in the implementation and optimization of a comprehensive solids collection program.

Type of Alternative:
Expected Change in
Hazardous Waste
Generation:

Operational Improvement
Studies conducted by the American Petroleum Institute have demonstrated that for every pound of suspended solids that enters the typical refinery waste water collection system, seven to nine pounds of oily sludge is generated, which can result in approximately two to three pounds of deoiled, dewatered sludge. Implementation of these methodologies have reduced the amount of oil/water separator sludge generated by reducing the solids loading to the waste water treatment system. Optimization of the identified economically viable methodologies would further reduce the sludge generation rate.

Technical Feasibility: All of the above methodologies have proven to be technically feasible and have been implemented at Unocal. This alternative involves an evaluation of these methodologies for modifications which are found to be both technically feasible and cost-effective, based on current sludge management techniques.

Economic Feasibility: The cost savings realized from the implementation of any of the identified economically viable methodologies would result in the reduction in cost to handle and transport these sludges from the waste water treatment plant to the coker unit for recovery. The cost of handling and transporting the oil/water separator sludges to the coker is approximately \$1.20 per bbl of sludge, determined on a wet weight basis. Assuming that the density of the sludge is 10 lbs./gallon, the handling and transportation cost is approximately \$5.60 per ton of sludge. This cost only accounts for sludge handling and transportation from Unit 100 (separators and sludge filtration process) to the coker unit; it does not account for the operation and maintenance of the Unit 100 sludge tankage.

As a result, the cost of handling the oil/water separator sludges to the coker unit, based on the amount of solids entering the waste water system, is approximately $\$5.60 \times 8 = \45 per ton of solids.

The potential cost saving by reducing the amount of sludge handling will be evaluated against the cost and effectiveness of implementing any of all of the solids control methodologies. Maintenance and cost data for each of these methodologies were

reviewed. For example, the catch basin and storm basin maintenance program led to the collection of approximately 180 tons of solids from the period January to August 1993, at a cost of approximately \$19,000, or about \$105 per ton of collected solids. The street sweeping program led to the collection of approximately 100 tons of solids from the period April 1990 to May 1994, at a cost of \$40,000, or about \$400 per ton of collected solids. The unit vacuuming program led to the collection of approximately 3.2 tons of solids in September 1992, at a cost of \$5,600, or about \$1,750 per ton of collected solids.

As a result, the costs for all of the solids control methodologies appear to outweigh the cost to handle and transport the oil/water separator sludges from Unit 100 to the coker, following the successful implementation of the sludge coking facilities. However, the costs shown for handling/transporting the sludges to Unit 200 do not account for the costs that will be necessary to handle/manage the sludge quantities currently accumulating in the Unit 100 influent tanks. Unocal should investigate modifications to these methodologies to reduce solids control cost and to increase the quantities of solids collected; if such modifications cannot be cost-effectively made, these solids control programs should be discontinued.

Effect on Product
Quality:

None expected.

Employee Health and
Safety Implications:

No change from current health and safety concern.

Permit/Variance
Required:

None.

Releases/Discharges:

None expected.

Selected Source Reduction Measure Abstract - 2

Waste Stream ID: **Stretford Solution/Stretford Solids
CWC: 132/181**

Quantity of Waste Generated, 1994: 3,620 tons of Stretford Solution
358 tons of Stretford solids

Process or Activity Generating the Waste: Maintenance changeouts of Stretford process vessels and tanks.

Measure Description: **Implement Modified Global Process:**
The Global process is a portable treatment process designed to regenerate spent Stretford solution by converting sodium thiosulfate to sodium sulfate and then removing the sodium sulfate from solution. This process effectively extends the life of the Stretford Solution. There are four implementation options proposed by Global Sulfur Systems, Inc:

1. Once-through regeneration of total Stretford solution inventory (requires shutdown of all three Stretford trains);
2. Once-through regeneration of Stretford from one train (requires shutdown of one of the three trains); and
3. Sidestream regeneration of Stretford solution from one train (requires no shutdown).
4. Once-through regeneration of one train with no shutdown (requires that a Stretford makeup solution of one train be on-hand in tankage).

Type of Alternative: Production Process Change

Expected Change in Hazardous Waste Generation: If the Modified Global Process proves feasible, full-scale implementation could achieve reductions approaching 50 % or more in the quantity of Stretford wastes generated by effectively extending

the service life of a given batch of Stretford solution.

Technical Feasibility: An attempt was made to implement the Global Process at Unocal, San Francisco refinery in 1992. However, the attempt was a technical failure for several reasons; the most prominent being that the Global equipment appeared to have inadequate capacity to regenerate the quantity of sodium thiosulfate contained in the Unocal's sulfur treatment trains. Had the Global process succeeded technically, it was felt that its implementation would not have been cost-effective.

However, since 1992 the Global equipment has been modified, and the Global Process has been successfully demonstrated at other refineries, including Unocal's Los Angeles Refinery. These successful demonstrations are not directly translatable to the Unocal, San Francisco because Unocal, San Francisco Stretford process is substantially different, both in design and operation. These tests however do indicate that Global is in the process of successfully developing a commercially viable technology. Unocal engineers recently completed a technical review of a revised proposal submitted by Global in June 1995, and made a decision to use the modified Global process on a pilot-scale basis for a once-through regeneration of the Stretford inventory from either one or all three trains (Option #1 or #2). It is anticipated that this pilot-scale implementation will be done at least twice, during the upcoming fourth quarter 1995 changeout and during a 1996 changeout. The technical data resulting from this pilot-scale implementation will allow Unocal engineers to better

evaluate the feasibility implementing the modified Global process on a long-term, full-scale basis at Unocal San Francisco.

Economic Feasibility:

The June 1995 proposal submitted by Global estimates that the first option would cost \$280,000 to fully implement the once-through treatment of the total Stretford solution inventory, and that the second option would cost \$300,000 to fully implement the once-through treatment of the solution inventory from one operating train. Unocal and Global are currently in the process of negotiating the actual costs of Global's services for the pilot-scale implementation. Unocal engineers will evaluate the results of the pilot-scale implementation to determine the cost-effectiveness to implement the modified Global process on a long-term, full-scale basis.

Unocal currently spends approximately \$1 million during each Stretford process changeout for offsite treatment/disposal of spent Stretford solution, Stretford solids, and Stretford-contaminated washwater. If implementation of the modified Global process proves successful, and the pilot-scale system can successfully be scaled up to full-scale, where reductions of 50% or more in the quantities of Stretford waste generation could be achieved. A 50% reduction in the amount of spent Stretford solution generated would translate into saving Unocal approximately \$500,000 per changeout, which occurs roughly every 12 to 18 months. Such a cost saving could effectively payback the cost of implementing the modified Global process within one or two changeouts (one to three years).

Effect on Product Quality:	None expected.
Employee Health and Safety Implications:	Beneficial. Process tanks and vessels would only be cleaned out half as often. Global workers will wear proper personnel protective equipment and observe Unocal contractor safety rules.
Permit/Variance Required:	Global Sulfur System, Inc. has verification from the California Department of Toxic Substances Control, that their mobile Stretford solution treatment unit does not require a hazardous waste facility permit or a transportable treatment unit permit. Section 25143.2 of the California Health and Safety Code exempts permitting requirements for treatment units which recycle material at the site where the material was generated. The Global process would return dilute Stretford solution on site for reuse in Unocal's Stretford process.
Releases/Discharges:	Besides the recycled Stretford solution, there are three effluent streams produced by the Global process. The first stream is a negligible vent gas stream of carbon dioxide and moist air that will be passed through simple caustic and activated carbon filters to prevent the escape of any odorous compounds. The second stream is a sulfur sludge consisting of sulfur filtered from the feed solution and sulfur produced during thiosulfate conversion. This sulfur will be returned to Unocal's sulfur froth tank or manifested off site for disposal. The third stream is moist crystals of hydrated sodium sulfate (Glauber) salt. These Glauber salts may be reclaimed once characterized to ensure they are non-hazardous.

Selected Source Reduction Measure Abstract - 3

Waste Stream ID: **Spent Catalyst**
CWC: **161**

Quantity of Waste Generated, 1994: 527 tons

Process or Activity Generating the Waste: Numerous refinery process units use catalysts, including UNOCAL's hydrocracker (Unit 240) unit and its associated catalytic reformer (Unit 244) and the unisar (Unit 248) unit, the isom unit, the midbarrel unifiner and its associated gasoline unifiner and catalytic reformer units, and the steam power plant. Spent catalysts are periodically removed from these processes during unit turnarounds and are replaced with new or regenerated catalysts.

Measure Description: **Repair heat exchanger leak thought to be responsible for generating spent catalysts and shortened runtimes in low temperature shift reactor (D-405):**

The low temperature shift reactor (Reactor D-405 at the Unicracker Unit) currently uses a copper and zinc based catalyst (United C18-7) and has historically achieved runtimes lasting approximately four years. However, over the last four to six years, runtimes lasting only one or two years have been achieved. An operational problem has been identified that may have potentially been the cause of these shortened runtimes; specifically a heat exchanger leak was found that, when combined with a newly changed chemical treatment of boiler water, may have resulted in the preliminary deactivation of the catalyst charge. The heat exchanger leak was repaired at the most recent unit turnaround and should enable the reactor to again achieve four year runtimes.

Type of Alternatives:	Operational Improvement
Expected Change in Hazardous Waste Generation:	If the reactor again achieves four year runtimes, a 50 to 75 percent source reduction of the portion of the spent catalyst waste stream originating at this particular reactor can be expected. Approximately 71 tons of spent catalyst is currently generated from Reactor D-405 during turnaround.
Technical Feasibility:	Unocal process unit engineers already determined that this alternative was technically feasible, and repaired the heat exchanger leak at the most recent unit turnaround.
Economic Feasibility:	Unocal process unit engineers already determined that this alternative was economically feasible, and repaired the heat exchanger leak at the most recent unit turnaround. The cost to replace the catalyst is approximately several hundred thousand dollars per turnaround; therefore, this measure to extend the runtime of the unit, which required no capital costs, was determined to be cost-effective.
Effect on Product Quality:	None expected.
Employee Health and Safety Implications:	Beneficial. Extension of runtimes means changeouts will be conducted less frequently with a lower employee health/safety risk.
Permit/Variance Required:	None.
Release/Discharges:	None expected.

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