INDEPTH SITE VISIT REPORT
DELAWARE REFINERY

CONTROL TECHNOLOGY ASSESSMENT OF PETROLEUM REFINERY OPERATIONS

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RADIAN
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DISCLAIMER

Radian Corporation prepared this report under Contract No. 210-81-7102 for the National Institute for Occupational Safety and Health, Physical Sciences and Engineering Division.

The findings presented are the result of two visits made to the Getty Refining and Marketing Company's Delaware Refinery. Mention of company names or products in this report does not constitute endorsement by the National Institute for Occupational Safety and Health nor by Radian Corporation.

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ABSTRACT

A major research area for NIOSH is the evaluation of control technologies which may be used to reduce occupational exposure to potentially toxic chemical substances and harmful physical agents. The primary purpose of this control technology assessment study was to identify and document examples of good employee exposure control techniques associated with five petroleum refining operations: lube oil, wax, and grease manufacture; lube oil and grease blending/packaging; naphtha reforming and aromatics recovery; oil-water separation; and acid alkylation.

During a preliminary visit conducted on June 3, 1982, a number of exposure control techniques of interest were noted at Getty Refining and Marketing Company's Delaware Refinery. A subsequent return visit was made to supplement work previously conducted in a NIOSH Health Hazard Evaluation around the Waste Water Treatment area, and to evaluate the exposure controls in place at the Refinery's benzene and aromatics loading facilities.

The indepth information obtained about these control techniques will be documented in a final study report and disseminated to interested members of the petroleum refining industry and industries to which it is applicable.

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ACKNOWLEDGEMENTS

Radian Corporation greatly appreciates the effort and time committed to this program by the Getty Refining and Marketing Company. Special thanks go to Gary Foster, Delaware Refinery Industrial Hygienist and Safety Representative. We also appreciate the help of engineering and operating personnel assigned to the Waste Water Treatment Plant and Aromatics Extraction Unit.

1.0 INTRODUCTION

This indepth visit report documents a visit by NIOSH and Radian Corporation to Getty Refining and Marketing Company's (GRMC) Delaware Refinery in Delaware City, Delaware. The purpose of this visit was to document good examples of controls used by the refinery in controlling worker exposure to potentially toxic chemical substances and harmful physical agents. The engineered controls studied during this visit were those implemented by the Refinery at the oil-water separation area around the Waste Water Treatment Plant and at the benzene and aromatics product loading facilities.

1.1 Study Overview

A major research area for NIOSH is the evaluation of control technologies which may be used to reduce occupational exposures to potentially toxic chemical substances and harmful physical agents. The primary purpose of this study is to identify and evaluate examples of good employee exposure control techniques associated with five petroleum refining operations: lube oil, wax, and grease manufacture; lube oil and grease blending/packaging; naphtha reforming and aromatics recovery; oil-water separation; and acid alkylation. The exposure controls studied include: engineering controls, monitoring programs, personal protective equipment, and work practices.

During a preliminary visit conducted on June 3, 1982 a number of exposure control techniques of interest were noted at the Delaware Refinery. A subsequent return visit was made to thoroughly document these control techniques.

Information obtained in visits to the Delaware Refinery will be presented in a final study report and disseminated to interested members of the petroleum refining industry and other industries to which it is applicable. Appropriate details also will be included as part of a catalogue for effective hazard control options being compiled by the NIOSH Engineering Control Technology Branch. These information transfer mechanisms are designed to promote the use of successful exposure control ideas in applicable industries.

1.2 Summary of Indepth Visit

On August 25 and 26, 1982, two Radian employees and the NIOSH project officer conducted an indepth visit at the Delaware Refinery. Photographs, sketches, drawings, and equipment specifications were acquired to document employee exposure control methods. Short term area sampling for benzene and hydrogen sulfide, and full-shift area and personal sampling for benzene, toluene, and xylenes were conducted in the Refinery's Waste Water Treatment Plant and at the benzene and aromatics loading facilities. Discussions were held with Gary Foster, Delaware Refinery Industrial Hygienist and Safety Representative, safety representatives of the Oil, Chemical, and Atomic Workers Union (OCAW) Local 8-898, and operating personnel assigned to the Waste Water Treatment Plant, the Aromatics Extraction Unit, and the benzene/aromatics loading facilities.

All Getty personnel were very helpful and their cooperation was greatly appreciated.

Oil-Water Separation Area

Indepth study in the oil-water separation area focused on evaluating the effects of recent (1980) modifications made at the Refinery's Waste Water Treatment Plant. Airborne levels of hydrogen sulfide and benzene, toluene, and xylenes were measured and the results compared to those obtained in a NIOSH Health Hazard Evaluation (HHE) conducted prior to the modifications.

Waste Water Treatment Plant (WWTP) modifications were made primarily to reduce the amount of pollutants discharged by the Refinery to the Delaware River. However, installation of improved oil-water separation facilities and a sour water stripper also was expected to significantly reduce employee exposure to hydrogen sulfide and hydrocarbons.

Sampling data collected during the indepth visit showed hydrogen sulfide levels of no greater than 1 ppm at sampling points located throughout the WWTP. Most points sampled registered hydrogen sulfide concentrations less than 0.1 ppm, the detection limit of the sampling method. Measurements made by NIOSH in the HHE indicated that hydrogen sulfide levels of 4 to 5 ppm were common in the area prior to its modification.

From the limited data base provided by the HHE and this study, it cannot be conclusively stated that the installation of a sour water stripper has reduced hydrogen sulfide levels in the WWTP. However, comparison of sampling data taken before and after installation strongly supports the premise that the sour water stripper is an effective employee exposure control for hydrogen sulfide.

Unscheduled maintenance of the CPI separators located in the WWTP prevented direct comparison between hydrocarbon levels before and after installation of improved oil-water separation facilities. However, WWTP operators' time-weighted average exposures to benzene were less than 1 ppm, the NIOSH recommended permissible exposure limit (PEL). The current OSHA PEL for benzene is 10 ppm. At only one area sampling point, the API separator discharge, did benzene levels exceed 1 ppm. The concentration of benzene measured (3 ppm), however, was well below the current PEL. Concentrations of toluene and xylenes were minimal.

Benzene/Aromatics Production and Loading

To minimize employee exposure to benzene and other aromatic hydrocarbons during tank truck loading operations, Getty has constructed loading facilities equipped with several engineered controls. Benzene and aromatics product are metered into tank trucks through a loading arm equipped with a dripless connector. When the loading arm is attached to a compatible dripless connector on the tank truck, a seal is formed which minimizes the potential for leaks and spills during loading.

At the Refinery's benzene loading facility, a vapor recovery system has been installed to minimize fugitive benzene emissions during loading. Fugitive vapors are recovered via a carbon dioxide eductor and a flexible hose attached to the tank truck. Recovered vapor is sent to an incinerator in the Reforming Unit.

Long-term personal and area samples were collected around the benzene and aromatics loading facilities and analyzed for benzene, toluene, and xylenes. Sampling results indicated that the OSHA PEL of 10 ppm was not exceeded at any sampling point. However, the truck loader's time-weighted average exposure to benzene and the area concentration of benzene at the benzene loading facility were significantly higher than the NIOSH-recommended PEL of 1 ppm. The truck loader's actual exposure was reduced by his use of a half-facepiece organic vapor cartridge respirator during loading operations.

1.3 Report Outline

Each of the controls studied during the indepth site visit is discussed in more detail in the remaining sections of this report. Additionally, brief descriptions of the Delaware Refinery, its safety and health programs, and each of the process units in which controls were examined are provided:

Section 2.0 Refinery and Health and Safety Program Descriptions
Section 3.0 Oil-Water Separation
Section 4.0 Benzene/Aromatics Production and Loading

2.0 REFINERY AND HEALTH AND SAFETY PROGRAM DESCRIPTIONS

2.1 Refinery Description

The Getty Delaware Refinery is located on a 5,000 acre tract near Delaware City, Delaware. This refinery has the capacity of processing up to 150,000 barrels per day of high sulfur crude. It was completed in 1957 as a new "grass roots" refinery and since start up has been extensively modified to add environmental and process innovations. These modifications include changes and new additions in the refining process, as well as in the petrochemical and environmental units.

All of its crude reaches the Delaware Refinery via a marine terminal on the Delaware River which can accomodate supertankers of up to 135,000 tons dead weight. Figure 2-1 is a simplified block flow diagram illustrating how the crude is processed into products.

From the marine terminal, crude is pumped to storage tanks. The Refinery has the capability to store 2.8 million barrels of crude. From storage crude is pumped to the Crude Distillation Unit, where lighter products (gas, gasolines, naphthas, and gas oils) are separated at atmospheric pressure and the heavy crude fraction is separated under vacuum into vacuum gas oil and residuum.

Light products are sent to the Refinery's desulfurizers and then receive downstream processing into fuels or petrochemicals. Vacuum gas oil from the Crude Unit goes to the Fluid Catalytic Cracking Unit where it is converted to high octane gasoline, fuel oils, and liquified petroleum gases (LPG). Residuum from the Crude Unit is transferred to the Fluid Coking Unit where it is thermally cracked to gasoline, gas oils, and coke. The coke is used as fuel by the Delmarva Power and Light Company, which supplies steam and electricity to the Refinery.

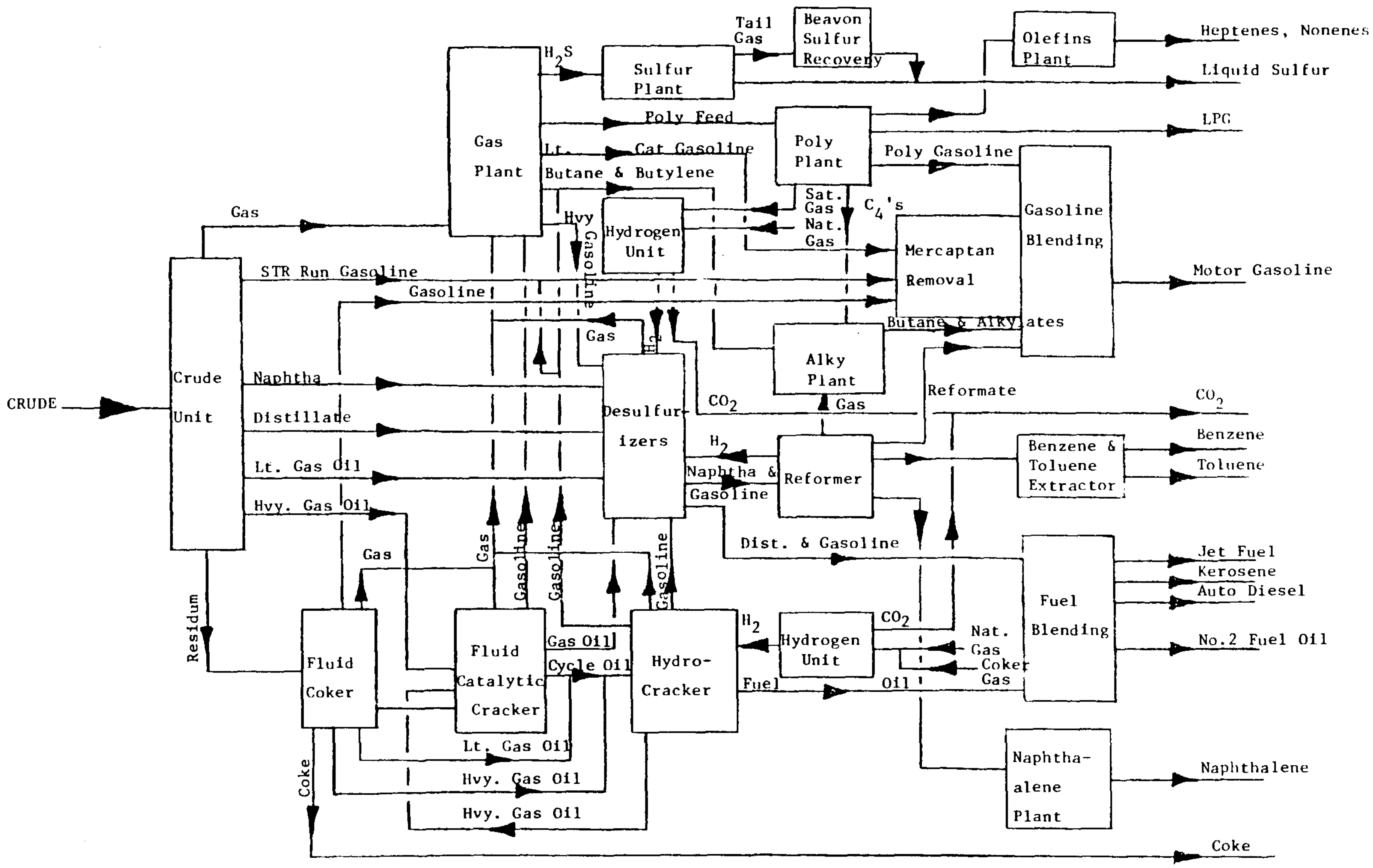

Figure 2-1 Refinery Block Flow Diagram

At the Hydrocracker, 19,000 barrels per day of high sulfur heavy oil is upgraded to low-sulfur gasoline type stock, essentially sulfur-free home heating oil (No. 2 fuel oil) and Fluid Catalytic Cracking Unit feed stocks. Hydrogen used in the Hydrocracker, the Desulfurizer and Naphthalene Unit is produced at two Hydrogen Units and the Reformer. Propane, refinery fuel gas, and natural gas are converted to 70 million cubic feet of hydrogen per day.

The Polymerization Unit receives short-chained products (i.e. propylene and butylene) from various refinery sources and upgrades them to good quality gasoline components. Gasoline from this unit is fractionated at the Olefin Fractionation Unit to produce C_7 - C_{10} olefins which are sold for plastics manufacture. Isobutanes and butylenes not converted to polymer gasoline are sent to the Alkylation Unit and converted to high quality motor gasoline blending stock.

Low octane naphthas are fed to the Reforming Unit to produce high octane gasoline components. Hydrogen produced in the process goes to the Desulfurizer Units. At the Aromatics Extraction Plant, aromatic compounds (benzene and toluene) are separated from the gasoline component in the Reformer product. High purity benzene and toluene are recovered and sold as petrochemical feedstocks. At the Naphthalene Unit, naphthalene is produced from heavy aromatics in the reformer product and sold to chemical manufactures.

Five Desulfurization Units remove sulfur and nitrogen compounds from various Refinery product streams. Hydrogen sulfide produced is converted to elemental sulfer in the Sulfur Recovery Plant.

An 11.4 million-gallon-per-day Waste Water Treatment Plant treats the Refinery's waste water streams. The primary treatment involves removing floating oils and settleable solids. This is accomplished by the use of an API separator and two CPI separators along with dissolved air flotation units. Secondary treatment includes activated sludge in which bacteria are used to remove dissolved organic material and clarification and filtration to remove solids. The treated waste water flows through a guard basin and is then combined with the water stream used for cooling and discharged to the Delaware River.

The Refinery employs about 700 people in operations, engineering, and administrative positions. Most Refinery maintenance is performed by contract labor.

2.2 Health and Safety Programs

The Getty Delaware Refinery conducts periodic exposure monitoring for the following substances and agents:

- Benzene
- Hydrogen sulfide
- Sulfur dioxide
- Carbon monoxide
- Toluene
- Ammonia
- Noise

Exposure monitoring is conducted by the Refinery's industrial hygienist. On the basis of potenital hazards and monitoring results, individuals are identified for inclusion in one or more of the Refinery's specialized medical surveillance programs.

Health and safety training is provided for all new employees. Special topics covered in this training include: firefighting, fit and use of respirators, self contained breathing apparatus, potential hazards in the workplace (hydrogen sulfide, noise), personal protective equipment, as well as refinery health and safety rules and guidelines. Initial safety training is provided by fire and safety inspectors and the plant industrial hygienist.

Periodic refresher training is provided for all plant workers in the use of self-contained breathing apparatus (SCBA), respirators, fire-fighting equipment and procedures, and hazards and precautions for hydrogen sulfide. Written refinery programs concerning hearing conservation, medical access, and fire protection are reviewed with supervisors periodically. Supervisors, in turn, review these programs with their work groups.

Weekly safety meetings, called "safety huddles" are conducted by supervisors. These meetings include an appropriate 15-minute presentation of a selected safety and health topic followed by a group discussion. Employees sign a sheet to document their presence at the meeting and indicate any questions or comments.

The Delaware Refinery uses a work permit system to assure the safety of maintenance operations. Work permits are issued by Operations and fire and safety inspectors issue permits for hot work and for work requiring confined space entry. For confined space entry, fire and safety inspectors test for adequate oxygen concentration and the presence of potentially toxic or flammable gases and vapors.

All refinery personnel are required to wear safety glasses with sideshields, hardhat, protective footwear, and fire-resistant coveralls at all times in all operating areas. Depending upon hazards that may be present in certain areas, the use of additional protective gear (e.g. gloves, goggles, faceshields, or acid-resistant suits) is required.

All employees receive pre-employment physical examinations. Annual physical examinations are available for all employees and are required of certain employees such as general service operators and bi-annual for truck operators. Physical examinations include full blood chemistry work-ups. A systematic review of blood chemistry data is performed for all persons who receive a medical exam. Audiometric testing is included in the annual physical exam for persons working in noise-hazardous areas.

An industrial physician is available at the Refinery for two hours a day, five days a week. A staff of two full-time nurses provides coverage during the day shift, seven days a week. During turnaround, nurse staffing is increased to provide 24-hour coverage, seven days a week. During regular operations, afternoon and evening shift coverage is provided by fire and safety inspectors who have completed courses as emergency medical technicians (EMT's).

3.0 OIL-WATER SEPARATION AREA

In August 1979, NIOSH conducted a Health Hazard Evaluation (HHE) at the Delaware Refinery Waste Water Treatment Plant. The HHE focused on measuring emissions of hydrogen sulfide (H_2S), ammonia (NH_3), hydrocarbons (benzene, toluene, xylenes) and biological agents from the biotreating units. Since the HHE was conducted, Getty has made extensive modifications to the Waste Water Treatment Plant which were designed to reduce emissions of H_2S, NH_3 and hydrocarbons. These changes, although implemented for environmental reasons, also represent engineering controls reducing worker exposures.

In an effort to evaluate the effects of the Waste Water Treatment Plant modifications as worker exposure engineering controls, Radian and NIOSH conducted a one-day follow up sampling effort.This effort focused on the measurement of the potential exposure of workers to H_2S, benzene, toluene and xylenes.

3.1 Past and Present Mode of Operation

In 1980, the Delaware Refinery Waste Water Treatment Plant (WWTP) was extensively modified to reduce the amount of pollutants discharged to the Delaware River. Additional modifications were made to reduce fugitive emissions of hydrocarbons to the atmosphere. Installation of improved oil-water separation facilities and a sour water stripper should have significantly reduced worker exposures to H_2S and hydrocarbons. Process descriptions of the WWTP before and after the 1980 modifications follow.

Past Process Configuration

Figure 3-1 presents a simplified flow diagram of the WWTP prior to modifications in 1980. This facility, started up in

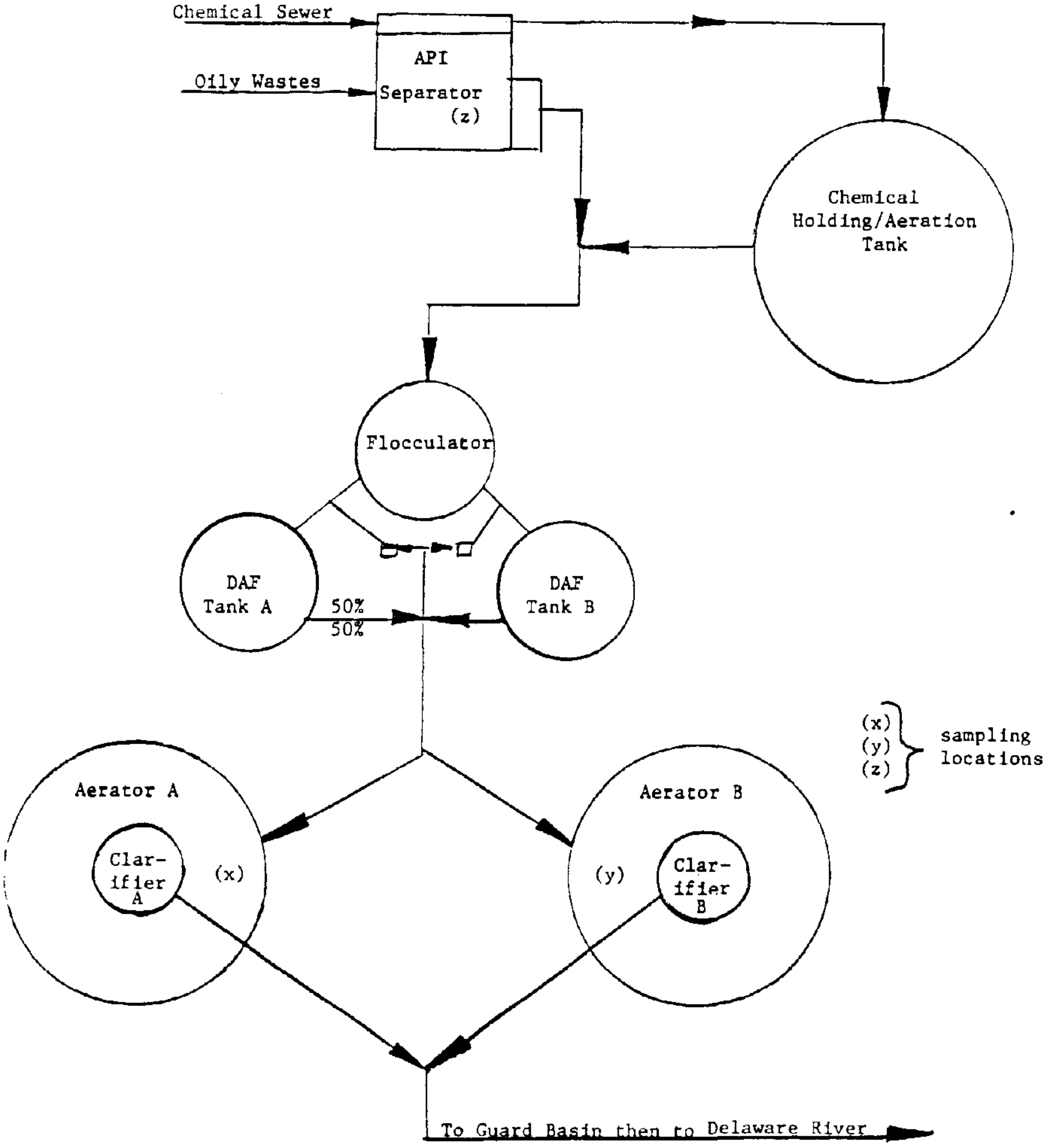

Figure 3-1 Waste Water Plant Flow Diagram

1974, treated an average waste water flow rate of 5.5 million gallons per day (MGD). Waste water flowed into the facility from two sewers, a chemical waste water sewer and an oily waste water sewer. The chemical sewer waste water flow was approximately one MGD and contained small amounts of H_2S and high concentrations of NH_3 and hydrocarbons. The oily sewer waste water contained significant amounts of oily wastes but only small amounts of H_2S and NH_3.

The waste water from the oily sewer flowed through the API separator where free floating oils were skimmed from the surface of the waste water and solids were collected at the bottom of the separator. The following is a general description for API separators:

> Oily water enters one end of a rectangular channel, flows through the length of the channel, and discharges at the the other end. A sufficient residence time is provided to allow oil droplets to float and coalesce at the surface of the wastewater. An oil skimmer is provided near the end of the separator to collect floating oil. Floating oil is advanced toward the skimmer by an oil and sludge moving devices. These devices consist of a series of moving flights which span the width of the separator. As the flights move over the survace of the separator, floating oil is advanced toward the skimmer. The flights return to the inlet of the separator on the bottom of the channel. Solids which have settled out of the water are thus scraped along the channel bottom to a sludge collecting hopper. Both the skimmed oil and the settled sludge are collected and treated for disposal or reuse. The water stream is either discharged to receiving waters or routed to additional treating facilities.

The chemical sewer waste waters were also processed through the API Separator, but in a separate bay from the oily waste waters. Waste waters from both sewers were combined in the afterbay of the API separator and flowed to the Dissolved Air Floatation (DAF) unit.

At the DAF unit, chemicals for pH control and polymers were added to the waste water to form a floc in the flocculation tank. Waste water flowing from the flocculation tank was combined with part of the waste water from the DAF unit that had been saturated with air under pressure. As these streams flowed into the DAF tanks, tiny air bubbles were released as the air-saturated waste water depressurized to atmospheric pressure. These air bubbles floated to the top of the tank forming a foam containing oil and fine suspended particulates. This foam was skimmed off and disposed of as an oily sludge.

Waste water leaving the DAF unit flowed to two activated sludge biological treatment tanks. These tanks were divided into an aeration section and a clarification section. In the aeration section, floating aerators churned up the waste water, providing the necessary oxygen to support biological destruction of the dissolved hydrocarbons in the waste water. Treated waste water overflowed into the clarification section where the bacteria responsible for the destruction of the hydrocarbons settled out of the waste water. The clarified waste water was then discharged to the Delaware River through a holding pond. The biological sludge from the clarifier was biologically reduced by aerobic digestion with final solids disposal in a landfill.

The WWTP was operated 24 hours a day requiring three shifts per day: 7:00 AM to 3:00 PM, 3:00 PM to 11:00 PM, 11:00 PM to 7:00 AM. Two operators and a foreman worked each shift. The operators rotated through two other refinery positions: utilities and pump station. Seven weeks were spent at each of the three operator positions. Both the WWTP position and the pump station position involved significant operator time in the oil-water separation facilities. Thus, 14 out of every 21 weeks were spent wholly or partially at the WWTP.

Present Process Configuration

Figure 3-2 presents a simplified block flow diagram of the present Refinery Waste Water Treatment Plant. This facility, started up in 1980, significantly reduced the waste water and fugitive emission pollutant discharges from the previous system.

The WWTP receives waters from three sources, the storm sewer, chemical sewer and oily sewer. The storm sewer system has a built in overflow that diverts excess water. A CPI separator is used to separate the oil and water; the oil skimmings are sent to the wet oil processing system, the bottom sludge is pumped to the sludge treatment area for further processing, and the water is pumped to an equalization tank. The following is a general description for CPI separators:

> Corregated-Plate Impact (CPI) separators are a relatively recent development which functions by reducing the distance oil droplets must travel before being collected and coalesced. The separator consists of a number of parallel plates set at an angle and approximately 4 inches apart. The oil droplets coalesce on the underside of the plates and creep up to the surface of the water. Conversely, solids accumulate on the top of the plates and travel to the bottom of the separator. CPI separators have the advantage of occupying less area than API separators to obtain the same oil and solids collection efficiency.

The chemical sewer oil-water separation is accomplished by an API separator, with the oil skimmings, bottom sludge, and water products going to the same units as the streams from the storm sewer CPI separator. Not shown on Figure 3-2, refinery

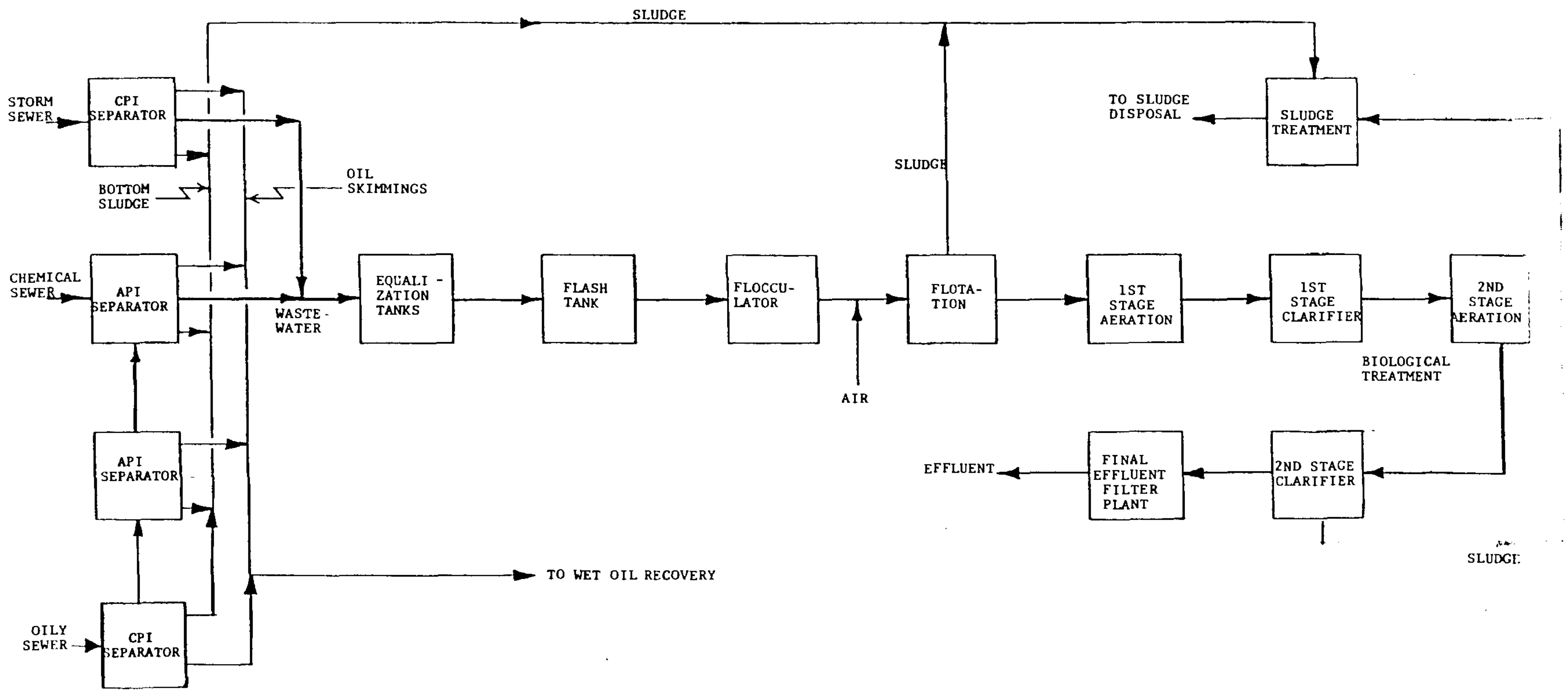

Figure 3-2 Refinery Waste Water Treating System

water products going to the same units as the streams from the storm sewer CPI separator. Not shown on Figure 3-2, refinery sour waters (containing high concentrations of H_2S and NH_3) are treated at a sour water stripping unit which removes essentially all the H_2S and NH_3 prior to discharge into the chemical sewer. The H_2S is then converted to sulfur and sold as a product.

The oily sewer utilizes a CPI separator and a API separator for oil-water separation and oil recovery. Waste water from the API and CPI separator join and flows to the equalization tanks to smooth out fluctuations in water flow. From the equalization tanks, water is taken to the flash mix tank where pH adjustment is made and flocculation chemicals are rapidly mixed with the waste water. The flocculator tank is next in the process and it allows residence time for dispersed oils and suspended impurities to clump together forming a floc.

A portion of the waste water from the flocculation tank is pressurized to 40 to 60 psi in the presence of sufficient air to approach saturation. This liquid-air mixture is recombined with the rest of the waste water and then released to atmospheric pressure in the floatation unit which causes minute air bubbles to rise up through water. As these bubbles pass through the waste water, oily floc and suspended solids attach themselves to the bubbles. As these bubbles reach the top they are skimmed off and the clarified liquid is removed at the bottom. The skimmed material is pumped to sludge treatment for processing.

The water flow continues to primary and secondary biological treatment where the waste water is mixed with air in the presence of microorganisms for decomposition of impurities. Waste sludge is removed from the second stage clarifiers and pumped to the sludge treatment plant. The waste water is then processed through final effluent filters before being discharged to a guard basin prior to its re-entry to the river.

Sludge treatment consists of a bio-sludge air floatation thickener, followed by an aerobic digestor, with the final step of sludge dewatering by gravity filtration. The sludge is then disposed of on-site by land treatment.

Figure 3-3 presents a simplified blockflow diagram of the wet oil processing system (CPI and API separator oil dewatering). This system receives oil from the tank farm and storm and oily sewers, CPI skimmings, chemical sewer API skimmings, and the primary sludge from sludge holding tanks. The wet oil is stored in day tanks (which include a recirculation heat exchanger) which are used to affect initial separation of oil and water. The remaining skimmings are fed to a pre coated vacuum filter that removes the solids, which are then disposed of in an on-site by land treatment. Additional oil is separated from the filtrate. The recovered oil is transferred into off-test tanks for reprocessing.

Each of the tanks described above is vented to a vapor recovery system where the hydrocarbon vapors are condensed by contact with refrigerated oil. The waste water separated at each tank is recycled through the storm sewer CPI separator and treatment plant.

Four operators and a foreman are assigned to each of the three daily shifts at the WWTP. With the expanded waste water treating facilities, the operators no longer rotate to other refinery units as part of their normal job assignments.

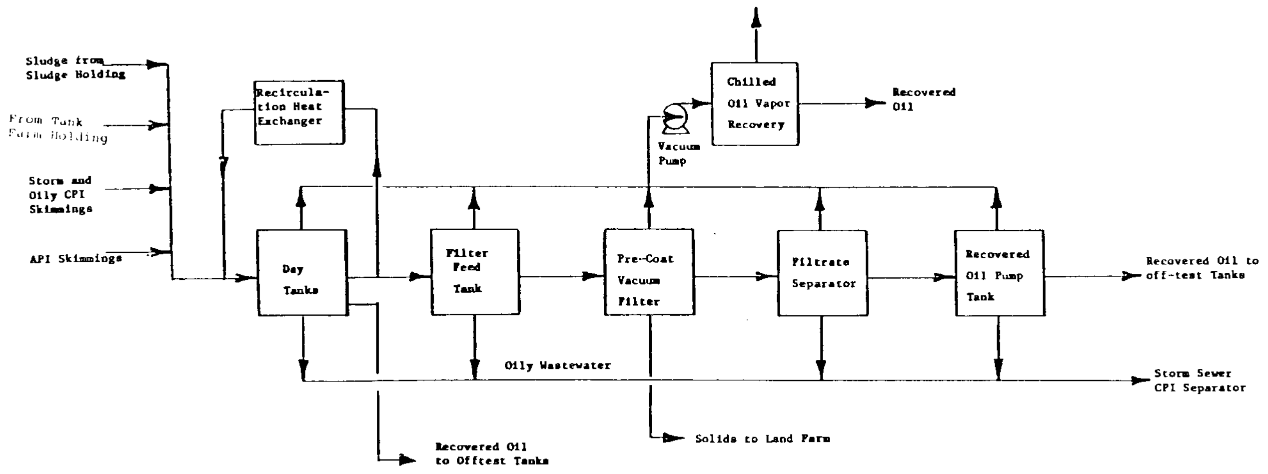

Figure 3-3. Wet Oil De-Watering System

3.2 Controls Reducing Worker Exposures

Three modifications made to waste water treatment facilities have significantly reduced worker exposures to H_2S, NH_3 and hydrocarbons:

- Improved sour water stripping
- Fugitive hydrocarbon emission controls
- Pressurized control room

Processing of refinery sour waters at the sour water stripper results in the removal of essentially all of the H_2S and NH_3 prior to final waste water treatment at the WWTP.

A number of hydrocarbon emission controls were implemented with the WWTP modifications. The new CPI separators significantly improve removal of free oils in covered facilities prior to the waste water flowing into the WWTP. Thus, less hydrocarbons are available for evaporation from the waste water in the downstream processing facilities (API separator, DAF unit, biological treating). Both CPI separators are covered reducing the ambient hydrocarbon levels around these oil-water separators. Hydrocarbons and oily sludges from the CPI and API separators are processed further to remove entrained or emulsified water from the oil. All of the facilities associated with this operation are tied into a vapor recovery system which recovers light hydrocarbons and reduces employee exposure.

A new control room was built to house the new process controls and monitors required to operate the WWTP. This modern control room is located in one corner of the WWTP and has a pressurized-recirculation air conditioning system. The old control room was located inside one of the WWTP sludge processing buildings in the center of the plant. The location and design of the new control room has reduced employee exposure to fugitive emissions from the WWTP facilities.

3.3 Industrial Hygiene Survey Results

This section presents the sampling results of the personal and area monitoring conducted by NIOSH in 1979 and by Radian in 1982. The 1982 survey was conducted to determine if a measureable reduction in employee exposures to H_2S, benzene, toluene and xylenes had occurred due to implementation of controls in the WWTP's 1980 modifications.

1979 Health Hazard Evaluation (HHE)

On November 24, 1978, NIOSH received a request to evaluate worker exposure to various chemicals at the Waste Water Treatment Plant (WWTP) at GRMC's Delaware Refinery. Workers were exposed to contaminants such as hydrogen sulfide, ammonia, benzene, hydrocarbons and other substances emitted during the various stages of the treatment process.

In August of 1979 NIOSH conducted an industrial hygiene and medical evaluation. Personal and area air samples for determination of organic vapors, amines and lead were obtained. Detector tube measurements were made to spot-check airborne contaminant concentrations. Airborne microorganisms were sampled to evaluate aerosol exposure in the area of the aeration tanks. The health of employees was evaluated through worker interviews, review of medical records, and consultation with the Refinery medical staff and private physicians.

Table 3-1 presents H_2S, benzene, toluene and xylenes area and personal sampling results from the 1979 HHE. Table 3-2 summarizes the range of these results.

TABLE 3-1 1979 HEALTH HAZARD EVALUATION BTX AND H_2S SAMPLING RESULTS

BTX CHARCOAL TUBE RESULTS - 8 HR TWA-PPM

	August 21, 1979						August 22, 1979					
	1st Shift			2nd Shift			1st Shift			2nd Shift		
	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
Personal Breathing Zone Samples												
Position												
WWTP Operator	.06	.06	<.02	.05	.05	<.02	.12	.15	<.02	<.03	<.03	.02
WWTP Operator	.02	.03	<.02	.12	.14	<.02	.20	.31	<.02	<.03	<.03	<.02
WWTP Operator	-	-	-	<.02	<.03	<.02	-	-	-	.12	.20	<.02
Utility Man							.14	.18	.05	-	-	-
Area Samples												
Location												
API Outlet	3.28	4.40	1.01	.06	<.03	<.02	7.22	10.3	2.32	5.9	8.7	.20
DCG	.22	.47	.19	1.70	6.20	-	.19	.30	.09	.14	.30	.19
Aeration TK Catwalk	1.89	2.37	.51	2.20	2.80	.53	1.74	2.6	.59	1.00	1.40	.31
Control Room	<.02	<.03	<.02	<.03	<.03	<.02	<.03	<.03	<.02	<.03	.03	<.02
Pump Area In Control Room Building	.06	.07	<.02	.15	.17	<.02	<.03	<.03	<.02	.10	.10	<.02

H_2S DETECTOR TUBE RESULTS - PPM

SUBSTANCE	AERATOR B, LOCATION (Y)				API SEPARATOR, LOCATION (Z)			
	9am, 8/21	9am, 8/22	5pm, 8/21	5pm, 8/22	10am, 8/21	10am, 8/22	4pm, 8/21	4 pm 8/22
Hydrogen Sulfide	4	0	4	4	<1	0	5	4

TABLE 3-2 SUMMARY OF HHE SAMPLING RESULTS

Substance	Personal Monitoring (ppm) 8-Hr TWA	Area Monitoring (ppm) 8-Hr TWA	OSHA Standard (ppm) 8-Hr TWA
Benzene	<.02 - .20	<.02 - 7.20	10
Toluene	<.03 - .30	<.03 -10.30	200
Xylenes	<.02 - .02	<.02 - 2.30	100
H_2S		< 1 - 5 (grab samples only)	20

Results of personal sampling indicated that 8-hour time-weighted average concentrations for unit operators during the four shifts sampled were less than 1 ppm for benzene, toluene and xylenes. Grab samples for H_2S using detector tubes showedmeasureable amounts (1-5 ppm) over the two-day sampling period at the API separator and the biotreatment unit (Aerator B).

NIOSH concluded from the HHE that no chronic health effects were evident but that the presence of benzene, although low, could have potential long term health effects. H_2S, NH_3, and amines were assumed to be the most probable cause of the alleged acute health effects which resulted in the request to conduct the HHE. NIOSH also indicated that many of the modifications ongoing in 1979 would result in lowering employee exposure to those substances of concern, particularly benzene, H_2S, and NH_3.

1982 Industrial Hygiene Survey

In an effort to evaluate the effectiveness of the WWTP modifications as engineering controls to reduce employee exposure, a one day area and personal sampling effort was conducted by Radian during its indepth visit to the Delaware Refinery. Four substances were the focus of this sampling: H_2S, benzene, toluene and xylenes (BTX).

Hydrogen sulfide area samples were taken using a new proposed NIOSH method (P & CAM 296) which uses a molecular sieve tube to capture H_2S (SKC Inc. Catalog Number 226-12-06). A sodium sulfate tube is used prior to the molecular sieve material to remove moisture (SKC Inc. Catalog Number 226-44-02). Short-term readings for H_2S were also made using an MSA Model 470600 hand held direct reading monitor. Area and personal samples for benzene, toluene and xylenes were taken using charcoal tubes and low flow pumps (NIOSH Method P & CAM 127).

Tables 3-3 and 3-4 present sampling results for BTX and H_2S, respectively. As Table 3-3 shows, breathing zone time-weighted average concentrations of benzene measured for the two separator operators were well below both the current OSHA permissible exposure limit (PEL) of 10 ppm and the NIOSH-recommended PEL of 1 ppm. Exposure to toluene and xylenes was minimal, about two orders of magnitude below the OSHA PEL for those substances.

TABLE 3-3 BTX SAMPLING RESULTS - AUGUST 25, 1982

	Benzene(ppm)	Toluene(ppm)	Xylenes(ppm)
Personal Samples, Breathing Zone			
"B" Operator	0.2*	0.9*	1.1*
Relief Operator Trainee	0.1*	0.7*	0.6*
Area Samples			
CPI Separator	0.9	3.0	3.1
API Separator	2.6	9.9	16
Old Control Room	ND	0.01	0.1
Pump Room	0.01	0.05	0.2
New Control Room	0.2	0.7	0.6

* 8-hr time weighted average concentration

ND - Not detected

TABLE 3-4 H_2S RESULTS - AUGUST 25, 1982

Area Sample Locations	Molecular Sieve Tubes (ppm)	MSA Monitor (ppm)
CPI Separator	ND	ND
API Separator	ND	0.1 - 1.0
Aeration Catwalk	--	ND
Old Control Room	--	ND
Wet Oil Filter Bldg.	--	0.4 - 1.4

ND - Not Detectable

Concentrations measured during area sampling were in the following ranges:

- Benzene - 0.01 to 2.6 ppm
- Toluene - 0.01 to 9.9 ppm
- Xylenes - 0.1 - 16 ppm

All of the higher concentrations were measured at the API separator.

Hydrogen sulfide long term (1-2 hour) samples collected using molecular sieve tubes showed no detectable levels of H_2S (<0.1 ppm). However, some difficulty with the analytical calibration technique cast doubt on the accuracy of these results. Spot readings using the MSA direct reading meter showed short term H_2S levels near 1 ppm at the API separator and wet oil separation building.

3.4 Exposure Control Evaluation

As was the case for the two day HHE sampling effort in 1979, the one day sampling effort conducted in 1982 can only provide screening results. No significant drop in BTX levels were observed. However, the BTX levels measured in both studies were low. Hydrogen sulfide sampling results indicate a measureable drop in ambient levels of H_2S. The impact of the three major exposure controls implemented as part of the 1980 WWTP modifications is discussed below.

Sour Water Stripping Unit

Environmental regulations directed toward reducing the amount of ammonia and sulfides discharged in waste water have resulted in more efficient removal of hydrogen sulfide (H_2S) and ammonia (NH_3) from refinery waste water. Generally, the technology used to remove these pollutants is steam stripping after which the H_2S is recovered as sulfur and the NH_3 incinerated.

A major benefit obtained by refiners which segregate and strip H_2S and NH_3 from process sour water streams is the reduction of fugitive H_2S and NH_3 from the waste water collectionand treatment systems. These fugitive emissions pose potentially acute and chronic health effects problems in refineries processing crudes with significant amounts of sulfur (greater than one weight percent sulfur).

The 1979 HHE concluded that one of the most probable causes of the alleged acute health problems reported by WWTP workers was low level H_2S exposure. Start-up of the sour water stripping unit in 1980 has resulted in lowering the average ambient concentration of H_2S at the WWTP, particularly around the API separator. Short-term measurements in August of 1979 showed 4 to 5 ppm H_2S concentrations several times during the four shifts sampled. Long-term (1-2 hour) and short-term measurements made in August 1982 showed a maximum H_2S level of 1 ppm with most results indicating no detectable levels of H_2S (<0.1 ppm).

It should be noted that since the start-up of the WWTP in 1974, area H_2S monitors have been in operation to warn employes of ambient concentrations of H_2S in excess of 10 ppm. The refinery industrial hygienist and WWTP supervisor indicated that the H_2S monitors at the API separator now rarely alarm, though still set at the 10 ppm level. The 1979 HHE indicated that several times a month 10 ppm H_2S levels were exceeded at the API separator monitor.

It can be conclusively stated that the start-up of the sour water stripping unit has reduced the H_2S concentration in the waste water going the WWTP. The 1979 and 1982 sampling results and the disappearance of the acute health effects alleged prior to 1980 indicate that the sour water stripping unit has been a highly effective employee exposure control.

Fugitive Hydrocarbon Emission Controls

The focus of the hydrocarbon fugitive emission controls evaluation made during the Radian/NIOSH indepth visit to the Delaware Refinery was the installation of covered CPI oil-water separators. During the 1979 HHE, only the API separator was used for primary oil-water separation. The 1980 WWTP modifications added two CPI separators to improve the effectiveness of the primary oil-water separation. Both of these new separators are covered as shown in Figure 3-4.

A direct comparison of the ambient BTX concentrations measured at the storm water CPI separators and the API separator would have provided a good measurement of the effectiveness of the CPI separator covers. However, because the oily sewer CPI separator was not in service due to normal clean-out maintenance, the oily sewer waste water during the onsite visit was bypassing the CPI separator directly to the API separator.

This situation impacted the Radian/NIOSH sampling effort in three ways. First, a direct comparison of the effectiveness of the oily water CPI separator fugitive control (i.e. cover) could not be measured versus the fugitive emissions from the API separator (which is mostly uncovered). Secondly due to the reduced oil-water separation efficiency obtained when both the CPI separator and API separator operate in series, fugitive hydrocarbon emissions from the API separator were probably somewhat higher than during normal operation since the 1980 modifications. Finally, because the storm sewer waste water is not as oily as the oily sewer waste water, direct comparison of fugitive emission measurement of the storm sewer CPI separator (covered) and the API separator (uncovered) handling both storm

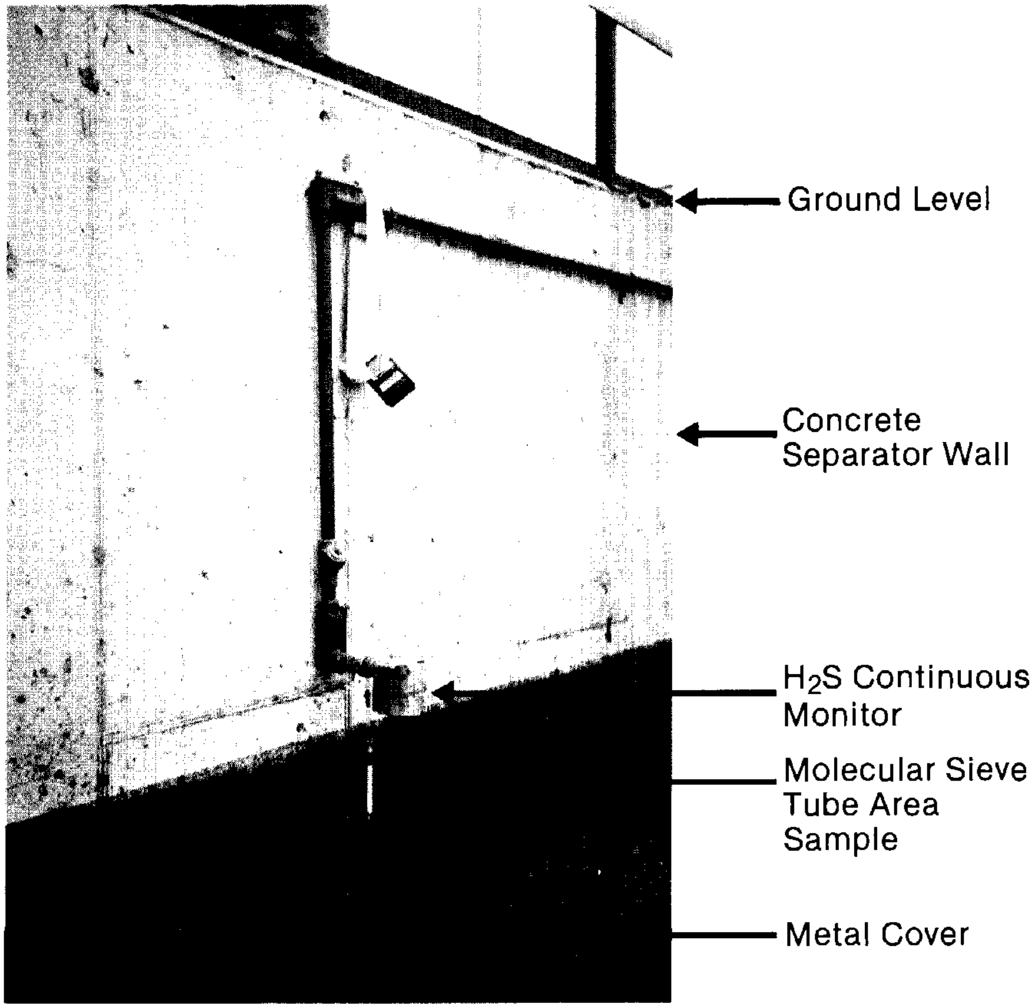

Figure 3-4 Storm Sewer CPI Separator

sewer waste water and untreated oily sewer waste water would not be meaningful as compared to the 1979 HHE results.

Area sampling of the storm sewer CPI separator indicated measureable quantities of BTX. However, benzene levels were 10 times less than the OSHA PEL of 10 ppm and just below the NIOSH-recommended PEL of 1 ppm. The API separator, probably operating at a slightly lower efficiency due to the non-operational oily sewer CPI separator, showed ambient BTX levels 3 to 4 times higher than the storm sewer CPI separator. These BTX levels were also well below the OSHA PEL for benzene, toluene, and xylenes.

Other area sampling results for BTX in the WWTP indicate that the primary exposure source for BTX is in the API separator area. Consequently, probably a great percentage of the WWTP employee exposure to BTX (between 0.1 and 0.2 ppm benzene) occurs during the less than 10 percent of the employee shift time spent around the API separator. If future research were to indicate that employee exposure levels to benzene should be much lower than 1 ppm, covers over the entire API separator and/or a respirator program could be implemented to lower potential benzene exposure.

Pressurized Operator Control Room

As part of the 1980 WWTP modifications, a separate central control room was constructed in the northwest section of the WWTP area. As is the case with most new unit construction at petroleum refineries, pressurized central controls rooms have replaced smaller controls rooms located in major equipment areas. These central controls rooms, if properly designed and located, can be very effective employee exposure controls for the following reasons:

- Pressurized recirculating air conditioning systems can reduce the concentration of air contaminants inside the control room.

- Control room location is usually not immediately adjacent or within the process equipment.

- Process controls and monitors incorporated in new control rooms can reduce the number of employees required or improve the effectiveness of the process control which results in fewer process upsets resulting in lowered employee exposure potential.

Area samples taken during the 1979 HHE at the old WWTP control room and area samples taken during the 1982 indepth visit at both the old and new WWTP control rooms indicate very low levels of BTX:

- Benzene $\leq$ 0.2 ppm
- Toluene $\leq$ 0.7 ppm
- Xylenes $\leq$ 0.6 ppm

The highest levels found were in the new control room.

Although the new control room BTX levels were higher than the 1979 and 1982 sampling of the old control room, BTX levels were well below 1 ppm. The increase may be due in part to normal sampling/analytical differences and to the new control room's proximity to the API separator. The new control room is located 100 - 200 feet east of the API separator, the major source of BTX emissions in the WWTP. Prevailing winds during the 1982 sampling effort were from the west due to a passing low pressure system. If future research indicates that employee exposure to benzene should be much lower than 1 ppm, reduction of hydrocarbon emissions from the API separator or use of a charcoal filter on the control room intake air system may be required to reduce the control room BTX levels below 1 ppm.

4.0 BENZENE/AROMATICS PRODUCTION AND LOADING

A potential employee health hazard in areas producing or handling aromatics is overexposure to benzene. A suspect human carcinogen which has been linked to leukemia and similar blood disorders, benzene is currently regulated by OSHA at a Permissible Exposure Level (PEL) of 10 parts per million (ppm). The NIOSH-recommended standard is 1 ppm.

To minimize employee exposure to benzene and other aromatic compounds during tank truck loading operations, Getty has constructed loading facilities which incorporate several engineered controls. These controls, used in conjunction with personal protective equipment, substantially reduce loading area employees' benzene exposure.

4.1 Process Description

The GRMC's Delaware Refinery utilizes a Union Carbide licensed Tetra process for aromatics extraction. The Tetra process is a liquid-liquid extraction system using tetraethylene glycol as a solvent. After heat exchange with hot raffinate, the feed, containing a mixture of aromatics, paraffinsand some naphthalenes is counter-currently contacted with aqueous tetraethylene glycol solution in the extractor column. The hot, rich solvent, containing benzene, toluene and xylenes (BTX) is cooled and introduced into the top of a stripper column. The aromatics are then purified by extractive distillation and recovered from the solvent by steam stripping. Both of these operations are performed in a single stripper column at atmospheric pressure.

The stripper overhead is condensed and the hydrocarbon phase containing some light saturated hydrocarbons is sent back to the extractor as reflux. The raffinate and the decanted extract product are washed with water to recover the solvent before it is sent to storage.

Benzene and aromatics products are sent to storage prior to their sale as petrochemicals. Raffinate goes to jet fuel or gasoline blending.

4.2 Description of Loading Facilities

In 1980, GRMC constructed two loading facilities equipped with engineered controls at the Delaware Refinery. One is dedicated to benzene loading; the other is used for loading Aromatics 150, a product of mixed xylenes heavier than C_{13}, containing less than 0.3 percent benzene. The design of each facility is essentially similar, as described in the following paragraphs.

Figure 4-1 is a photograph of the Delaware Refinery's benzene loading "rack," located adjacent to the Refinery's benzene storage tanks. The facility is a partially-enclosed corregated metal shelter which houses a heated cabinet for the product loading arm, an automatic metering system, a vapor recovery system, and an electrical grounding system.

The loading arm is shown within its cabinet in Figure 4-2. A dripless connector is attached to the arm's end to minimize leaks. The loading arm is stored in a heated cabinet to prevent benzene solidification during loading operations in winter months.

Other equipment in the loading facility (shown in Figures 4-3 and 4-4) include a metering system which automatically controls the amount of benzene transferred to each truck, and a vehicle grounding mechanism. To ensure proper vehicle grounding, the loading arm discharge valve will not open unless a secure

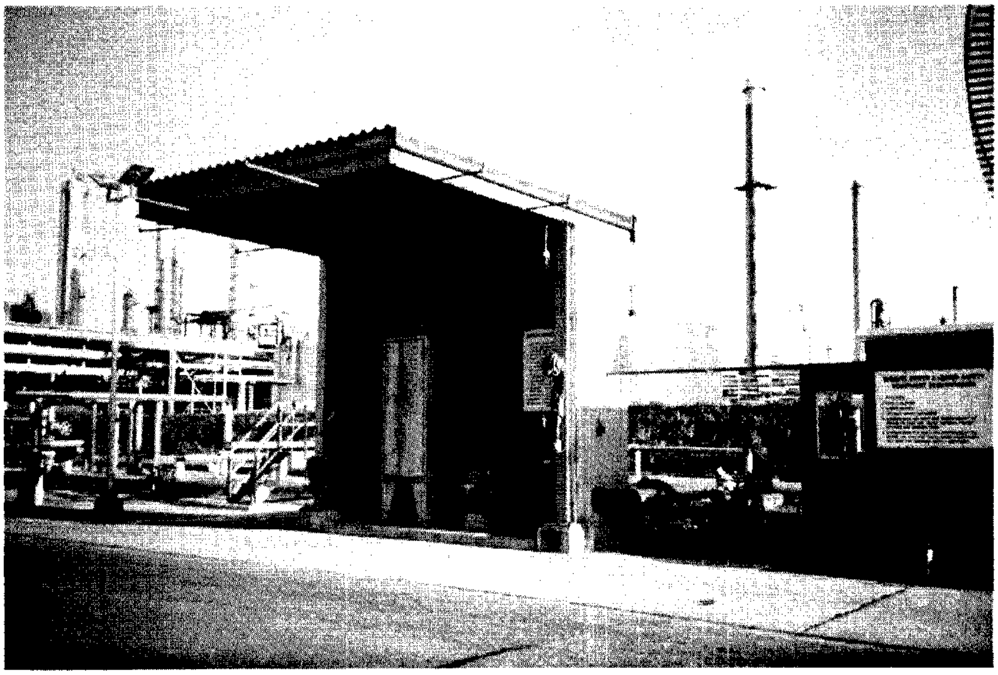

Figure 4-1 Delaware Refinery Benzene Loading Facility

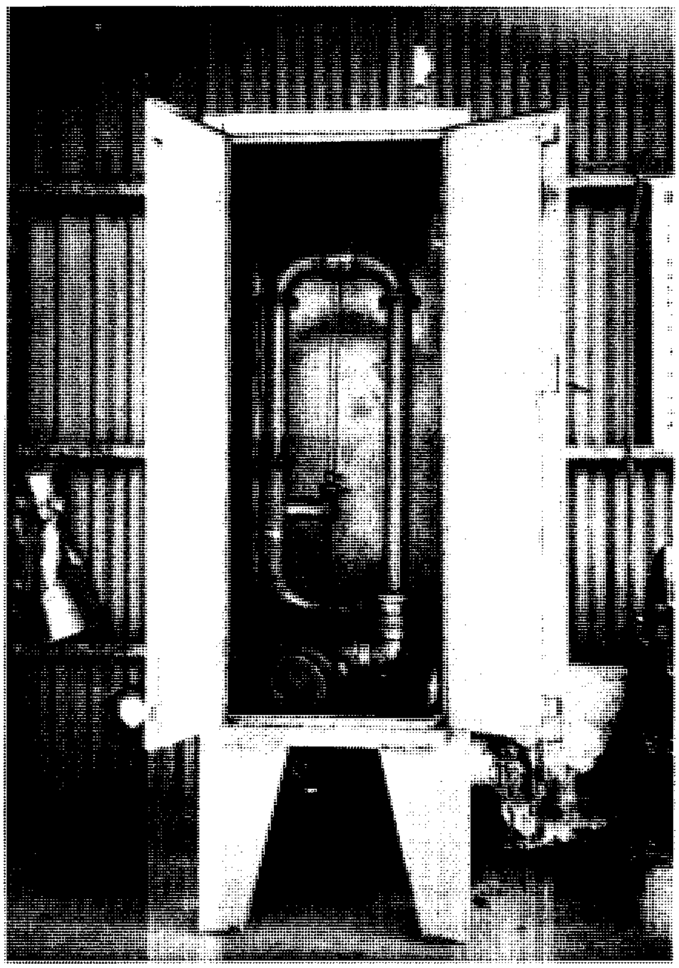

Figure 4-2 Benzene Loading Arm Inside Cabinet

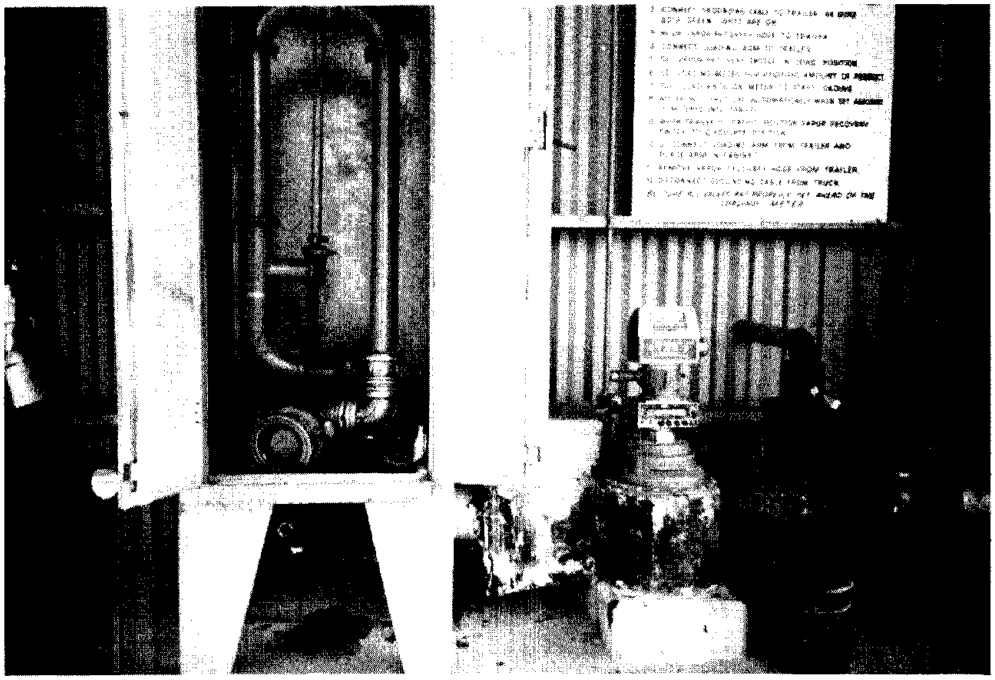

Figure 4-3 Automatic Product Metering System

Figure 4-4 Vehicle Grounding Mechanism

grounding connection is made. A visual signal (dual green lights) is displayed on the meter panel when a proper ground connection has been achieved.

GRMC has installed a fugitive emissions collection system for the benzene loading facility. A simplified diagram of the system at the benzene loading rack is shown in Figure 4-5. Fugitive vapors are a flexible hose attached to each tank truck. The system is actuated with the loading facility's delivery meter. Recovered vapor is sent to furnaces where it is incinerated.

GRMC personnel estimate the cost of each loading facility in a range between $40,000 and $50,000 (1980 dollars). The total cost is divided evenly between equipment and installation costs. The loading arm, dripless connectors, meter, and electrical grounding system were obtained from Liquid Loading Systems, King of Prussia, Pennsylvania.

4.3 Typical Loading Activities

During the indepth visit, Radian and NIOSH personnel observed benzene and Aromatics 150 loading activities on what was described by Getty employees as a typical day. On this day, five trucks were loaded with benzene and two were loaded with Aromatics 150. Based on our observations, typical loading activities are summarized in the following paragraphs.

One employee is responsible for loading activities at both the benzene and aromatics loading racks. This employee works an eight-hour shift which begins at 7:00 AM and ends at 3:00 PM. Trucks are loaded only on this shift five days per week (Monday through Friday). Although an operator's shack is located in the loading area, the truck loader remains in the area only when trucks are being loaded. All other time is spent in the Aromatics Extraction Unit's positive pressure control room.

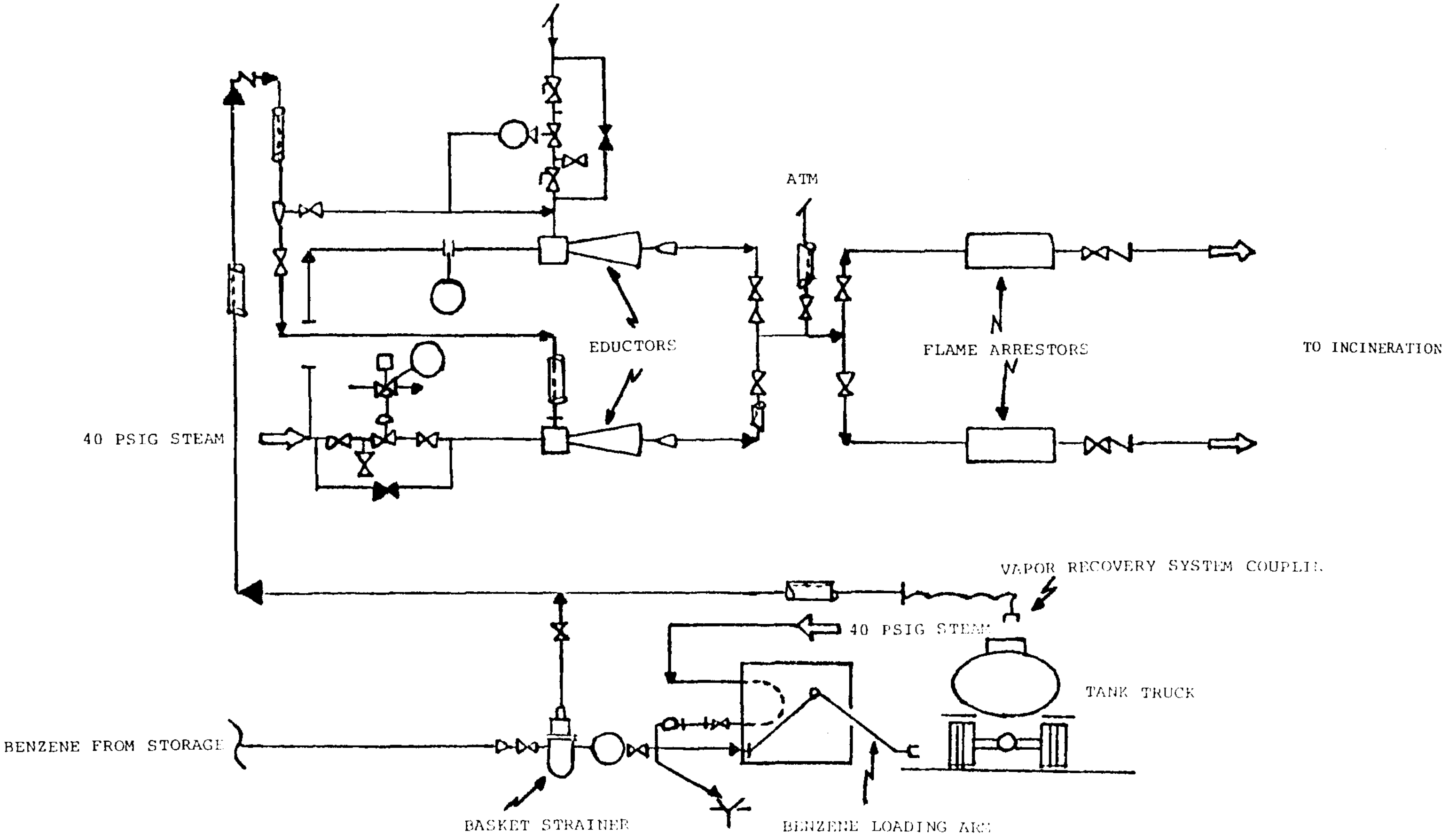

Figure 4-5 Diagram of Vapor Recovery System

When a truck arrives at the Refinery gate, a guard notifies the truck loader in the control room. Each truck requires about 15 minutes for loading. Although the loader has some knowledge of how many trucks are scheduled each day, the number often varies because unscheduled trucks are typically added to the schedule as the day progresses.

The loading procedure is the same for benzene and Aromatics 150. When a truck is positioned at the loading rack, its driver turns off the motor and leaves the vehicle. From this point until the loaded truck is ready to leave the refinery, the loader is completely responsible for the loading operation. The driver may assist if necessary, provided he is equipped with personal protective equipment equivalent to that worn by the truck loader: safety helmet, safety glasses or goggles, rubber gloves, and an organic vapor cartridge respirator.

The loader first connects the loading rack's vehicle grounding mechanism to the truck (Figure 4-6), making sure that the dual green lights on the meter panel are illuminated to indicate that the truck is properly grounded. Next, the flexible vapor recovery system hose is attached to the truck, as shown in Figure 4-7. Figure 4-8 illustrates the next step in the procedure, attaching the loading arm to a corresponding dripless connection on the side of the truck. The loader next sets the meter to transfer the required amount of product into the truck. The vapor recovery system is actuated with the meter.

When the product has been fully loaded into the truck, the loading arm discharge valve automatically closes. At this point, the loader disconnects the loading arm, the vapor recovery hose and the electrical grounding cable, and the truck may leave the Refinery.

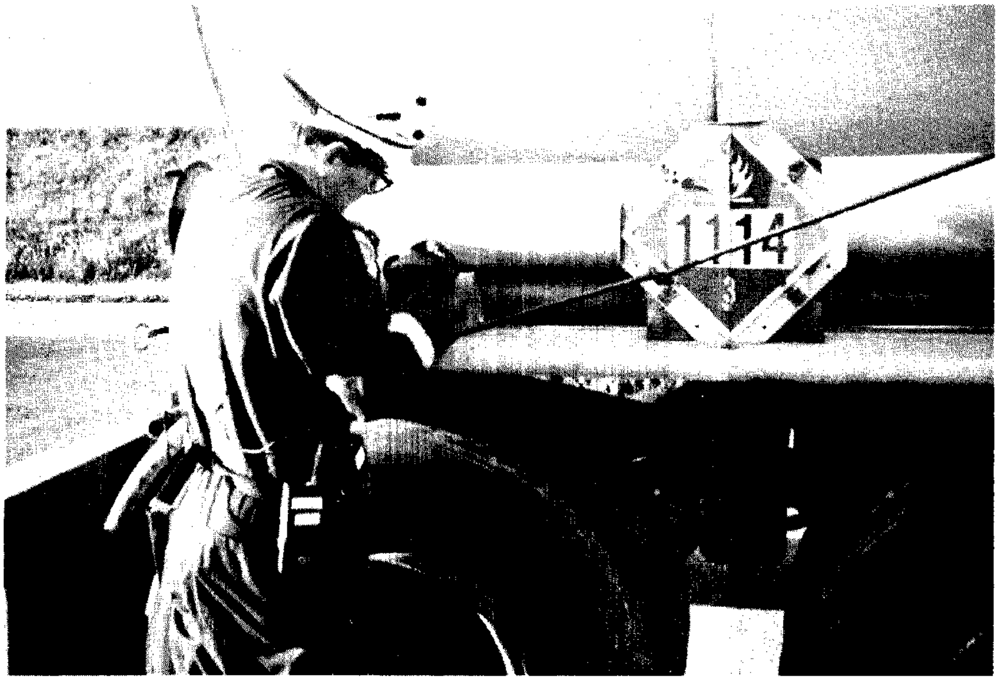

Figure 4-6 Truck Loader Connects Grounding Cable to Truck

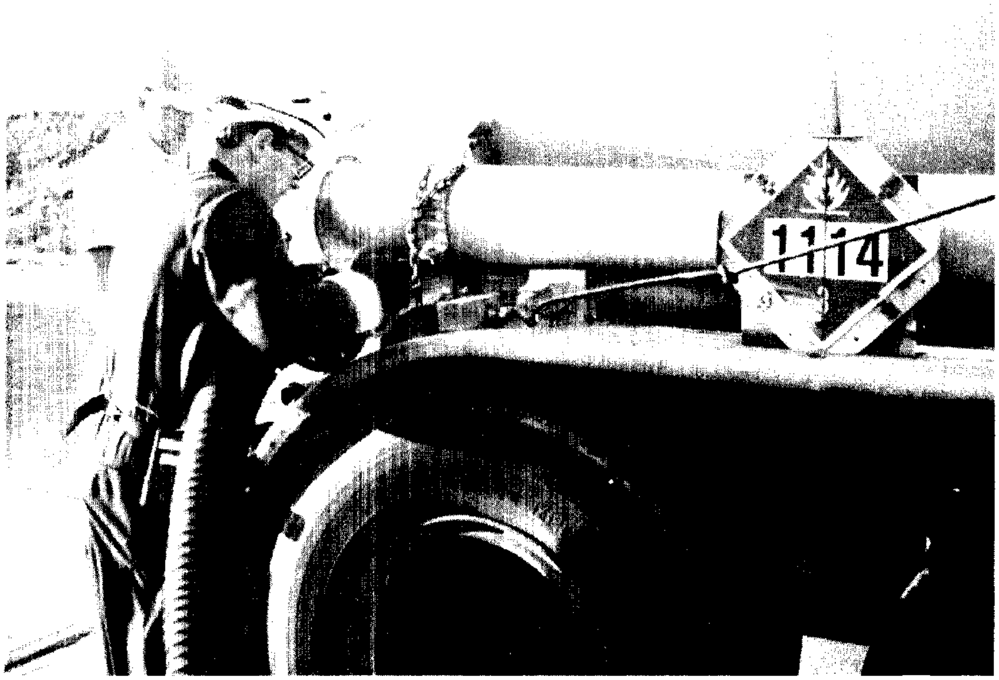

Figure 4-7 Vapor Recovery Hose Attached to Truck

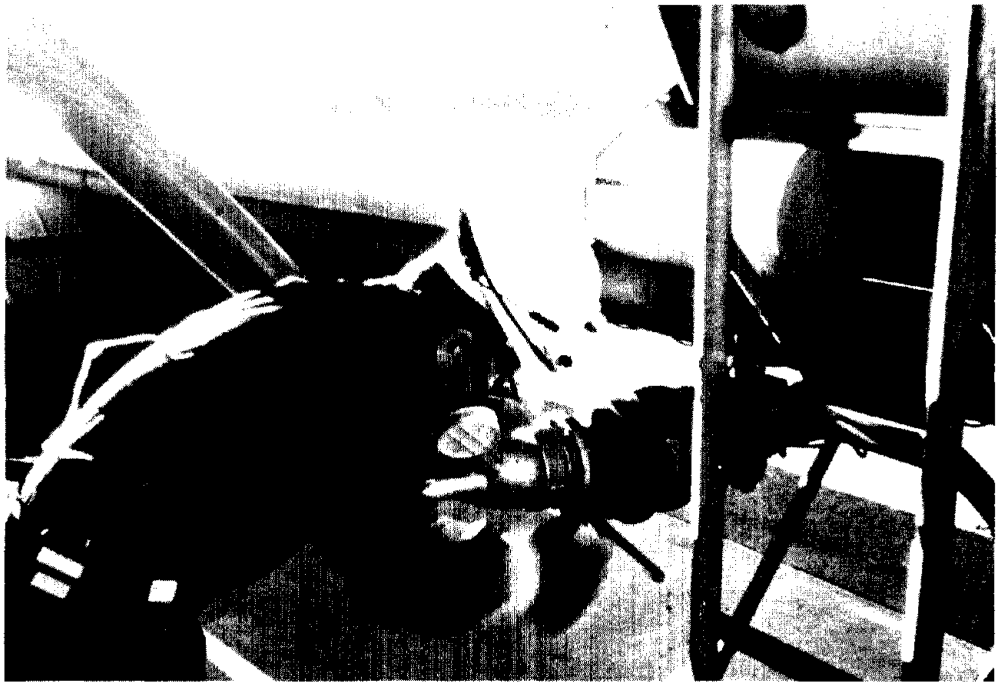

Figure 4-8 Truck Loader Connects Loading Arm to Truck

At times (e.g. at the beginning of the shift) when several trucks may be loaded in sequence, the loader remains in the area for an extended period of time. During non-peak times, however, the loader returns to the control room immediately after loading a truck and may remain there for several hours before the next truck arrives.

4.4 Aromatics Product Sampling Procedure

Benzene and aromatics process stream sampling is normally conducted once per day during the 7:00 AM to 3:00 PM shift. One-liter stainless steel sample collection bombs are used to collect samples. The bombs have been redesigned by the Refinery to make them easier to use and to prevent leaks. Each is fitted with a carrying handle and double seal quick-connect fittings that are color-coded to ensure that they are used in sampling only one type of process stream. The closed sampling loop in which each bomb is connected is a low-pressure, flow-through design (Figure 4-9).

Two sampling bombs are filled during each sampling period. The operator connects each bomb to the sampling loop and draws sample through the bomb for about 30 seconds. He then clears each of the sampling lines and disconnects the bomb.

Personal protective equipment worn by the operator during process sampling includes a safety helmet, safety goggles, rubber gloves, coveralls, and a half-facepiece organic vapor cartridge respirator.

Process sampling for benzene was observed during the indepth visit. Short-term sampling conducted using detector tubes indicated only a trace amount of benzene during sampling. One drop of benzene liquid fell from the end of each connector when the sampling bomb was removed from the sampling loop.

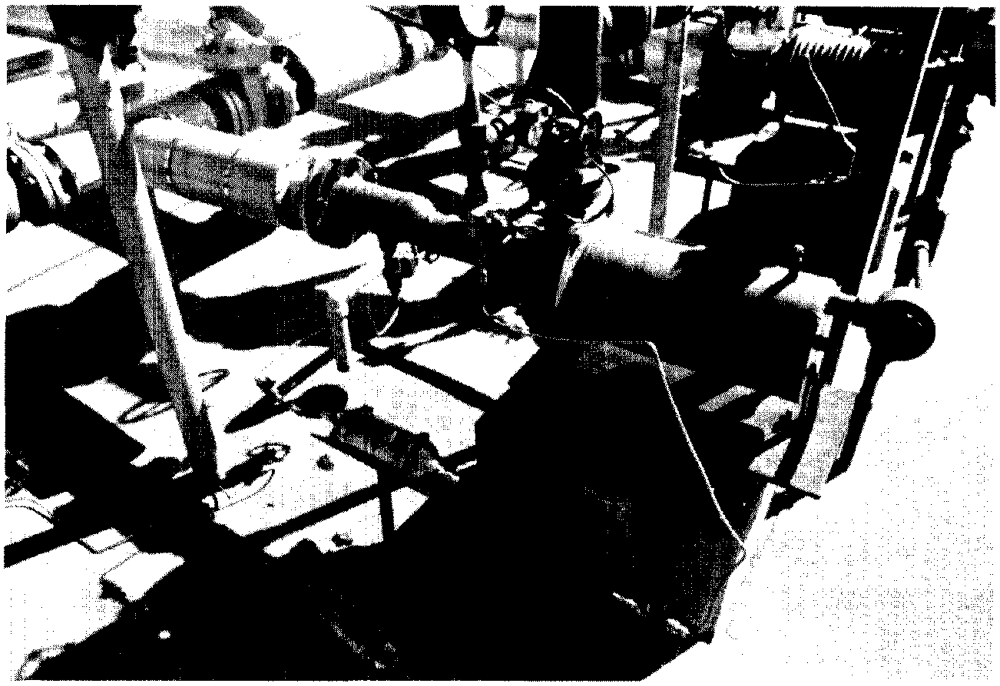

Figure 4-9 Benzene Process Stream Sampling Apparatus

4.5 Sampling and Analytical Results

Long-term personal and area samples were collected around the benzene and Aromatics 150 loading facilities during the Radian/NIOSH indepth visit. Sampling pumps (MDA Scientific Model 808) were positioned inside each loading facility. Air to be sampled was drawn through a charcoal tube (SKC, Inc., Lot 120) at a nominal rate of 100 cc/minute. Additionally, a breathing zone full shift sample was collected on the truck loader. NIOSH Method P & CAM 127 was used to analyze the samples for benzene, toluene, and xylenes.

Sampling results are shown in Table 4-1. As the table shows, all benzene concentrations are below the current OSHA Permissible Exposure Level of 10 ppm. However, the area concentration at the benzene loading rack and the truck loader's time-weighted average concentration exceeded the NIOSH-recommended standard of 1 ppm. The truck loader's actual exposure to benzene is less than 5.5 ppm because of his use of a half-facepiece organic vapor cartridge respirator during loading operations.

TABLE 4-1 LOADING AREA SAMPLING RESULTS

		(ppm)	
Sample Point	Benzene	Toluene	Xylenes
Benzene Loading Rack	9	0.1	0.1
Aromatics Loading Rack	0.5	0.1	0.02
Truck Loader Relief Operator	5.5*	0.1*	0.04*

* 8-hr. Time-Weighted Average Concentration

The Refinery's industrial hygienist ran parallel samples on the same employee with similar sampling techniques and found a 8-hour TWA of 119 ppm. Previous employee samples taken by the company during this operation have shown consistent reading below 1 ppm of benzene. Concentrations of toluene and xylenes at all sample points were well below the OSHA permissible exposure limits of 200 ppm for toluene and 100 ppm for xylenes.

4.6 Evaluation of Controls

The use of engineered controls and personal protective equipment at the Delaware Refinery appeared to be effective in reducing employee exposure to benzene and other aromatic hydrocarbons. Engineered controls such as the vapor recovery system and the loading arm equipped with dripless connectors did much to minimize airborne hydrocarbon levels resulting from fugitive emissions and spills or leaks. Use of appropriate respiratory protection provides a further element of employee protection, particularly against overexposure to benzene.

Proper maintenance of engineered controls is necessary to ensure the controls' integrity and continued effectiveness. The loading facilities appeared to be extremely well-maintained, as did the dripless connectors and vapor recovery system connectors on tank trucks owned by GRMC. However, other tank trucks observed during the indepth study were not well-maintained. The truck loader had difficulty in establishing a good seal on two trucks in particular, and benzene was spilled as a result. It is probable that most of the truck loader's exposure to benzene may be attributed to these spills.

The truck loader can (and reportedly does) refuse to load trucks with incompatible or poorly maintained connectors. However, in many instances, the truck loader does not know a connector is bad until he has attempted to initiate loading. To alleviate this problem, the truck loader should keep a log of loading activities and record in the log those trucks or independent haulers with which he had difficulty. GRMC management should periodically review the log to identify haulers with chronically-poorly maintained loading facilities. These haulers then should be contacted and requested to upgrade their equipment.