CONTROL TECHNOLOGY ASSESSMENT
OF SELECTED
PETROLEUM REFINERY OPERATIONS

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ABSTRACT

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 conducted by Radian Corporation was to identify and evaluate examples of good employee exposure control techniques associated with several petroleum refining operations: Lube oil and wax processing and packaging; catalytic reforming and aromatics extraction; oil-water separation; alkylation; and hydrogen sulfide handling.

Indepth visits were conducted at seven petroleum refineries across the U.S. and successful employee exposure controls were documented and evaluated:

- HF Alkylation Unit Exposure Controls
  - protective clothing change room to manage HF protective clothing and work practice programs
  - separate maintenance facilities designed specifically to handle HF contaminated equipment
  - emergency decontamination shower designed to wash down protective clothing while still on the employee

- Process Sampling Engineering Controls
  - valve and spigot enclosure designed to prevent exposures to operators due to splashed liquid and released vapors.
  - density measuring chamber enclosure designed to prevent operator exposure to acid and hydrocarbon vapors at sulfuric acid alkylation units.

- Hydrogen Sulfide and BTX Area Monitoring Systems - description of newly installed state-of-the-art area monitoring systems employing new sensor technologies and advanced warning and data handling systems.

- Emission Controls at Oil-Water Separators
  - dissolved air flotation unit covers vented to a carbon absorber.
  - sour water stripping and separator covers to reduce exposures to H_2S, NH_3 and hydrocarbons.

- Emission Controls at a Benzene Loading Facility - includes vapor recovery system and dripless connectors.

- Equipment Maintenance Controls - preventive maintenance programs which can reduce employee exposures include valve and rotating equipment inspection/maintenance, exchanger head leak prevention and acoustic testing programs.

- Catalyst Dust Wet Scrubber - skid mounted two stage wet scrubber used to reduce catalyst dust emissions during catalyst dumping.

- Lube Oil and Wax Processing and Construction Changes
    - comparison of employee exposure potential at a new lube oil process (hydrogenation) which replaced furfural extraction and clay filtering processes.
    - benefits of open air unit construction and remotely located control rooms.

The information obtained from the program will be disseminated to the industry and other interested parties. This information transfer is designed to promote the use of successful exposure control ideas.

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ACKNOWLEDGEMENTS

Radian Corporation and NIOSH greatly appreciate the time and effort committed to this program by representatives of the American Petroleum Institute, the National Petroleum Refiners Association and the participating petroleum refining companies. Special thanks go to all of the refinery personnel who were very supportive of this program.

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) develops and disseminates information concerning the effectiveness of control technologies which can be used to reduce occupational exposures to toxic chemical substances and harmful physical agents. This report documents a research program which identified and evaluated examples of successful employee exposure control techniques implemented at seven petroleum refineries which participated in the study. Hopefully, the information provided here will facilitate earlier application of available employee exposure controls in the petroleum refining industry and other industries having similar processing technologies.

The U. S. petroleum refining industry is made up of over 150 refineries ranging in size from processing several thousand barrels of crude oil per day to processing half a million barrels of oil per day. Although a wide range of processing technologies are utilized, most refineries, regardless of size, use modified versions of the same processes. Most processes are continuous and under pressure necessitating closed processing systems (i.e., liquids, gases, and solids are completely contained in process equipment). Primary employee exposures occur:

- Due to process leaks (fugitive emissions)
- Due to equipment failures
- During sample collection/analysis
- During final product and process chemical loading/unloading
- At waste treatment facilities which are typically not closed processes, and
- During equipment maintenance.

This program was conducted in three phases. Under Phase I the project scope of work was developed with input from various government agencies, industry, and organized labor. At a tripartite meeting held in April 1981, five petroleum refining processing areas were selected as shown in Table 1. These processing areas were selected based on industry interest and the lack of previous NIOSH work in these areas. One additional area (H_2S area monitoring systems) was added later, due to industry input subsequent to the tripartite meeting.

During Phase II of the program, one day visits were made to each of the seven refineries which agreed to participate in the program. The purpose of this program phase was to identify specific employee exposure controls of interest for indepth documentation and evaluation. After making the seven refinery visits plus a one day visit to a refinery process licensor, eight employee exposure control techniques were selected for indepth study.

During Phase III of the program, all seven of the participating refineries were revisited to collect design and operating information regarding the selected controls and to collect sampling data to evaluate the effectiveness of the controls whenever possible. This program final report summarizes the pertinent information obtained on the eight employee exposure control areas studied indepth.

TABLE 1
PROCESSES SELECTED FOR PRELIMINARY STUDY

Lube Oil and Wax Processing: Characterize controls applicable to: (1) solvent (phenol, furfural) extraction of lube oils to remove aromatics and resins, (2) dewaxing involving solvent (propane, methyl ethyl ketone, toluene, benzene, chlorinated hydrocarbons) extraction, subsequent recrystallization, and removal by vacuum filtration, (3) clay treatment of specialty lube oils including clay filtering operations and (4) hydrotreating.

Lube Oil/Wax and Grease Packaging: Characterize controls applicable to batch and in-line blending of lubricating oils and greases. Attention was given to exposure problems created by additives used in these processes.

Catalytic Reforming/Aromatics Extraction: Characterize controls applicable to fugitive emissions (e.g., benzene, toluene, xylenes) from catalytic reforming equipment (valves, flanges, pumps, etc.) and similar equipment associated with aromatics extraction, handling and storage.

Liquid Waste Separators (Oil-Water): Characterize exposure control options for work associated with oil-water separators (hydrogen sulfide, ammonia, hydrocarbons).

Alkylation: Characterize controls used to reduce exposure potential to hydrofluoric and sulfuric acid catalysts used in the alkylation process.

H_2S Area Monitors: Characterize new technologies now being employed by refiners in the areas of sensor/detectors, controllers, graphic alarm systems and data handling systems.

SECTION 2

SUMMARY OF CONTROL TECHNOLOGY AREAS STUDIED

Employee exposure control technology as defined for this program consists of: (1) engineering controls for the elimination or control of exposure to toxic chemicals and harmful physical agents; (2) work practices which lessen employee contact with harmful agents; (3) process or operation monitoring systems for warning of a process or control failure which would create a health hazard; and (4) personal protective equipment for individual worker protection from uncontrolled toxic chemicals harmful physical agents, and safety hazards.

Engineering controls are methods of applied technology used to reduce or eliminate emission of a toxic chemical or a harmful physical agent into the workplace. Examples include:

- Substitution of a non-toxic or less toxic substance for a toxic one
- Process design or modification
- Equipment design or modification (pumps, seals, fittings, etc.)
- Isolation of a process or worker
- Dilution, local, or general exhaust ventilation
- Maintenance procedures for the above (where appropriate).

Work practices are defined as specific work and management techniques which minimize the generation and subsequent emission of a toxic chemical or harmful physical agent, or which prevent or minimize worker contact with these agents.

Monitoring devices are used to warn of a process or engineering control failure which would result in excessive concentrations of a contaminant in the workplace. Examples include:

- Exhaust system failure monitors
- Continuous workplace environment monitors
- Warning devices which are tied into process control systems that indicate process phases, malfunctions, or failures which may result in employee exposure.

Personal protective equipment includes devices worn by a worker to protect against uncontrolled toxic chemicals or harmful physical agents. Examples include:

- Respirators
- Protective clothing (gloves, suits, etc.),
- Hearing and eye protection.

Although the petroleum refiners rely on the full range of employee exposure control methods, engineering controls, to contain all substances within the process equipment, are the primary method used. Other control methods are used as back-up to engineering controls.

REFINERY PARTICIPATION

Working closely with representatives of American Petroleum Institute, National Petroleum Refiners Association and representatives from individual companies, refinery participation in the study was arranged. Over forty refining companies were contacted about participating in an indepth visit at one of the company's refinery locations. Seven refineries agreed to participate and Table 2 provides a brief profile of each refinery.

Based on the one-day preliminary visit to each refinery, fourteen employee exposure control applications were documented and evaluated during 2-3 day indepth visits at each refinery. Table 3 summarizes the fourteen control areas studied. More detailed discussions of each area are found in Sections 3 through 10.

TABLE 2

PROFILE OF PARTICIPATING REFINERIES

Refinery Location	Size MBPD*	Union	Processes Reviewed
Gulf Coast	200	None	Naphtha Reformer, BTX Extraction, HF Alkylation, Oil-Water Separation
East Coast	7	OCAW	Lube Oil/Wax Manufacture (MEK Extraction, Furfural Extraction, Clay Filters), Lube Oil/Wax Blending and Packaging
East Coast	12.5	OCAW	Lube Oil/Wax Hydrotreater, MEK Dewaxing Lube Oil/Wax Blending and Packaging
Gulf Coast	30	None	Lube Oil Hydrofinisher, HF Alkylation, Naphtha Reformer, Oil-Water Separation, H_2S Monitoring System
West Coast	120	None	Naphtha Reformer, Oil-Water Separation, H_2S Monitoring System
West Coast	400	OCAW	Naphtha Reformer, Benzene Recovery, H_2SO_4 Alkylation, Oil-Water Separation, H_2S Monitoring System
East Coast	150	OCAW	Benzene Recovery, Oil-Water Separation, H_2SO_4 Alkylation

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* Thousands of barrels per day

TABLE 3 FOURTEEN EMPLOYEE EXPOSURE CONTROL APPLICATIONS STUDIED

Control Applications	Description of the Employee Exposure Control	Refiner's Reason for Implementing Control
HF Exposure Controls at Alkylation Unit	Protective Clothing Change Room - A modern facility to effectively manage HF acid protective clothing and work practice programs.	Refinery has just started up a newly constructed HF alkylation unit. The best engineering, protective clothing, and work practice controls have been implemented to minimize employee exposure potential to HF acid.
	Separate Maintenance Facilities - A maintenance facility specifically designed to handle HF contaminated equipment.	
	Emergency Decontamination Shower - An emergency shower booth located within the battery limits and designed to decontaminate protective clothing while still on the operator.	
Process Sampling Engineering Controls	Valve and Spigot Enclosure - A box enclosure around a sample tap. The system has a closed drain to process sewer, vapor vent line, and door with window.	Refinery has installed enclosures around open sampling systems containing hazardous chemical substances: caustic, acid, phenol, sour water (H_2S, NH_3), etc. Enclosures reduce the potential for inhalation and dermal exposures to employees during process sampling.
	Density Measuring Chamber Enclosure - An enclosed system for measuring sulfuric acid density by alkylation unit operators.	

TABLE 3 (continued)

Control Applications	Description of the Employee Exposure Control	Refiner's Reason for Implementing Control
Hydrogen Sulfide and Hydrocarbon Area Monitoring Systems	Hydrogen Sulfide Area Monitoring System - A newly installed system employing new sensor technology and advanced alarm and data handling systems.	Installation of area monitoring systems employing newly developed sensor/analytical technologies which are low in cost and very reliable. Very effective warning systems and inexpensive data handling systems provide a high degree of effectiveness.
	Hydrocarbon Area Monitoring System - A gas chromatograph used to monitor benzene, toluene, and xylenes at six locations in aromatics processing units.	
Emission Controls at Oil-Water Separators	Controls on a Dissolved Air Flotation Unit - A covered DAF system (mix tank, flocculation tank, DAF tank) vented to a carbon absorber.	Covers on DAF system were required to meet local fugitive emission laws but also reduced employee exposures to hydrocarbons.
	Sour Water Stripping and Gravity Separator Covers - Installation of a sour water stripper and covered oil-water separators to reduce environmental emissions of H_2S, NH_3, and hydrocarbons.	Modernizing an existing wastewater treatment plant handling sour waters to meet water discharge standards also reduced employee exposures to H_2S, NH_3, and hydrocarbons.
Emission Controls at a Benzene Loading Facility	Emission and Safety Controls - These include vapor recovery system, dripless connectors, heated loading arm, and automatic grounding system.	Refinery designed the loading facility in 1978 to comply with now-rescinded OSHA PEL of 1 ppm benzene.

TABLE 3 (continued)

Control Applications	Description of the Employee Exposure Control	Refiner's Reason for Implementing Control
Equipment Maintenance Controls	Aggressive Preventive Maintenance Programs - Includes: inspection for hydrocarbon and steam service valve leaks and subsequent repair with thermosetting compounds; heat exchanger head leak prevention program which prevents head warpage by calculation and measurement of proper bolt extension; rotating equipment vibration monitoring and equipment balancing program; acoustic testing program which reduces down time for maintenance inspection.	Refinery has implemented a number of aggressive preventive maintenance programs for economic and safety reasons. Program should also reduce worker exposures to fugitive hydrocarbons and noise from steam leaks.
Catalyst Dust Wet Scrubber	Skid-mounted Two Stage Impingement Type Wet Scrubber - Device is used to reduce catalyst dust emissions from drums as catalyst is dumped from reactors for replacement.	To reduce maintenance worker occupational exposure to catalyst dust containing toxic metals, the refinery fabricated the wet scrubber which significantly reduces dust emissions during dumping of fluid bed and pellet type catalysts.
Lube Oil and Wax Processing and Construction Changes	Processing Changes - Comparison of exposure potential at a new lube oil process (hydrogenization) which replaced the more traditional processes of furfural extraction and clay filtering. Construction Changes - Present practices employ open air construction and remotely located control rooms.	Refinery construction trends since the 1950's implemented for economic and safety reasons also result in lower operator occupational exposures from fugitive emissions.

SECTION 3

HYDROGEN FLUORIDE EXPOSURE CONTROLS

As with most refinery processes, the primary exposure control method used in hydrofluoric acid alkylation units is the containment of all process substances within the unit equipment (i.e., vessels, piping, and pumps). Greatest exposure potential occurs:

- During process stream sampling
- During unloading of hydrofluoric acid from trucks
- Due to process leaks (fugitive emissions)
- Due to equipment failures (e.g., pump seals)
- During equipment maintenance.

Dermal and respiratory exposure to hydrogen fluoride (HF) acid is of concern due to the severity of chemical burns obtained even with low HF concentrations.

Because of the chemical burn hazard present with HF, refineries have incorporated many or all of the following engineering controls at HF alkylation units:

- Construction of concrete containment curbs around reactor and HF storage vessels.
- Installation of segregated sewer systems designed to contain spills and runoff from HF acid areas. Effluent is treated for HF neutralization/removal before release to refinery main sewers.
- Routing all vents from the unit to a soda ash scrubber to neutralize HF.
- Installation of soda ash solution vats for neutralizing equipment that is to be removed from the unit for maintenance or disposal.
- Installation of feed drying and HF acid regeneration systems to keep moisture content of acid less than 4 percent to prevent corrosion of equipment.
- Potassium hydroxide scrubbing of light products leaving unit for neutralization of trace amounts of HF that may be stripped overhead with the light products.

- Incineration of HF acid sludge in process heaters.

The above controls are designed to contain HF inside the unit area, thereby minimizing exposure potential to workers outside the alkylation unit.

Because of the severe chemical burns caused by exposure to HF, refineries have extensive protective clothing measures and work practices as back up measures to engineering exposure controls. These operator and maintenance personal protective clothing/work practice measures were the focus of the two indepth visits conducted under this program. Three areas were identified as being of most interest and are discussed in the following sections:

- Protective Clothing Change Room
- Separate Maintenance Facilities
- Emergency Decontamination Showers

PROTECTIVE CLOTHING CHANGE ROOM

Because of the extensive use of protective clothing to protect workers from HF exposure at alkylation units, it is necessary to provide facilities for the care and storage of the protective clothing at the unit. One of the refineries visited had just completed construction of a new facility to provide for proper maintenance and use of the protective clothing required in the alkylation unit. This facility probably represents a state-of-the-art facility in the petroleum refining industry for HF alkylation unit change rooms. The following sections describe and evaluate this new facility.

Description of Change Room

All personnel working or coming within the battery limits of the HF alkylation unit are required to wear protective clothing. Four classes of protective clothing are provided based on the degree of protection required for different types of work. Table 4 briefly describes the protective clothing worn and the type of work in which the clothing is to be used.

Figure 1 is a photograph of the alkylation unit change room as seen from the alkylation unit. Figure 2 shows a plot plan of the change room building which is 36 feet by 22 feet. Anyone entering the HF alkylation unit area is required to pass through the control room (adjacent building) and suit up in the change room with the appropriate class of protective clothing before entering the unit area.

The air conditioning system for the change room is a specialized unit located on the roof. The fresh air intake duct extends to approximately 30 feet above ground level. Intake air passes through an aqueous sodium bicarbonate scrubber to neutralize and

Table 4 Personnel Protective Clothing

Regularly assigned operators must wear the special clothing conforming to the following schedule:

CLASS A PROTECTIVE CLOTHING

Hard hat with face shield; 14-inch neoprene gloves with gauntlet sleeves; latex neoprene jacket and work pants; neoprene-soled boots with #12-inch top.

TYPE OF WORK

Routine operating work under normal conditions: reading meters and pressure gauges; assembling equipment which has been neutralized and washed; and visual inspection of area by supervisors and operators.

CLASS B PROTECTIVE CLOTHING

Hard hat with face shield; neoprene latex coat and overall slicker pants; 14-inch neoprene gloves with gauntlet sleeves; 12-inch neoprene overboots (pants over boots).

TYPE OF WORK

All phases of routine and non-routine operating work under normal conditions except those noted under Class C clothing: starting up or shutting down sections of the unit in the acid area; greasing valves; washing down; adjusting packing, routine switching of pumps; and opening and closing valves in closed systems. (Not bleeders or sample points.)

CLASS C CLOTHING

Air-supplied HF hood; neoprene latex coat with 14-inch neoprene gloves with gauntlet sleeves; overall pants; neoprene overboots.

TYPE OF WORK

In all operations where it is possible to have HF leaks to the atmosphere: taking HF samples; removing plugs from opened valves during operation or during cleanup for a shutdown; breaking unions and flanges or tightening fittings; pressuring equipment with HF without otherwise testing; and obtaining gaugings by use of rotary gauges or tricocks without long tail pipes.

CLASS D PROTECTIVE CLOTHING

Full-coverage, acid-resistant, pressurized suit with either self-contained breathing unit or with complete air supply system, including a control valve on body harness, a lifeline, and a belt.

TYPE OF WORK

Extreme emergencies where it is necessary to enter areas having a high concentration of acid vapor or where there is an acid spray: during pump or valve packing failure and large leaks where it is necessary to shut off equipment.

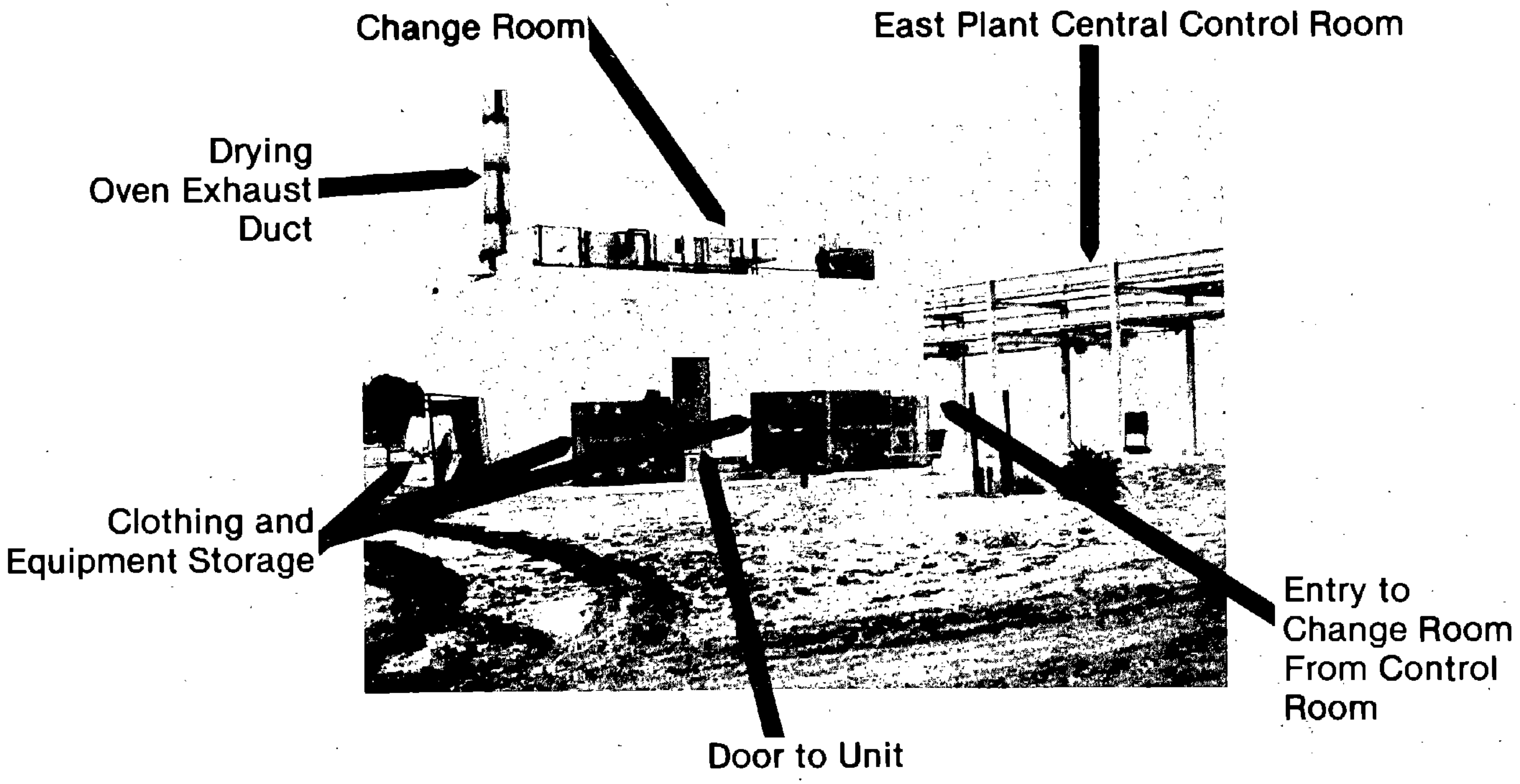


FIGURE 1 - HF ALKYLATION UNIT CHANGE ROOM

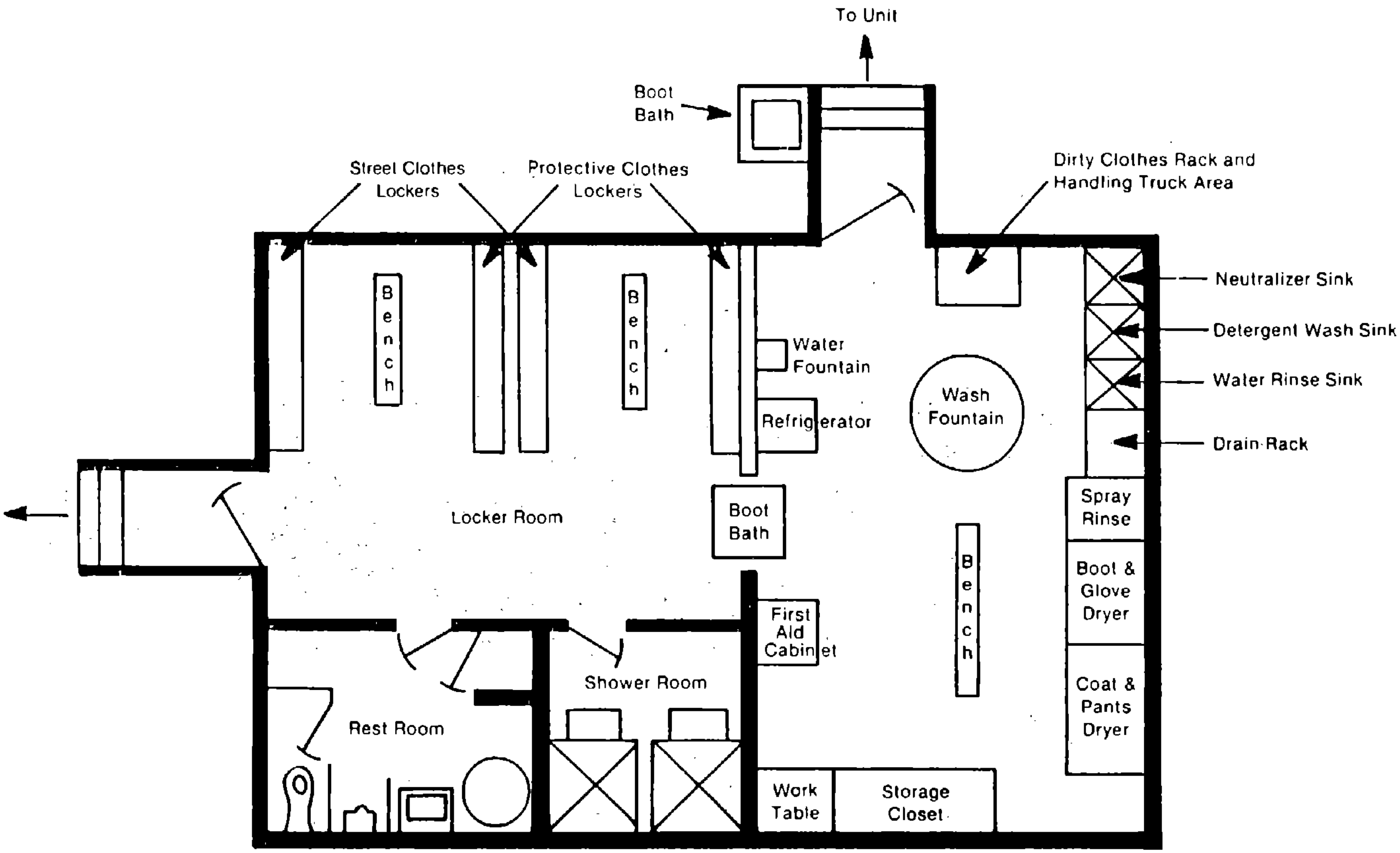


FIGURE 2 - HF ALKYLATION UNIT OPERATOR CHANGE ROOM

remove any HF in the ambient intake air. This protects unit personnel in the change room from HF exposure in the case of a massive spill or leak. The air conditioning system maintains the change room at a positive pressure with respect to the ambient, minimizing the possibility of HF vapor entry through the doors.

As shown in Figure 2, the change room is divided into a "clean" locker room and a "less clean" wash room. Fresh conditioned air is discharged into the locker room and flows through the door above the boot bath into the wash room. This provides an air flow that would minimize any HF vapor migration from the wash room into the locker room. Recirculated, conditioned air is also passed through the intake air scrubber to remove HF before reintroduction into the locker room.

Locker Room Area --

Upon entering the change room building from the central control room, one enters the locker area. The locker room area consists of four banks of lockers in pairs, facing each other. Between each pair of facing lockers is a sitting bench. One set of lockers is for storage of street clothes and the other set of lockers is for Class A and B protective clothing (hard hat with face shield, 14" neoprene gloves, latex neoprene jacket, work pants and boots). Each operator is assigned two lockers across from each other.

Additionally, two Class D "zoot" suits ready for emergency use hang on the wall of the locker room near the entrance to the wash room. Figure 3 is a photograph of these full coverage, acid resistant, pressurized suits using either a self-contained breathing unit or air supply line. These suits, and two others stored outside of the change room building, are used during extreme emergencies to enter areas where high concentrations of HF vapor or spray are present. The Class C clothing and air supplied HF hoods, which are worn over Class B clothing bib-type overall pants, are also stored in the outside lockers.

Wash Room Area --

The locker room area including the rest rooms and showers are considered acid free areas. The remaining half of the change room building is the wash room area, in which protective clothing that has been exposed or potentially exposed to acid is worn and cleaned for reuse. Entry into the wash room area is from both the locker room area and outside from the alkylation unit.

Figure 4 is a photograph taken from the locker room door of the wash room area which contains the following facilities:

- A rack for contaminated protective clothing next to the door to the alkylation unit

FIGURE 3 - CLASS D PROTECTIVE CLOTHING READY FOR USE IN LOCKER ROOM

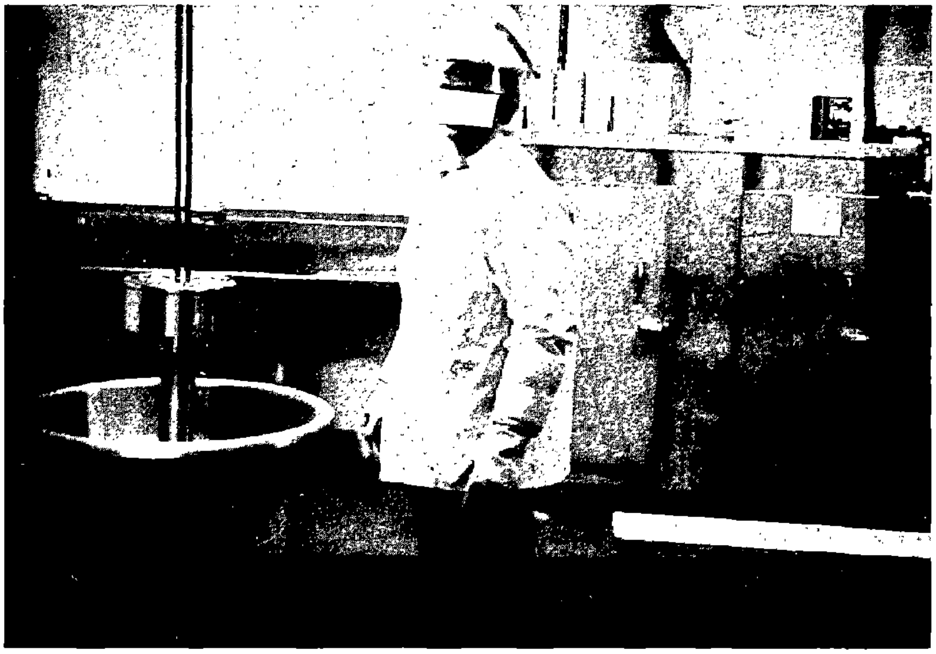


FIGURE 4 - WASHING FOUNTAIN AND DRESSING BENCH

- Three stainless steel sinks used for neutralization and washing of protective clothing (shown)
- Three protective clothing dryers (shown)
- Washing fountain and dressing bench (shown)
- Storage cabinets for dry clothes and new equipment first aid cabinets, and stand up work desk, and
- Drinking fountain and refrigerator containing first aid equipment.

Before entering the wash room from the alkylation unit or leaving the wash room through the locker room, neutralization sumps are used for neutralization of acid on boots. Figure 5 shows an operator neutralizing his boots before entering the locker room area. Figure 6 shows an operator neutralizing his boots before entering the wash room from the unit.

Change Room Procedures --

Refinery personnel enter or exit the change room building through only two doors. Anyone wishing to enter the HF alkylation unit area must first notify the central control room operating personnel to obtain permission to enter and obtain a unit status report. Entry to the unit must be through the change room building located adjacent to the central control room.

Upon entering the locker room side of the change room, an operator removes his street clothes and puts on cotton surgical shirt and pants provided by the refinery. Street clothes are stored in one set of lockers provided to each operator; Class A and B protective clothes are stored in another locker across the dressing bench from the street clothes locker. Normally the operator dons Class A or B clothing before leaving the locker room area through the wash room area.

Upon leaving the unit area, the operator neutralizes his gloves and boots in neutralization baths provided at the edge of the unit (Figure 7) and at the door to the wash room of the change room building. The washing fountain is used to rinse off rubber gloves. If the possibility exists that any acid has contaminated the operator's protective clothing, the clothing is carefully removed and hung on the rack next to the wash room door. These clothes are then neutralized and washed in the stainless steel sinks provided in the wash room. The washed clothes are then placed in the dryers located adjacent to the washing sinks.

Each operator is responsible for cleaning and maintaining his own Class A and B protective clothing. Clean-up of Class C and D suits is the responsibility of the personnel on the shift that uses them.

FIGURE 5 - BOOT NEUTRALIZATION BATH BETWEEN LOCKER ROOM AND WASH ROOM

FIGURE 6 - BOOT NEUTRALIZATION BATH BEFORE WASH ROOM ENTRANCE FROM UNIT

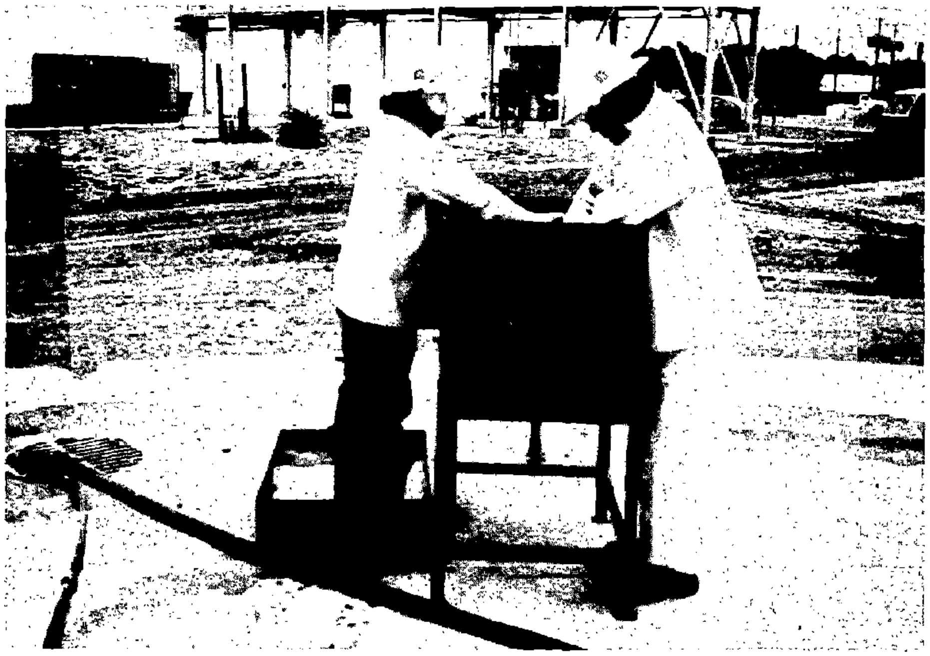


FIGURE 7 - GLOVE AND BOOT NEUTRALIZATION BATHS AT EDGE OF UNIT

When an operator wishes to leave the unit or use the facilities in the locker room area, all potentially acid contaminated protective clothing must be left in the wash room area. A neutralization foot bath in the wash room-locker room doorway is used to ensure that any acid picked up from the wash room floor is neutralized before entry into the locker room area. Several times during the shift, the pH of the boot neutralization baths inside and outside of the change room building is checked to ensure that sufficient alkalinity is available for acid neutralization.

Cleaned and dryed Class A and B protective clothing is stored in the individual operator lockers at the end of each shift. Used surgical smocks are laundered by an outside firm at company expense.

Exposure Control Evaluation

An integral part of any protective clothing program is the proper care and handling of the protective clothing. To facilitate proper handling and work practices, the refinery built an operator change room facility in conjunction with the construction of the HF alkylation unit.

The limited access rules employed provide a necessary control toward effectively managing the protective clothing/work practices program. In accordance with fire and safety practices commonly used by the industry, a physical barrier has not been placed around the unit to prevent unauthorized access to the alkylation unit. However, the unit boundaries will be marked clearly with bright-colored warning strips when road construction has been completed.

The general layout of the change room building appears very workable. Approximately 45 percent of the change room building includes the protective clothing decontamination and clean up area (wash room). Adequate room has been allotted for protective clothing removal, cleaning, and drying. A final boot neutralization bath is built into the floor at the locker room-wash room doorway. Except for boots, all other protective clothing items are left in the wash room or shower room facilities until cleaned and dried at the end of each shift.

One additional feature of note was the air conditioning system employed at the change room building. The air intake to this building passes through an aqueous sodium bicarbonate scrubber to neutralize and remove any HF acid in the intake air. This, plus the positive pressure on the inside of the building, prevents HF vapor from entering through the air conditioning system or doors. These features are highly desirable in being able to safely handle a situation where a large release of HF vapor can occur.

The change room facilities and protective clothing/work practices used by this refinery were primarily based on recommendations provided by the alkylation unit process licensor (Universal Oil Products, Inc.). Modifications were made based on previous experience by the unit superintendent and other refinery personnel.

Industry Applicability

The change room facility described includes innovations developed over 40 years of industry alkylation experience. The facilities are primarily outside the unit battery limits and are not an integral part of the process. Retrofit or upgrading of existing change room facilities could easily be made anywhere, except where existing plants have severe space limitations. The change room facility design philosophy also should be applicable for plants handling other hazardous liquids or solids.

SEPARATE MAINTENANCE FACILITY

In an effort to reduce worker exposures to HF, a separate maintenance facility is being constructed adjacent to the unit change room discussed in the previous section. The alkylation unit maintenance facility will have:

- A locker room including showers and rest rooms
- Protective equipment clean-up area, and
- Equipment work shop and spare parts and tool storage.

These facilities will allow most all unit maintenance to be conducted adjacent to the unit in a facility specifically designed to handle acid contaminated equipment. This approach should reduce accidents where workers may be exposed to HF acid through inadequate handling of acid-contaminated equipment at a larger maintenance facility and/or accidental use of non-HF resistant parts (i.e., gaskets) in equipment maintenance.

Maintenance Facility Description

Figure 8 is a drawing of the maintenance facility, which will be 46 feet by 22 feet, and is planned for completion late 1982. A brief description of each area follows; no photographs of the facilty are available because construction had not begun during the indepth visit.

Locker Room Facilities --

As in the previously described change room building, all maintenance personnel will enter and leave the alkylation unit through the locker room. The maintenance locker room will be similar to the unit operations locker room just described.

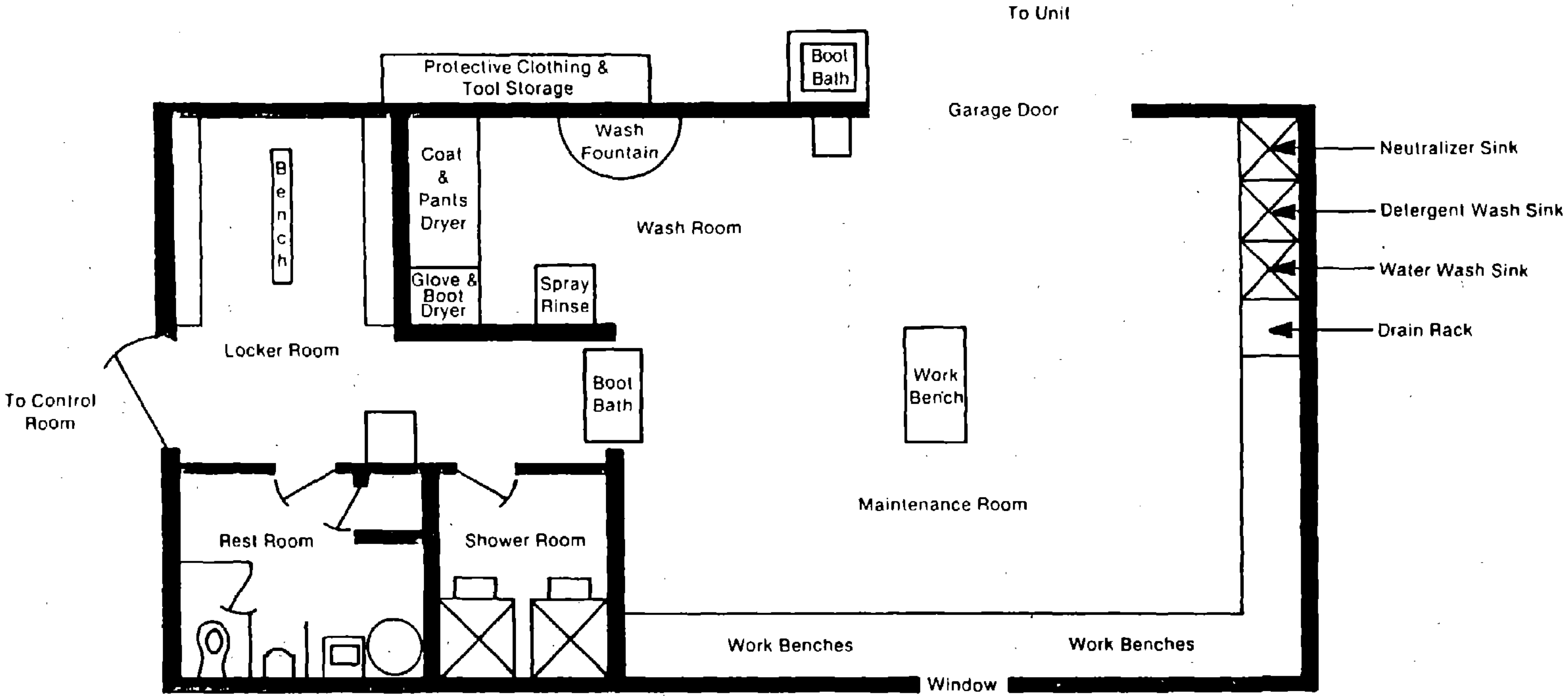


FIGURE 8 - HF ALKYLATION UNIT SEPARATE MAINTENANCE FACILITIES

The locker room, restroom, and shower areas will be considered acid free; and protective clothing which has not been properly neutralized and cleaned will not be allowed in any of these areas.

Maintenance Room --

After donning proper protective clothing for the job, maintenance personnel will leave the locker room area and enter the maintenance room. Here tools and equipment will be stored for most maintenance jobs required by the HF alkylation unit. Large amounts of work bench area will be provided as well as three sinks and a drain rack for neutralizing and cleaning small equipment parts and protective clothing. Access to the alkylation unit will be through a garage door. A foot bath will be provided just outside the garage door for boot neutralization before entering the maintenance room.

Prior to being brought into the shop area, all equipment to be repaired in the maintenance rooms will be neutralized at the HF alkylation unit in large neutralization baths. However, pieces of equipment that cannot be completely taken apart or which have many cavities may be difficult to neutralize in the baths within the unit battery limits. Special precautions will be taken by maintenance personnel when working on these equipment items.

Wash Room --

The wash room alcove off the maintenance room will provide facilities for proper cleanup of protective clothing. Maintenance personnel leaving the HF alkylation unit or maintenance room will neutralize, detergent wash, water wash and drain all protective clothing which may have been exposed to HF acid. After draining, gloves, jackets and pants will be dried in dryers similar to those used in the operator change room building.

The wash room area also will include a wash fountain, spray rinse unit and drinking fountain. After cleaning their protective clothing and after boot neutralization in the foot bath in the locker room to maintenance room doorway, maintenance personnel can enter the locker room area.

Battery Limits Maintenance Facilities --

Prior to removing any acid contaminated equipment from the HF alkylation unit battery limits, all items will be neutralized in a large caustic bath (sodium bicarbonate or soda ash and water) which is about 4 feet deep, 5 feet wide and 10 feet long. Equipment items are slowly immersed in the solution by a mobil crane. After the bath neutralization, equipment items will then be transferred to the HF alkylation unit out maintenance room.

Exposure Control Evaluation

Maintenance personnel have a much higher probability of being exposed to HF because equipment maintenance frequently requires the dismantling of an equipment item and associated piping. Because HF will escape containment, workers must be protected from dermal and respiratory exposures.

A good way to control protective clothing use and good work practices during alkylation unit equipment maintenance is to handle all unit equipment maintenance at a facility specifically designed to handle acid contaminated parts. All maintenance workers in this shop area would be required to follow work practices designed to prevent acid exposures. Isolation of all maintenance work at the unit will provide better control over such operations. It would reduce the potential for employee exposures to HF acid due to use of improper work practices or casual workers passing by as could occur in a general maintenance facility.

The corrosive nature of HF acid requires that metal parts exposed to HF be of acid resistant materials. If a non-acid resistant part were accidentally placed in HF service, quick failure of the part would be likely. Consequently all replacement parts kept at the refinery alkylation unit separate maintenance facility will be of HF resistant materials. This should significantly reduce the accidental use of a non-acid resistant material in HF service.

Upon completion, the separate maintenance facility for the HF alkylation unit should significantly reduce maintenance employees' potential for dermal or respiratory exposure to HF. This facility should provide excellent means for the proper use and care of protective clothing. Additionally, the facility should provide better management control of maintenance work practices requiring protective clothing and use of HF-resistant spare parts.

Industry Applicability

The vast majority of petroleum refineries with HF alkylation units probably make some effort to separate alkylation unit equipment maintenance. Both refineries visited during this program had either separate rooms or areas in the central maintenance shop for handling only HF contaminated equipment. For the refinery building the separate maintenance facility, this was only a temporary situation. Procedures more typical of the industry are:

- Equipment disassembly and neutralization at unit
- Repair at unit if possible

- Move to central shop if major repairs needed
- Mark off area in central shop where acid contaminated equipment is repaired.

Although an effective protective clothing and work practices program can be administered whether a separate maintenance facility is used or not, administration of the work practices program should be made easier by having a separate maintenance shop at the alkylation unit. This exposure control method could be used wherever severe space constraints would not prohibit locating a new building next to the unit. The separate maintenance facility philosophy could be used at any plant where hazardous liquids/solids are processed and contaminated equipment must be repaired along with other plant equipment not contaminated.

EMERGENCY DECONTAMINATION SHOWER

Although emergency showers typically are not installed to prevent worker exposures, they are an effective method in reducing the effects of an exposure. At an HF alkylation unit, emergency showers may aid in reducing the effects of exposures by quick removal of acid from protective clothing. At one of the refineries visited three emergency shower booths have been installed in the alkylation unit area. These showers are much more sophisticated than the normal emergency shower and eye wash units located in most refinery processing units and in the non-acid side of the alkylation unit. The main purposes of the three shower booths are to provide controlled decontamination of HF acid exposed protective clothing and to serve as an initial first aid point if dermal acid exposure has occurred.

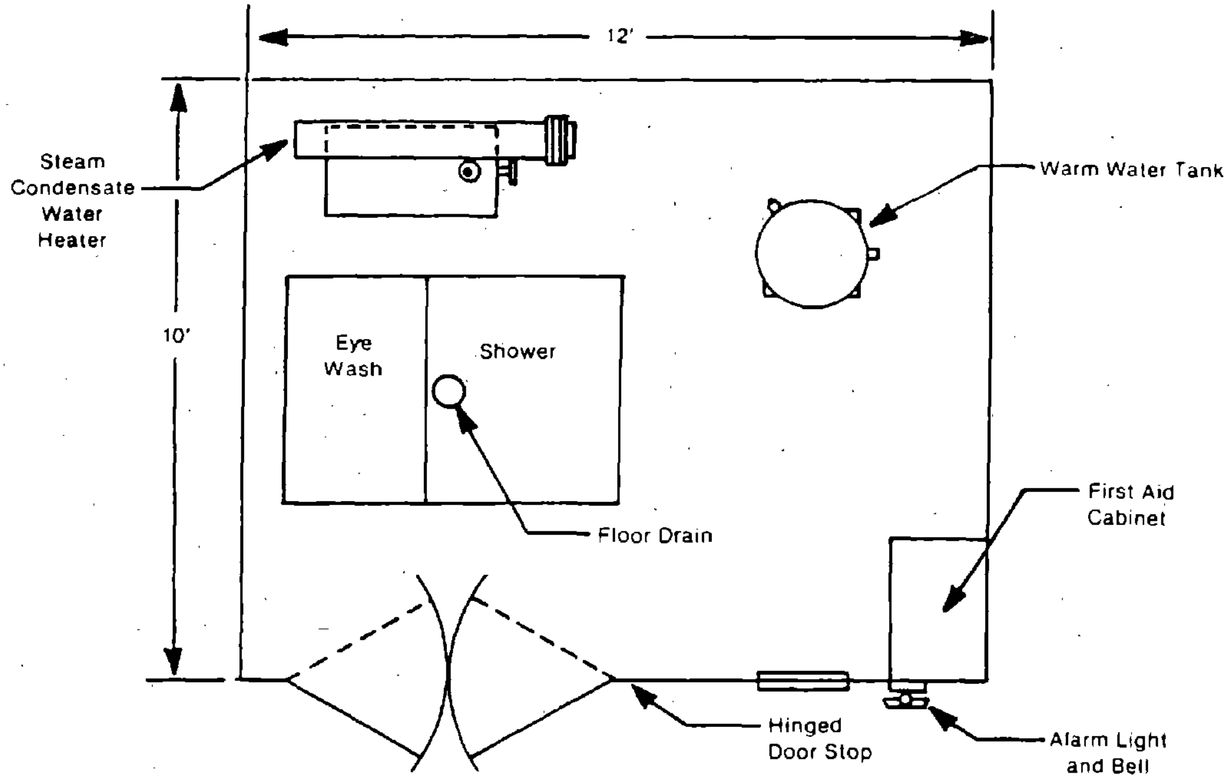
Emergency Shower Description

Figure 9 shows a simplified schematic diagram of the three 10 feet by 12 feet by 10 feet emergency shower booths installed at the alkylation unit. These booths are equally spaced along the acid side of the unit near the:

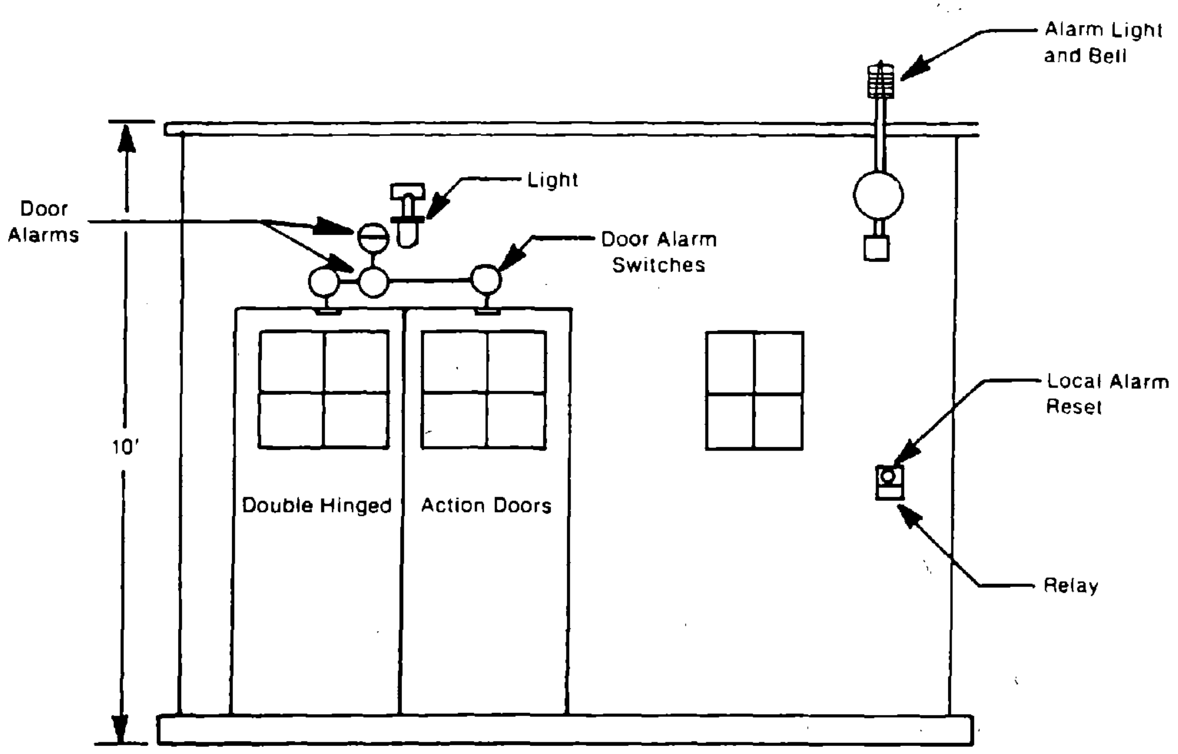
- HF loading area
- HF acid regeneration area
- HF acid sampling station and alkylation reactor area.

Entrance into each booth is through two large double action hinged doors.

The shower spray unit in the booth sprays lukewarm water (about 80°F) from all directions and is activated when someone steps into the shower area. The face and eye wash unit, also activated by treads in the shower, directs a stream of lukewarm water at an angle towards the face and eyes.



Top View



Front View

FIGURE 9 - EMERGENCY SHOWER BOOTH

Because lengthy wash downs may be required to completely decontaminate protective clothing, warm water is supplied to the shower. The water circuit heats up potable water by heat exchange with steam condensate from the unit. A "pump around" circuit with temperature sensors and a warm water tank ensure that the shower water is not too hot or too cold. Use of lukewarm shower water ensures worker comfort during 15 to 30 minute wash down periods.

When the emergency shower booth is entered, an alarm system actuated by door movement signals a local alarm (light and sound) and an alarm in the control room. Additionally, circulating water temperature and flow rate are monitored by alarms in the control room to ensure full operability of the system at all times. Daily testing of the door alarms and shower also ensures operability.

The tempered water system includes a warm water tank, a circulation pump and a steam condensate/circulating water heater. Potable water is made up to the circulating water which is warmed by the condensate heater before being circulated through a warm water tank. The system water temperature is controlled using a temperature sensor in the circulating water line to control steam condensate flow to the circulating water heater. Previous systems not employing this circulating water system (similar to home water heaters) did not supply sufficient warm water needs or occasionally provided water that was too hot for comfort.

General specifications for the emergency shower booth were provided by the alkylation unit process licensor (Universal Oil Products, Inc.).

Exposure Control Evaluation

The three emergency shower booths are conveniently located in the HF alkylation unit battery limits. These booths provide excellent facilities for decontamination of protective clothing. The location of these shower booths provides easy access (less than 75 feet) from any of the HF equipment areas.

The well-designed emergency shower booths have the following advantages:

- Wide double-hinged doors for easy access into the shower stall area
- Door alarm switches with local and control room light/alarm
- Tempered water system which instantly supplies 80°F shower water for as long as is needed

- Tempered water system circulating flow and temperature read outs in the control room
- Easily entered and actuated shower stall/eye wash.

Additionally, the building protects both the shower equipment (stall, eye wash, water heater, etc.) and anyone using the shower from the elements.

By providing a well designed emergency shower facility, the refinery should reduce the severity of HF burns which can be prevented by quick and effective decontamination. The use of tempered water improves worker comfort during wash-down, reducing the chance of HF exposure due to an inadequate washdown period and eliminates the physiological impacts of a cold water shower, eye wash, or bath.

Industry Applicability

A wide range of sophistication exists in the petroleum refining industry for emergency removal of HF from an employee's protective clothing:

- Tempered water shower booths
- Conventional shower/eye wash units
- Neutralization tubs filled with sodium bicarbonate solution
- Water hose.

If properly maintained and located, the use of tempered water emergency shower booths has advantages over the other options. Retrofit or installation of new units would be easy and would provide an adequately prepared facility for emergency decontamination.

SECTION 4

PROCESS SAMPLING ENGINEERING CONTROLS

A high potential for employee exposure to toxic substances exists during sampling of process streams. Although process streams are typically sampled only one to three times a day, the potential is great that an employee will have dermal or respiratory exposure to substances in the sampled stream.

Streams containing toxic gases such as hydrogen sulfide (H_2S) and hazardous chemicals such as strong acids and bases, ammonia (NH_3), phenols and benzene are quite common in the petroleum refining industry. Most refineries use the standard valve and spigot arrangement for process sampling, relying on work practices and protective equipment to prevent employee exposures during the short time (less than 1 minute) required to collect most process samples.

Several different sample collection systems in use at one of the refineries visited were studied indepth. These systems rely on engineering controls designed and fabricated by the refinery to reduce worker exposure to toxic substances during process sampling. The process sampling systems studied were:

- Valve and spigot enclosure - for sour water treating unit sampling of refinery water containing H_2S, NH_3 and hydrocarbon vapors.
- Acid density measuring chamber enclosure - for sulfuric acid (H_2SO_4) alkylation unit acid density measurements.

As designed, these systems significantly reduce the potential for worker exposure to toxic chemicals (H_2S, NH_3, and H_2SO_4) by venting gases and vapors away from the operator and/or shielding the operator from accidentally splashed or spilled material. The systems are relatively inexpensive and have been used for many years. All were designed by the refinery staff (engineering, safety, and operating personnel) and can be fabricated and installed by either a refinery or local contractor.

VALVE AND SPIGOT ENCLOSURE

At most of the valve and spigot sampling stations in the refinery where the potential for operator exposure to hazardous liquids (phenol, caustic, acid, etc.) is high, stainless steel boxes enclose the spigot reducing the potential for employee exposure. The most sophisticated of these systems was studied at the sour water treating unit.

The sour water treating unit receives process water contaminated with H_2S and NH_3 and strips these gases from the water. The recovered gases are processed and sold as sulfur and ammonia products. The stripped waste water is further treated for hydrocarbon removal before reuse or discharge. Three of the unit water streams are sampled regularly to ensure good process control: the sour water feed stream, the stripper bottom stream (degassed waste water), and the ammonia concentrate stream. The sour water feed stream sampling box system was the focus of this study because it has an eductor system which vents H_2S and NH_3 released during the sampling operation well away from the unit operator.

Sampling System Description

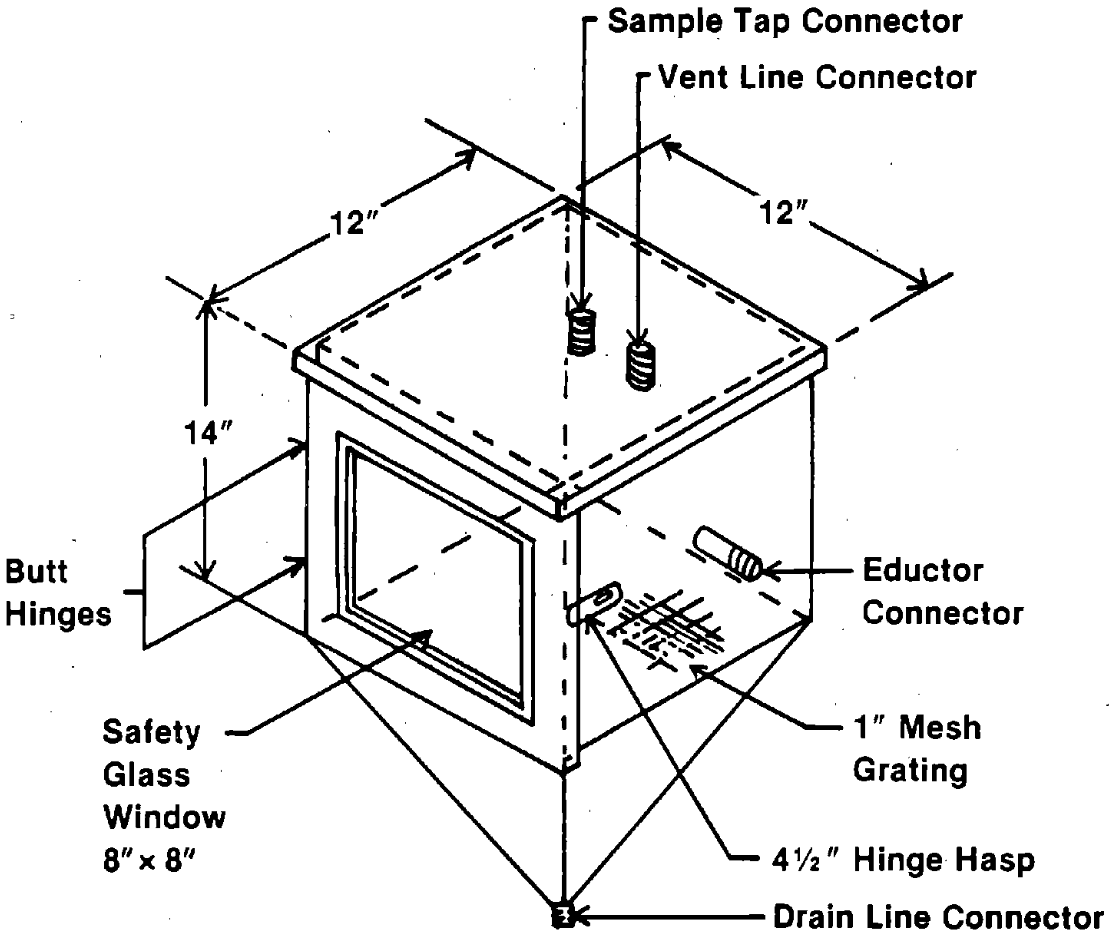
The sour water sampling system, (Figure 10) consists of a stainless steel box (12 inches wide, 12 inches deep, and 14 inches high) that encloses the sampling spigot. The box has a hinged door with a safety glass window for viewing inside the box. The bottom of the box is funnel-shaped to allow for drainage of any liquid spilled during sampling.

Figure 11 shows the layout of this sampling station at the sour water treating unit. The sampling line enters through the top of the box ending in an open spigot. The sampling line valve is located just above the box. The sampling box has a drain line from the bottom of the box to a nearby process drain. The sampling line has a continuous flow created by connecting the sample lines upstream and downstream of a process control valve. This reduces the amount of dead space in the sampling line and means that little or no line flushing is required prior to sample collection.

As shown in Figure 12, the sampling box has an additional safety feature not used at the unit's other sampling boxes. This feature is a large handle which actuates an eduction air valve. Plant air flows through the eductor which vents vapors in the sampling box about 50 feet above the sampling area. To open the box door to insert or remove a sample bottle, the air valve handle must be pushed down. This actuates the eductor and ensures that while the sampling box door is open the eductor is exhausting H_2S or NH_3 away from the operator.

As is the case for most refinery operations, sampling of the sour water process stream occurs infrequently, normally once a day. Actual sampling time per sample is about one minute. The following paragraphs describe the sampling of the sour water feed stream observed during the indepth visit.

Because of the potential for exposure to high concentrations of H_2S evolving from sour process waters, the sour water feed stream sampling box is located in an open area with easy access from the unit perimeter. Prior to sampling, the sampling box door is closed, with the air eductor valve handle blocking the access to opening this door. To take a sample, the operator pushes the air



(Not to Scale)

FIGURE 10 - SOUR WATER TREATING UNIT SAMPLE BOX DESIGN

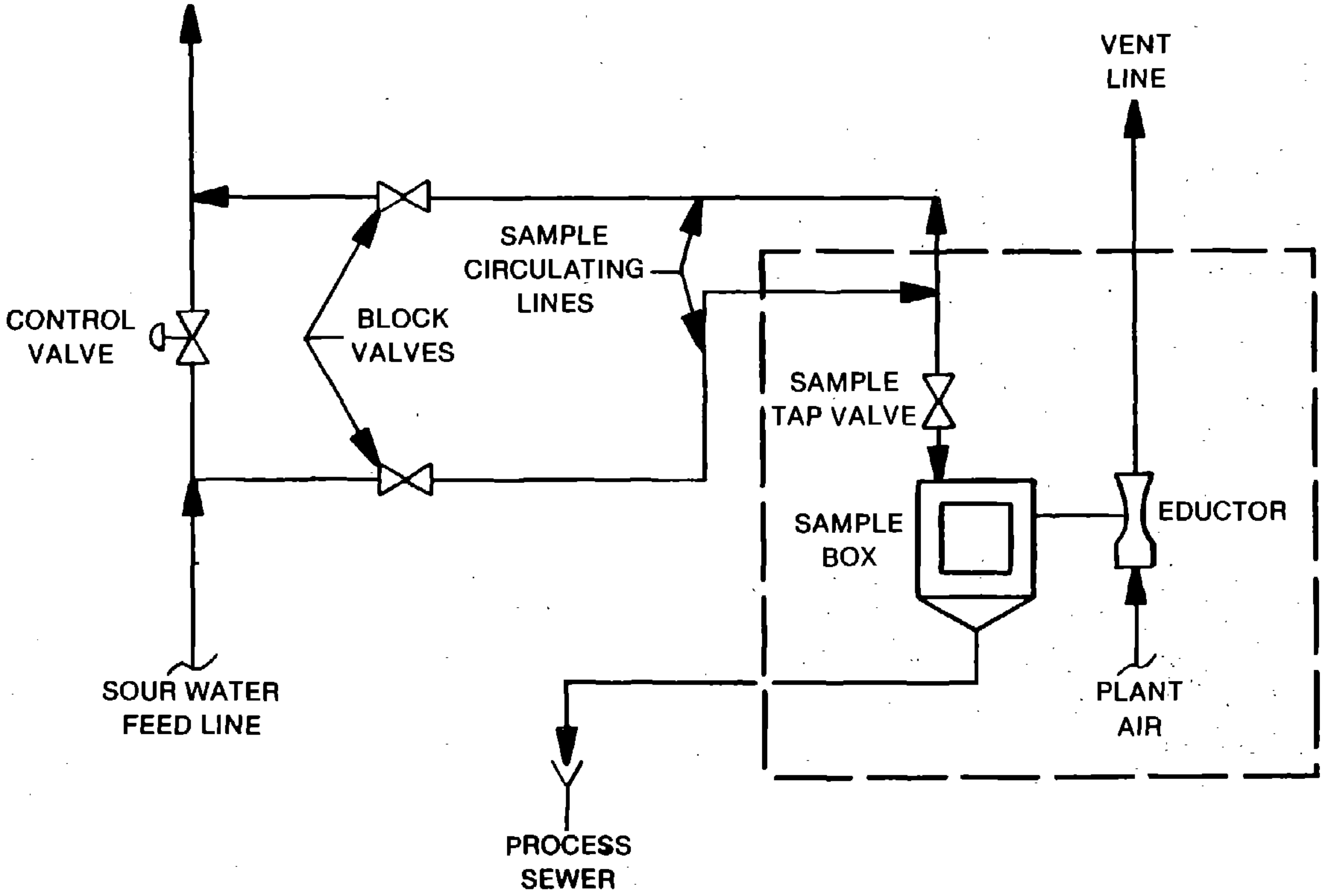


FIGURE 11 - SOUR WATER FEED SAMPLING SYSTEM

FIGURE 12 - SOUR WATER UNIT FEED SAMPLING BOX

eductor handle down, activating the air eductor. The sampling box door is opened after releasing the door latch, and the sample bottle is placed under the sample tap. The sample bottle rests on a stainless steel screen which allows any spilled material to flow to the process drain. Before sampling, the operator closes and relatches the sample box door.

The operator then turns the sample tap valve above the box to collect the sample. This valve is attached to the circulating sour water loop and minimizes the chance for collecting a stagnant sample. As the sample is taken, the operator peers through the sampling box door to observe the sample level in the bottle. When the bottle is nearly full, the sample tap valve is closed. After unlatching and opening the sampling box door, the operator caps and removes the sample bottle. The air eductor operates continually throughout this procedure, collecting any gases released and venting them 50 feet above the sampling box. The box door is closed and latched before the operator closes the air eductor valve by pulling the air eductor handle in front of the sampling box door.

Control Evaluation

To evaluate the effectiveness of the sampling box used to collect the sour water feed sample, Radian conducted short term sampling using colorimetric indicator tubes to measure ambient H_2S concentrations. Three samples were taken:

- o Ambient H_2S concentrations before sampling
- o Ambient H_2S concentrations during sampling
- o Ambient H_2S concentration from sour water sample.

Short term (1 minute) samples were collected because the sour water sampling procedure requires only a short time to complete. Additionally, velocity measurements were made at the face of the box. Table 5 presents the colorimetric indicator tube sampling results and results of velocity measurements taken with the sample box door open and the air eductor in operation.

Colorimetric indicator tube testing indicates that significant amounts of H_2S (greater than 200 ppm) evolve from a sour water sample after collection. The sampling indicated that most of the H_2S evolved from the sour water sample is removed from the box area during sampling. This is due to the effect of the air eductor system. Air velocity measurements indicate a minimum door face exhaust velocity of 60 feet per minute with the sample box door completely open.

Industrial Applicability

The refinery visited had several different sample box enclosure systems in use, as shown in Table 6. The degree of enclosure box sophistication (e.g., air eductor, drain system, vent height)

TABLE 5 AMBIENT H_2S CONCENTRATION - ppm

Before Sampling:	None Detected after 10 strokes
During Sampling:	None Detected after 3 strokes
Above Sour Water Sample:	Greater than 200 after one stroke

VELOCITY MEASUREMENTS - FEET PER MINUTE**

Around Door Face when Open:	60 - 75
Edge of Door when Closed:	200

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*Draeger Tube No. 67 19001 (Hydrogen Sulfide 1/c)

**Alnor Jr. Velometer

TABLE 6 VARIATIONS IN SAMPLING BOX DESIGN

Process Stream	System Description
Sour Water Feed	Box with tall vent line, air eductor system with safety handle over door.
Stripped Bottoms and Ammonia Concentrate	Box with medium height vent line and air eductor system.
Caustic	Box with short vent and no eductor.
Sulfuric Acid	Box with medium height vent and no eductor system.

is a function of the hazardous chemical properties (gaseous, liquid, degree of toxicity, sampling frequency, etc.). However, all of these systems are variations of the box enclosure design. Consequently, the design should have a wide range of applicability in the petroleum refining industries and other industries sampling liquid streams from valve and spigot samplers. Figure 13 is a photograph of a caustic sampling station box enclosure with a short vent and a piped drain system.

The enclosure box system is simple, low in cost and can be readily fabricated and installed by refinery or local maintenance shops. The refinery personnel estimate the fabrication and installation cost of the average sample box system to be about $5,000. Factors impacting this cost are:

- Sample line material and distance from process line
- Vent line height and use of air eductor
- Sample box materials of construction.

The stainless steel sample box systems have been in use at the refinery visited for 5 years. Many of these systems replaced older systems fabricated from carbon steel. The stainless steel boxes reportedly have been very reliable and have required little maintenance.

ACID DENSITY MEASURING CHAMBER ENCLOSURE

At a sulfuric acid alkylation unit olefins (C_3 - C_4) are reacted with butanes using sulfuric acid as a catalyst. An acid strength in excess of 88 percent must be maintained to produce the desired gasoline product octane number. Thus acid density, which is relatable to the acid strength, must be measured frequently. Because acid samples are under pressure and contain dissolved light hydrocarbons, the potential for worker exposure to acid spray and vapor, and to light hydrocarbons can be great. One of the participating refineries has developed a special sampling system which greatly minimizes the potential for employee exposure to sulfuric acid and light hydrocarbons while measuring sulfuric acid density.

Control Description

Figure 14 shows a simplified schematic of the sulfuric acid density measurement sampling system. Acid from the discharge of a process acid pump flows through a small sampling line to the sample settling pot. From the bottom of the sample settling pot, the acid flows back to the suction of the process acid pump. The pressure differential between the pump suction and pump discharge causes a stream of acid to be circulated throughout the sample settling pot. A sight glass is attached to the inlet and outlet lines of the sample settling pots so that the operator can see the extent to which the settling pot is full.

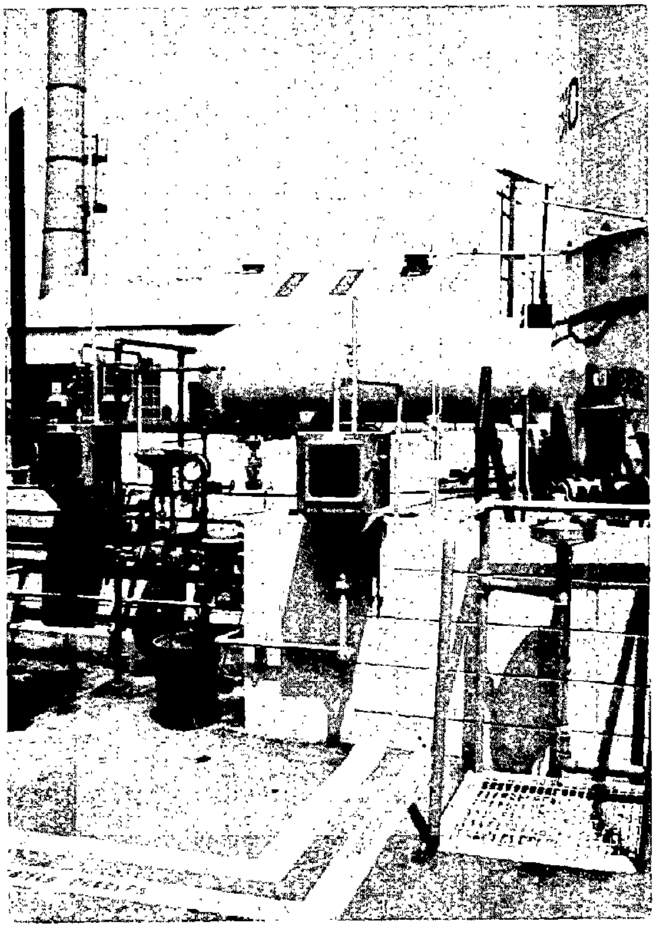


FIGURE 13 - CAUSTIC SAMPLING STATIONS

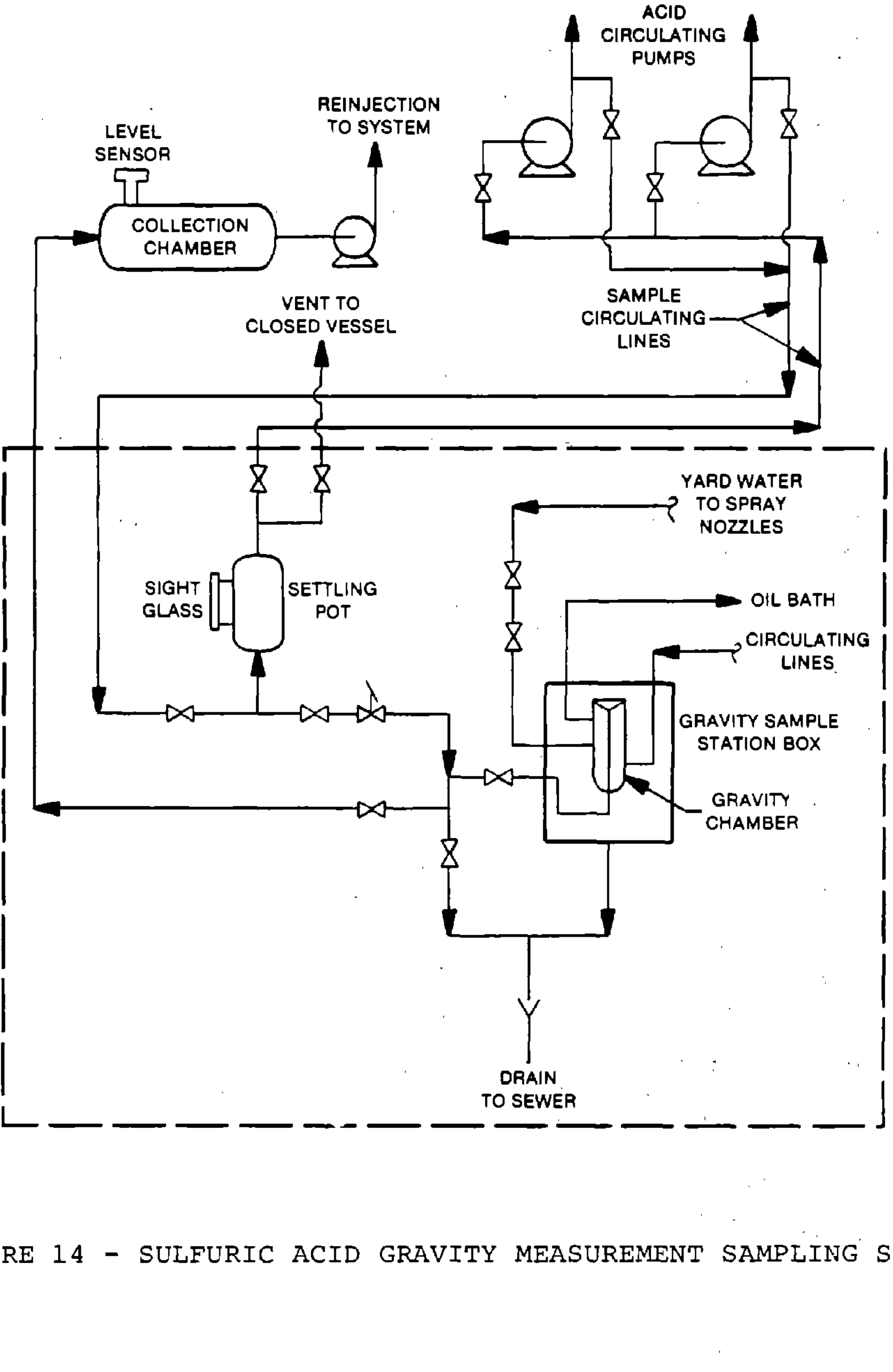


FIGURE 14 - SULFURIC ACID GRAVITY MEASUREMENT SAMPLING SYSTEM

A vent line is connected to the top of the settling pot to allow for weathering (depressurizing and vaporization of light hydrocarbons) of the acid sample. Another line is connected to the bottom of the settling pot to allow the weathered acid sample to flow into a gravity measuring chamber. This chamber is open at the top and surrounded by a circulating oil bath. The entire chamber apparatus is enclosed in a stainless steel box which has a door with a window. A hydrometer in the gravity chamber is used to measure the density of a weathered acid sample.

Before acid density is measured, circulating oil heats the weathered acid to the desired temperature. The hot oil circulating system consists of a pump and electric heating system which maintains the circulating oil at the desired temperature.

When acid density and temperature have been measured, the gravity measuring chamber is drained to an acid collection system. This system consists of a small vessel about 14 inches in diameter and 3 feet long, a level sensing probe, sight glass and pump. Weathered acid from the sulfuric acid sampling system flows by gravity into the collection vessel. When the vessel is full (determined either by the level sensor or sight glass), the pump is actuated either automatically or manually and the weathered acid is pumped back into the process acid system. If this system is not functioning, the weathered acid flows to a sump. It is then collected and trucked to a nearby unit where it is neutralized.

Figure 15 is a photograph of the sulfuric acid sampling station at the alkylation unit. Twice per shift, under normal conditions, a circulating acid sample is trapped in the settling pot by blocking the valves into and out of the settling pots. The sample is allowed to settle for several minutes before the vent line to the acid blowoff vessel is slowly opened. Light hydrocarbons dissolved in the acid sample vaporize to a hydrocarbon vapor recovery vessel. Release of hydrocarbon vapors from the acid causes foaming. Observations of the sample through the sight glass allows the operator to accurately determine when most of the light hydrocarbons have "weathered" off.

After the acid sample has weathered, the bottom drain valve of the settling pot is slowly opened to allow the acid to gravity flow into the gravity measurement chamber. The hot oil circulating system is required only on cold days. After transfering the weathered acid to the gravity chamber, acid density and temperature are read through the glass window of the gravity chamber box. Afterwards, the gravity chamber is drained through a small line to a nearby collection vessel (Figure 16).

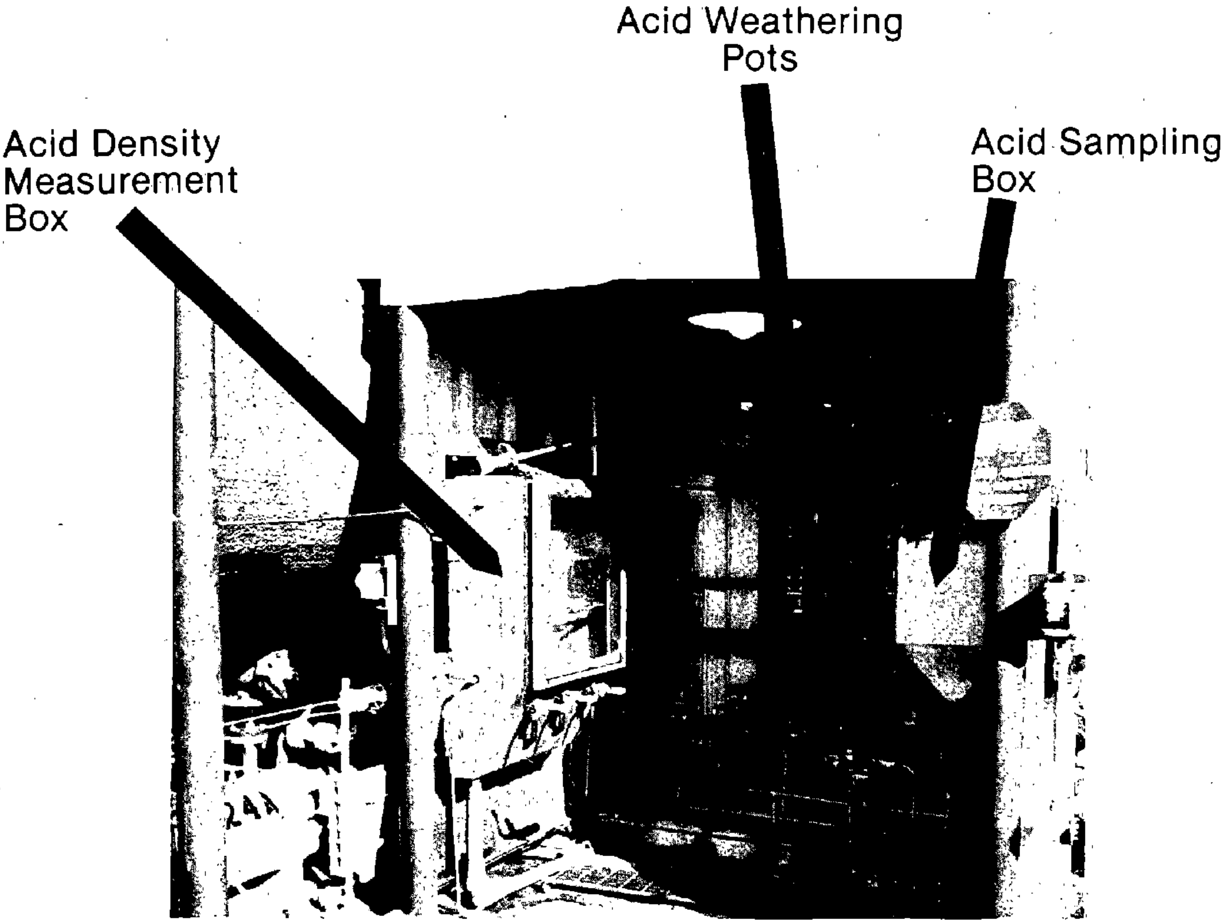


FIGURE 15 - SULFURIC ACID SAMPLING STATION

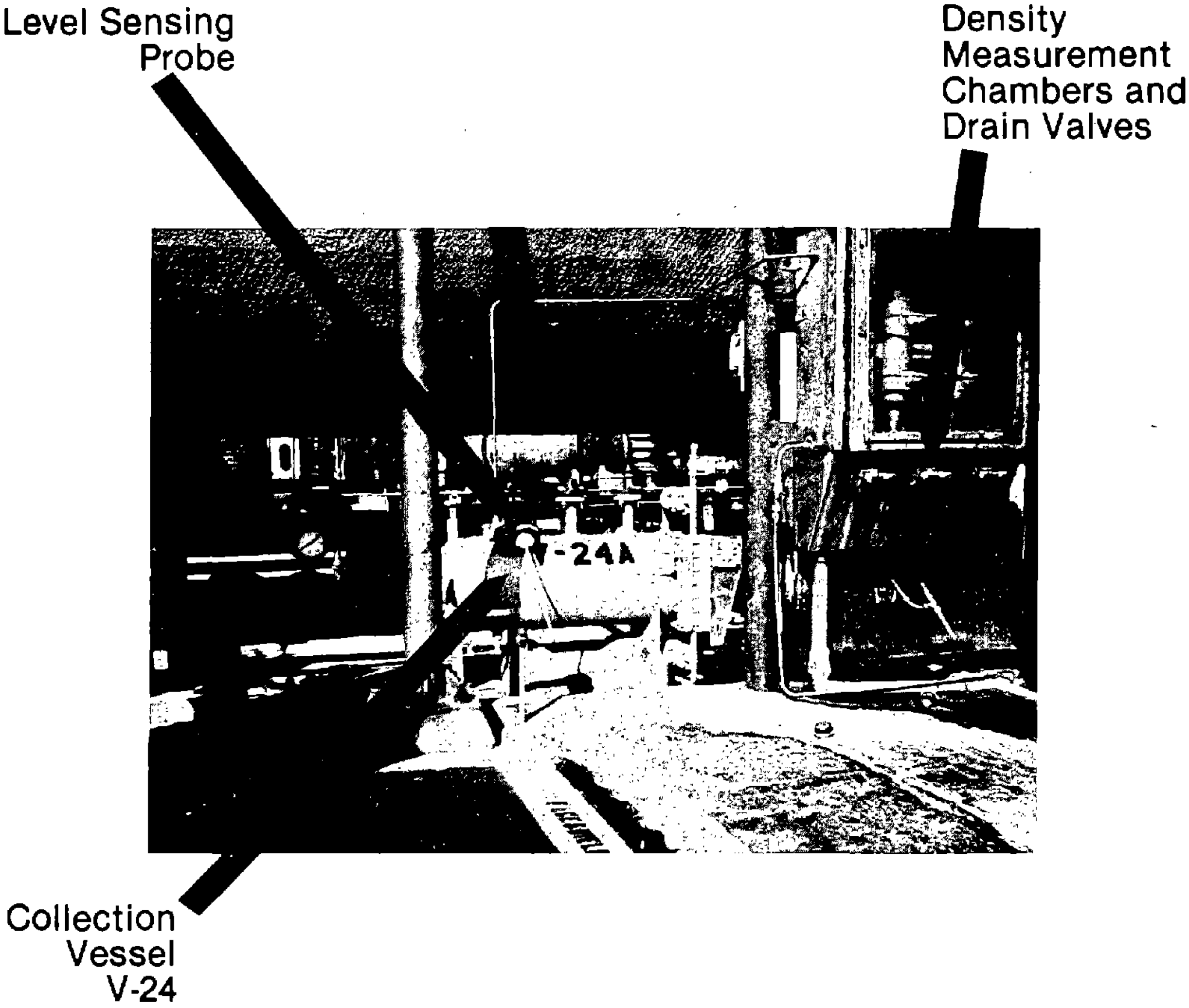


FIGURE 16 - SAMPLED ACID COLLECTION VESSEL

Control Evaluation

Throughout the entire procedure, the operator is not exposed to sulfuric acid or light hydrocarbons. During sampling and degassing, the acid is contained within conventional process equipment (valves, pipe, site glass, and vessels). As density measurements are made, the operator is shielded from acid and hydrocarbons by a stainless steel and glass enclosure surrounding the gravity measuring chamber.

Discharge of weathered acid samples is also accomplished through a completely closed system. Operator exposure to sulfuric acid and/or hydrocarbons can occur only due to leaks in the system and if the gravity chamber enclosure door is open. Additionally, clean up of the gravity chamber enclosure box and acid sample box is accomplished with water sprays inside both boxes.

To evaluate the effectiveness of the density measurement sampling system, ambient hydrocarbon measurements were taken using an organic vapor analyzer (OVA). Sulfuric acid mist samples were not taken because the short time periods required for process sampling precluded obtaining measurable amounts for detection by colorimetric indicator tubes or other short-term air sampling methods. Table 7 summarizes the results of the OVA measurements made during the density measuring sample procedure.

TABLE 7 SUMMARY OF OVA MEASUREMENTS

Sample Location	OVA Reading PPM	Comments
Outside Sample Station House	10	Unit background concentration
Inside Sample Station House near Settling Pot	10 - 15	Operator exposure during weathering
Inside Sample Station House near Gravity Measuring Chamber Box	10 - 30	Operator exposure during density and temperature measurement
Inside the Gravity Measuring Chamber Box	100 - 150	Operator exposure if protective box is not used

OVA sampling results indicate that the closed acid sampling system significantly reduces ambient concentrations of hydrocarbons to which the operator is exposed during acid density measurement sampling. Additionally, the closed system virtually eliminates the possibility of an operator being splashed or sprayed with acid during the sampling procedure.

Industry Applicability

The refinery acid gravity sampling system probably is limited to reducing employee exposure potential while making simple analytical measurements (specific gravity and temperature) at atmospheric pressure. While the system could easily be adapted to other refinery sulfuric acid alkylation systems, most other lab analyses performed on industry process streams may not easily lend themselves to this approach. These analyses can only be performed by on-line analyzers (e.g., gas chromatographs) which are also closed systems or in conventional analytical laboratories. However, this system could be used by other industries where liquid density measurements are required and if the liquid and/or dissolved gases are hazardous.

The visited refinery installed two acid gravity sampling systems in 1977. One system consists of three settling pots and three gravity measuring chambers; the other consists of only one settling pot and gravity chamber. The installed cost for these systems in 1982 dollars was:

- Single system - $27,000
- Triple system - $40,000

These costs include the following equipment items:

- Sampling lines piping and utilities (water and power)
- Settling pots
- Gravity chambers including surrounding box
- Hot oil circulating system
- Acid sampling box
- Sampling station house.

System maintenance costs have been minimal. The only problem has been finding a replacement for the level sensing probe on the collection vessel that holds the acid after the gravity has been measured and before it is returned to the operating system. The relatively high cost of this system probably limits its use to those plants which have generous health and safety program funds and/or plants having very hazardous streams requiring frequent physical measurements.

SECTION 5

H_2S AND BTX AREA MONITORING SYSTEMS

Area monitoring systems are used at many refinery units to warn operators of high concentrations of hazardous gases due to fugitive emissions and equipment failures. Several of the refineries visited had hydrogen sulfide (H_2S) area monitoring systems which are the most common type of systems found at refineries. Three of the systems studied indepth have just recently been installed and incorporate recently developed sensor technology and very effective warning/monitoring systems.

Another type of area monitoring system studied utilizes a conventional gas chromatograph to monitor benzene, toluene and xylene (BTX) concentrations in two units. This system was initially installed in 1979 to address the now rescinded OSHA PEL of 1 ppm for benzene. The system has worked quite well and is actively used by the refinery to minimize worker exposures to BTX.

Descriptions of the H_2S and BTX monitoring systems evaluated during the indepth refinery visits follow.

HYDROGEN SULFIDE MONITORING SYSTEM

Hydrogen sulfide (H_2S) is a dangerous chemical asphyxiant. Acute exposure to H_2S can cause death. Sub-acute exposure can cause eye and respiratory irritation, headache, dizziness, and gastrointestinal distress. Despite its characteristic odor of rotten eggs, hydrogen sulfide gas is considered to have poor warning properties. This is because it can paralyze the olfactory system so that its odor can no longer be detected. Some people cannot detect the odor at all.

Since dangerous quantities of hydrogen sulfide may be released into the workplace as a result of equipment failure, continuous monitors are used at refineries to detect hydrogen sulfide. This section presents a description of a new monitoring and alarm system installed in a refinery in February of 1982.

Monitoring System Description

The hydrogen sulfide monitoring system serves four processing areas all handling H_2S: Claus sulfur plant units with tail gas treaters, diethanolamine (DEA) and di-isopropylamine (DIPA) regeneration units, sour water stripping units and a waste caustic neutralization unit. Since hydrogen sulfide gas is present in high concentration in many of the process streams, leaks and equipment failures can result in the release of dangerous concentrations of hydrogen sulfide into the workplace.

The hydrogen sulfide area monitoring system used at the refinery sulfur handling facilities is a multichannel system which provides continuous independent monitoring of 18 locations. The system consists of 18 independent area sensors; several multichannel controllers located in an instrument shelter; area, shelter, and control room alarms; and the refinery central computer which processes the data generated. The electrochemical sensors and the multichannel controllers were recently developed and manufactured by Mine Safety Appliances Company. The audiovisual area alarms, the instrument shelter panel alarms, and the central control room computer system alarms were developed by the refinery.

The system was carefully selected and designed by refinery personnel prior to installation. The new system replaced a 16-point lead acetate tape sensing system. The new system was selected after a 6-week trial against two other monitoring systems which used a metal oxide semi-conductor as the sensing element. The electrochemical system was selected because of its rapid sensor response time and its reliability in a high moisture environment. Figure 17 shows an H_2S sensor located near one of the sulfur pit areas.

The sensor operates on the principle of an electrochemical polarographic cell. The cell electro-oxidizes hydrogen sulfide to sulfur dioxide (SO_2) as it diffuses through a gas porous membrane. The oxidation of H_2S to SO_2 creates an electrochemical signal proportional to the partial pressure of H_2S diffused into the cell, and this signal is amplified to drive the meter and alarm systems.

Location of Sensor--

Selection of sensor locations was based on input from refinery maintenance, safety, and engineering groups. The sensors are located near equipment where the highest concentrations of H_2S would be released and near equipment having the highest probability for leaking. To determine the degree of hazard (leak rate and concentration) for each equipment area, dispersion calculations were developed using a method presented by Ledbetter (Ledbetter, J. O., "Exclusion area for safety from high-pressure sour gas leaks", AIHA Journal 39:586 (1978)). A relatively high density sensor pattern was selected due to the highly variable weather conditions.

Figure 18 presents a plot plan of the four processing areas covered by the H_2S monitoring system. Six sensors in the Claus plant area are strategically located to detect H_2S leaks from the sulfur pits and converter equipment areas. Three sensors are located near the reboiler, flash drum and exchanger equipment areas in the DEA regeneration area. Three sensors are in the DIPA regeneration area, located near the DIPA regenerator, sour water flash drum and water stripper areas. Six sensors are located in the sour water and caustic/acid loading areas near the sour water treating area, sour water holding tank, caustic

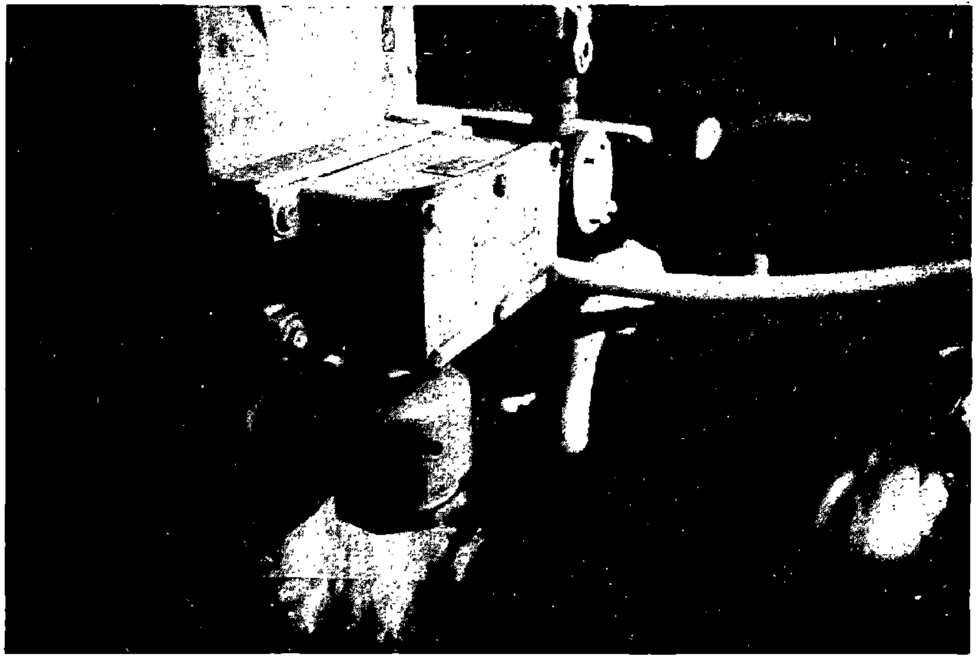


FIGURE 17 - ELECTROCHEMICAL SENSOR FOR H_2S DETECTION

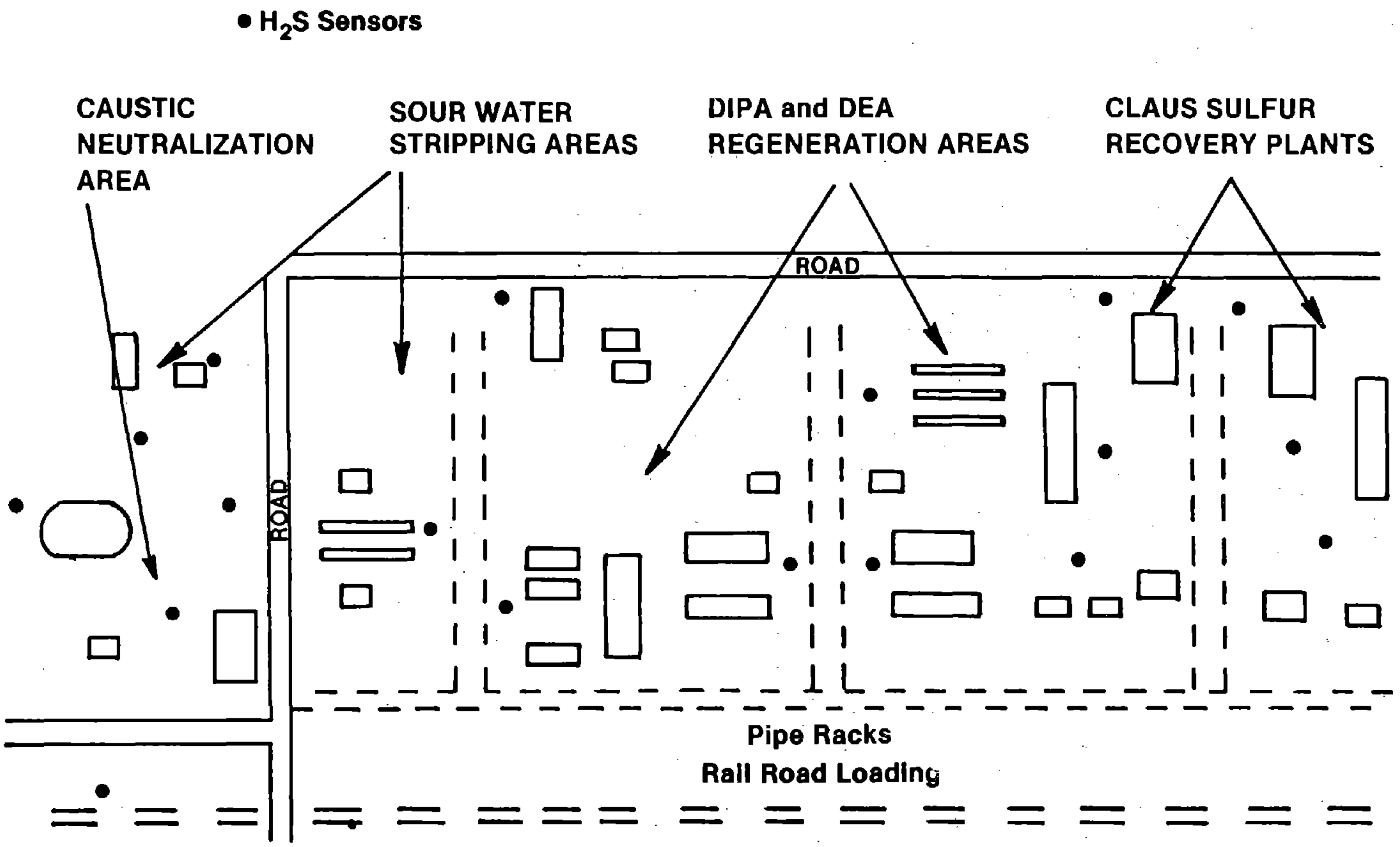


FIGURE 18 - H_2S HANDLING AREA PLOT PLAN

neutralization tank, spent caustic tank and caustic/acid loading racks.

Warning and Alarm Systems --

The 18 remotely-located H_2S sensors are tied into a group of controllers located in an instrument shed at the corner of the hydrocracking unit. The shed is located midway between the H_2S processing areas and the central refinery control room. This location allows area operators quick, safe access to the controllers during a detected H_2S release. An LED display built into each of the controllers continuously displays the H_2S concentration measured by each sensor. Also in the instrument shed is a panel board showing the location of each sensor in the four processing areas.

When one or more of the sensors detects an H_2S concentration greater than 10 ppm, the controller actuates the system alarms. These alarms include:

- Audible alarms in the caustic neutralization area and the central control room
- Flashing lights at the instrument shed and one in each of the four processing area entrances
- Flashing light for each of the sensors detecting over 10 ppm on the panel board in the instrument shed.

Additionally, the refinery central computer can display plot plans of the four processing areas showing the H_2S concentration at each sensor on a CRT terminal and by printing a hard copy.

The unit operator responds to alarms by donning a self-contained breathing apparatus in the unit or at the control room before investigating the cause. Operators at the coking unit area provide back-up support to the unit operator. All operators are in radio contact with the control room.

Computer Monitoring System --

The refinery uses a process control computer to aid operating personnel in controlling and tracking unit processes. The output from the H_2S monitor controllers is scanned once a minute by the process computer, and the H_2S concentration at each sensor is stored in the computer. Presently, these 1-minute readings are stored as 6-minute averages, 1-hour averages and 24-hour averages.

Four area plot plans, showing the location of each H_2S sensor scanned each minute, are also available on the computer. These plot plans can be visually displayed one at a time either on the CRT and/or on hard copy from one of the central control room printers. Because the board operator for the H_2S handling areas is in radio contact with the unit operator, the board man can quickly relay updated H_2S levels monitored by the sensors during an alarm situation.

Calibration and Operation --

Since the system's startup in February 1982, the refinery has corrected a number of operating problems. Major problems included:

- Replacement of all controller circuit boards
- Failure of several sensor heads
- Short shelf life and long delivery time of sensor heads.

However, early detection of a pump seal failure by the H_2S monitoring system has resulted in a high level of confidence in the system by the operating personnel.

The monitoring system is calibrated once a month using a standard gas. Each sensor is tested, as are the system's electronic functions. A test of one of the sensors during the indepth visit demonstrated the quick response capability of the chemical sensor and the system functions (the audible alarm in the control room, the process area light, and the computer functions). About two man-days per month is required for a calibration check.

Installation Costs --

Refinery personnel designed the overall system and subcontracted the installation work. Items provided by venders included: H_2S sensors and controllers, instrument shed, instrument shed panel board, and miscellaneous systems (e.g., alarms and lights). All computer programming was conducted by refinery personnel on the refinery's central process computer. The total system cost was $190,000 (February 1982 dollars) which includes:

- Instrument shed
- Panels and alarms
- Monitor sensors and controllers
- Installation equipment and labor
- Computer programming
- Engineering.

Sensor and controller costs alone were estimated at approximately $19,000. About half of the system's cost was incurred by the extensive engineering and computer programming effort.

H_2S Monitoring System Evaluation

The H_2S monitoring system recently installed at this refinery is highly sophisticated. Operating personnel report a high degree of satisfaction with the new system which replaced a lead-acetate tape system. The following summarize the key features of this system:

- Location of 18 sensors provides a high degree of coverage over the four processing areas.

- An extensive alarm system effectively warns if H_2S concentrations greater than 10 ppm are detected. Each processing area has a visual (blinking light) alarm and the control room and the caustic neutralization area have audible alarms.

- Use of the refinery computer to handle the H_2S system monitoring data provides a high degree of emergency and long term monitoring information.

- The rapid response time of the sensor and low cost ($400 each) has contributed to a high degree of satisfaction with the new system.

Area monitoring systems can be highly effective controls in reducing worker exposure to toxic substances. This refinery's new H_2S monitoring system appears to be well designed and implemented. It uses state-of-art technology for sensors, controllers, alarms, and data handling. The health hazard associated with H_2S is one of the petroleum refining industry's major concerns. This refinery's H_2S monitoring system makes use of many new technologies to effectively address this concern.

Industry Applicability

The new generation of H_2S sensor technology using electrochemical sensors and metal oxide semiconductor sensors appear to be very reliable and low in cost. Three refineries visited were very pleased with their new installations which replaced lead acetate tape systems. A brief description of the two systems studied but not discussed above follows:

- Sixteen General Monitor remotely located sensors with four multichannel controllers in the sulfur recovery plant area. System uses metal oxide semiconductor sensor with display panel in operator shed and computer handling of data. Sensors are located near equipment which might release high concentrations of H_2S. System installed in February 1982 at a cost of approximately $50,000. New system replaced an existing lead acetate monitoring system.

- Fourteen General Monitor remotely located H_2S monitors (sensor and controller together) with visual alarm (red flashing light) at each sensor/controller location in the sulfur recovery unit. Sensors are located near process equipment along the battery limits of H_2S processing unit. Unit wide audible alarm and control room panel alarms for each monitor location included in the 1981 installation cost approximately $5000 per monitor ($70,000 total). The metal oxide semiconductor type sensor was selected due to the good performance experience at another refinery unit and replaced an existing lead-acetate tape system.

Each of the three refinery monitoring systems studied were installed by the refinery maintenance department or by local contractors.

As petroleum refiners process more sour crudes, expansion of existing H_2S handling facilities will be required increasing the need for H_2S area monitoring systems. Continued industry concern regarding occupational exposure to H_2S and the advent of the new technology H_2S sensor/controllers should result in a more widespread use of area monitoring systems. Many other industries handling H_2S should also benefit from the new sensor/controller technologies.

BENZENE/TOLUENE/XYLENE AREA MONITORING SYSTEM

At one refinery's aromatics extraction processes, small quantities of benzene, toluene, and xylene escape to the workplace because of leaks from pumps, valves, or process lines. Due to the toxicity of benzene, a relatively minor leak could result in airborne concentrations great enough to produce overexposure to workers assigned to the aromatics extraction and thermal hydrodealkylation units. To reduce the potential for overexposure to benzene (as well as toluene and mixed xylenes), this refinery installed an extensive monitoring system which was studied during a 2-day indepth visit.

Monitoring System Description

This refinery has a Universal Oil Products licensed unit designed to extract the aromatics fraction from light reformate produced in the catalytic reforming unit. Sulfolane (tetrahydrothiophene-1,1-dioxide) is the solvent used to extract the aromatic fraction of the feed, producing the following products:

- Benzene-toluene mixture
- Xylenes and heavy aromatics mixture (C-8 aromatics)
- Light raffinate
- Heavy raffinate.

The benzene-toluene concentrate is used as a feed stock to the thermal hydrodealkylation (THD) unit to maximize the production of benzene.

The refinery uses a Beckman Model 6750 processor and analyzer to monitor for benzene, toluene and mixed xylenes in the two aromatics processing units. Three sampling points are located near charge or reflux pumps in each of the above units, as illustrated in Figure 19. The refinery chose these locations because sampling data indicated that these pumps are more prone to leak than other process equipment in the unit. Additionally, the pumps are centrally located in the two units.

The sampling head at one end of the sample conduit is protected by a 3-inch diameter cartridge particulate filter. The other end of the conduit is connected to the gas chromatograph analyzer (shown in Figure 20).

The automated system takes a grab sample from each point once every 40 minutes, or about 12 times per 8-hour shift. The analyzer has been programmed by the refinery personnel to alternate units so that hourly sampling data are available for each unit. Using this sampling scheme ensures prompt detection of leaks or other problems.

The sampling scheme currently in routine use is shown in Table 8. The analyzer program may be altered so that a point of concern can be monitored more frequently (e.g., if one sampling point records persistently high readings).

TABLE 8 ROUTINE BTX AREA SAMPLING SCHEDULE

Sample Point No. (in order sampled)	Process Unit	Hydrocarbon Pumped
1	Aromatics Extraction	Benzene-Toluene-Xylenes
4	Thermal Hydrodealkylation	Benzene-Toluene
2	Aromatics Extraction	Benzene-Toluene-Xylenes
5	Thermal Hydrodealkylation	Benzene-Toluene
3	Aromatics Extraction	Benzene-Toluene-Xylenes
6	Thermal Hydrodealkylation	Benzene-Toluene

The control panel of the data processing portion of the Beckman Model 6750 displays information regarding the status of the system, including the sample point currently being analyzed; the amount of elapsed time in the sample program; and the number of active sampling points being monitored. Collection and analysis of each sample requires 400 seconds. Prior to analysis, the stream to be sampled is purged with nitrogen for 370 seconds to ensure that no residual air remains in the sample line from the previous analysis.

Five seconds into the analysis cycle, the sample valve is closed and the analytical portion of the cycle begins. The sample goes to the Beckman analyzer, which is located in an enclosed area in

FIGURE 19

BTX SAMPLING LOCATION - BETWEEN BENZENE/TOLUENE REFLUX PUMPS

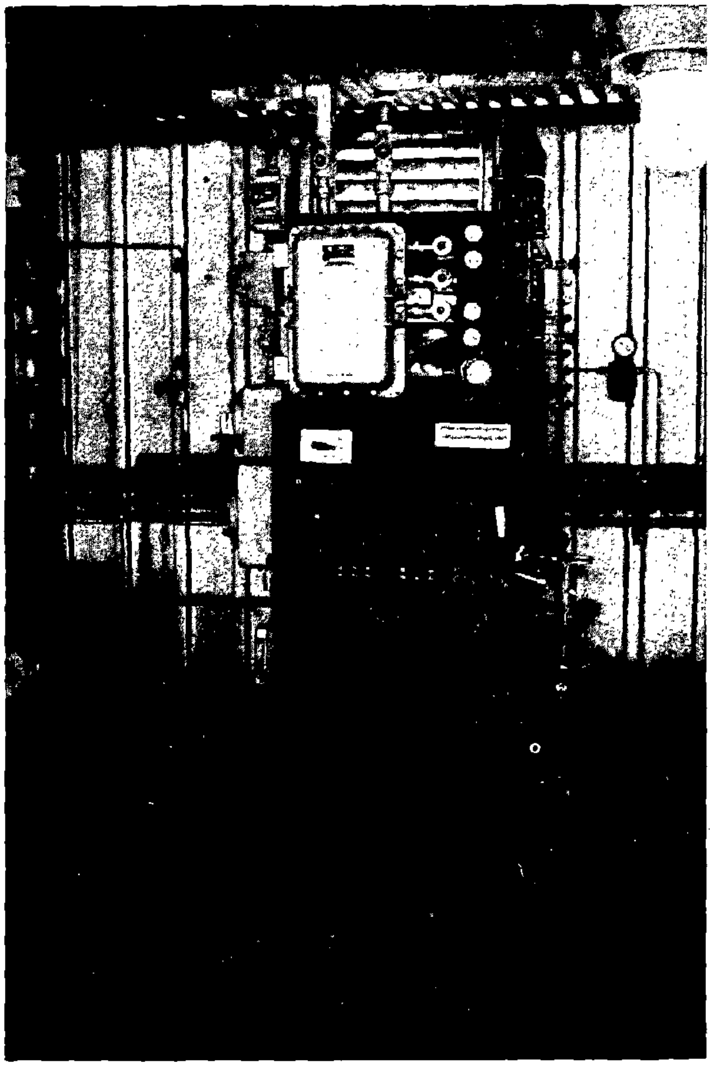


FIGURE 20

GAS CHROMATOGRAPH PORTION OF
BECKMAN MODEL 6750 ANALYZER/MICROPROCESSOR

the aromatics extraction unit. The analyzer measures the benzene, toluene and xylene fractions in the sample via a flame ionization detector (FID). The refinery currently uses an OV 101/60-80 mesh chromatographic column for separation. The analyzer requires zero-grade nitrogen as the carrier gas, zero-grade air as the purge gas, and zero-grade hydrogen for the flame.

Analysis for benzene is complete within 2 minutes into the collection/analysis cycle. The toluene and xylene fractions elute within 3-1/2 minutes into the cycle. The remaining three minutes provide time for removal of heavy hydrocarbon impurities from the chromatographic column so that "ghost" compounds will not appear in subsequent analyses.

Analytical results may be displayed on a strip chart recorder or printer (plotter) integrator. Additionally, after each analysis, results are stored in the microprocessor's memory. The microprocessor may be programmed to generate a hard copy of results immediately following analysis, or results may be averaged and a hard copy summary generated at regular intervals.

Routinely, the system is not programmed to print results after each analysis. Instead, results are averaged for each sampling point and summarized in hard copy generated at the end of each 8-hour shift (at 3 PM, 11 PM, and 7 AM). These data summaries, similar to that shown in Figure 21, are reviewed by operating personnel assigned to the aromatics extraction and THD units and by the refinery's environmental department.

If the measured concentration of benzene, toluene or xylenes in a sample exceeds 10 ppm set point, an alarm panel lights and an alarm sounds on the control panel which monitors the aromatics extraction and THD units. A strip chart recorder on the control panel indicates the compound of concern, the sampling point at which the high concentration has occurred, and the concentration measured. The operator responsible for the area in which the high concentration has been measured will investigate the area to locate the cause of the problem and clear the alarm.

A second alarm system is programmed in the microprocessor. Should the concentration of benzene, toluene or xylene exceed 25 ppm in a sample, an alarm on the control board of the microprocesor is activated. When this situation occurs, the microprocessor automatically prints a hard copy of the analysis results, indicating the compound(s) in high concentration.

Unit operating personnel immediately review alarm data as an aid in monitoring process conditions, to check for equipment problems such as pump seal failure, and as a check on the reliability of the sampling system.

```
BECKMAN 6750 GC          SHIFT TIME AVERAGES      15:00 05/22/82

COMP 01 Benzene

A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG
1  1   12  .000020       1  2   12  .000126       1  3   12  .000315       1  4   12  .000015       1  5   12  .000033
1  6   12  .000470


COMP 02 Toluene

A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG
1  1   12  .000018       1  2   12  .000034       1  3   12  .000890       1  4   12  .000037       1  5   12  .000013
1  6   12  .000071


COMP 03 Xylene

A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG         A ST  CNT    AVG
1  1   11  .000033       1  2   12  .000003       1  3   12  .000066       1  4   11  .000021       1  5   12  .000055
1  6   12  .000038
```

FIGURE 21 - EXAMPLE OF ANALYTICAL DATA SUMMARY

COMP = COMPONENT
ST = SAMPLING POINT
CNT = NO. OF TIMES SAMPLED DURING SHIFT
A = ANALYZER NO.
AVG = AVERAGE CONCENTRATION TIMES 10,000 EQUALS PARTS PER MILLION

The system has not required extensive maintenance since its installation in 1979. Routine maintenance requirements include replacing the sampling head particulate filters (once every two months unless filters are damaged or splashed with water or hydrocarbons) and regular calibration of the gas chromatograph portion of the system.

Refinery personnel estimated that the system has been on-stream about 80 percent of the time since its installation. Most of the downtime occurred shortly after installation when microprocessor programs were de-bugged. Occasionally, operating problems occur due to heavy rainfall or abrupt changes in humidity and temperature.

In planning for the system's installation, the refinery personnel paid particular attention to locating the sample points. Costs and practicality of installation were weighed against location for optimum employee protection. The sample points are located immediately adjacent to pumps with high leak potential, but are protected enough to avoid damage during normal refinery operation and maintenance. Additionally, the sample points are centrally located in the aromatics extraction and THD units.

Ambient air from each sample point is analyzed about 12 times per 8-hour shift or once every 40 minutes. Refinery personnel said that each point could be sampled more frequently if the analysis program were altered, for example, to exclude toluene and xylene, or to minimize column-conditioning time at the end of the cycle. However, refinery personnel feel that obtaining more detailed and better quality information is more important than adding more sampling periods during each shift.

The BTX monitoring system cost approximately $30,00 installed (1979 $). This cost excludes construction and utility costs for enclosures to house field analytical equipment because such enclosures were already available. Operating costs for the system include maintenance of a supply of spare parts and calibration gases, and labor costs for an instrument technician responsible for operating the system. Refinery personnel estimated that about two hours per day of instrument techician time is dedicated to operating the BTX monitoring system.

Control Evaluation of the BTX Monitoring System

The refinery personnel report that the BTX monitoring system works efficiently and is an effective means of preventing employee overexposure to benzene and other aromatic hydrocarbons which could be present in the aromatics extraction and THD units. Observations made during the indepth survey confirmed refinery reports.

As a check on the reliability of data collected by the BTX monitoring system, area samples were collected of ambient air at each of the system's six sampling points. Samples were collected using low-flow sampling pumps and charcoal tubes. The tubes were analyzed for benzene according to NIOSH Method P & CAM 127. Analytical results are shown in Table 9.

Although continuous sampling results cannot be compared directly to results obtained from "grab"-type sampling by the BTX monitoring system, similar trends should be evident. Average monitored concentrations for benzene over the 8-hour time period in which the continuous samples were taken are also shown in Table 9. Grab sampling average values taken by the monitoring system at sampling points 2, 3, and 6 are actually higher than concentrations obtained through continuous sampling. Average concentrations obtained from either method are well below the current OSHA permissible exposure limit of 10 ppm. Only three of the twelve average concentrations exceeded 1 ppm.

TABLE 9 BENZENE CONCENTRATIONS OBTAINED FROM CONTINUOUS AND GRAB SAMPLING

Sample Point No.	Average Concentration Continuous 8-hr Sampling (ppm)	Average Concentration of GC Samples Taken Over 8-hr Shift (ppm)
1	0.015	0.020
2	0.09	1
3	1	3
4	0.04	0.015
5	0.14	0.03
6	2	5

Response time of the BTX monitoring system was demonstrated as excellent in spiking tests conducted during the survey. In these tests, small quantities of mixed xylenes and benzene/toluene product were splashed in the area near (but not directly on) one of the sampling heads. Each "spike" was made within 3-1/2 to 2-1/2 minutes prior to the beginning of the analysis cycle for the area. In each spiking test, analyzer response was immediate; high concentrations of the spiked compound were detected in the analysis cycle; alarm systems were activated; and hard copy results were automatically printed.

Since its installation in late 1979, the BTX monitoring system at the refinery has been an effective engineering control in protecting employees from potential overexposure to benzene and other aromatic hydrocarbons. The system protects aromatic extraction and thermal hydrodealkylation unit employees in two ways. First, it provides an early warning that elevated concentrations of benzene, toluene or xylenes are present in the area near the sampling point. If necessary, employees may be evacuated from the area or may be warned to avoid the area until the problem is solved and aromatic concentrations decrease to safe levels.

The second way in which the system protects employees is its ability to detect relatively small increases in aromatics levels which may be indicative of pending equipment failure. For example, small increases in toluene levels over several hours may indicate that a pump seal is about to fail. The BTX monitoring system aids refinery personnel in locating the emission source and initiating appropriate maintenance procedures.

Refinery personnel stated that one of the system's major assets is its flexibility. The microprocessing portion of the system can accommodate up to six analyzers, although currently it only uses two: one for BTX monitoring and one for hydrogen sulfide monitoring in fuel gas streams. Each analyzer can sample up to 16 streams or sample points.

Industry Applicability

The use of gas chromatographs as analytical instruments in refineries has found widespread use for many years in laboratories and on process streams. However, the cost and reliability of these instruments now makes them cost effective for use in area monitoring systems for a wide range of hydrocarbons. These systems can be valuable not only in monitoring worker exposures to toxic chemicals but also in reducing the chance of major equipment failure (e.g., pump seals) through early detection followed by preventive maintenance. With proper calibration and maintenance, these systems can prove cost effective to any plant where the uncontrolled release of such chemicals can cause environmental, health, and safety problems.

SECTION 6

EMISSION CONTROLS AT OIL-WATER SEPARATORS

All refineries employ oil-water separators as part of the wastewater facilities. Oil-water separation typically consists of gravity type separation and dissolved air-flotation (DAF) type separation. Most of these separators are open to the atmosphere at some point and allow gaseous emissions from the wastewater to escape into the ambient environment. Employees responsible for the operation of oil-water separation facilities are typically exposed to various hydrocarbon vapors, hydrogen sulfide (H_2S) and ammonia (NH_3). Typically, time-weighted exposures are low because operator time requirements at these facilities are very short.

In many cases, stringent air and water environmental regulations have required refineries to install equipment that significantly reduces the air emissions from oil-water separation facilities. At two of the refineries visited, the impact on worker exposures due to the installation of emission controls was evaluated. A discussion of these findings follows.

EMISSION CONTROLS ON A DAF UNIT

One of the refineries visited covered its DAF unit in 1977 as a part of the hydrocarbon emissions control program. The fiberglass/steel tank covers and the ventilation system exhausting trapped hydrocarbons also provide an effective engineered control which shields the refinery's effluent treatment plant operators from overexposure to hydrocarbon vapors emitted from the unit.

Control Description

The DAF unit consists of two parallel trains which operate independently. Each train has the capacity to treat approximately 2000 gallons of oily water per minute, for a total DAF throughput of 3600 to 4000 gallons per minute. Figure 22 is a simplified process flow diagram which illustrates the DAF process described in the following paragraphs.

Effluent from the refinery's API separator (oil-water gravity type separator) flows to a surge tank from which the DAF unit is fed. Effluent oil concentration is about 400-500 ppm. Material from the surge tank, at a temperature of about 100°F, goes to one of two parallel flash/mix tanks. In these tanks, acid or base is added to adjust the pH for downstream treatment, and polymer is added to improve the flocculation of suspended solids and dissolved oils in flocculation tanks. The flocculation tanks provide sufficient residence time and slow agitation to promote optimum flocculation.

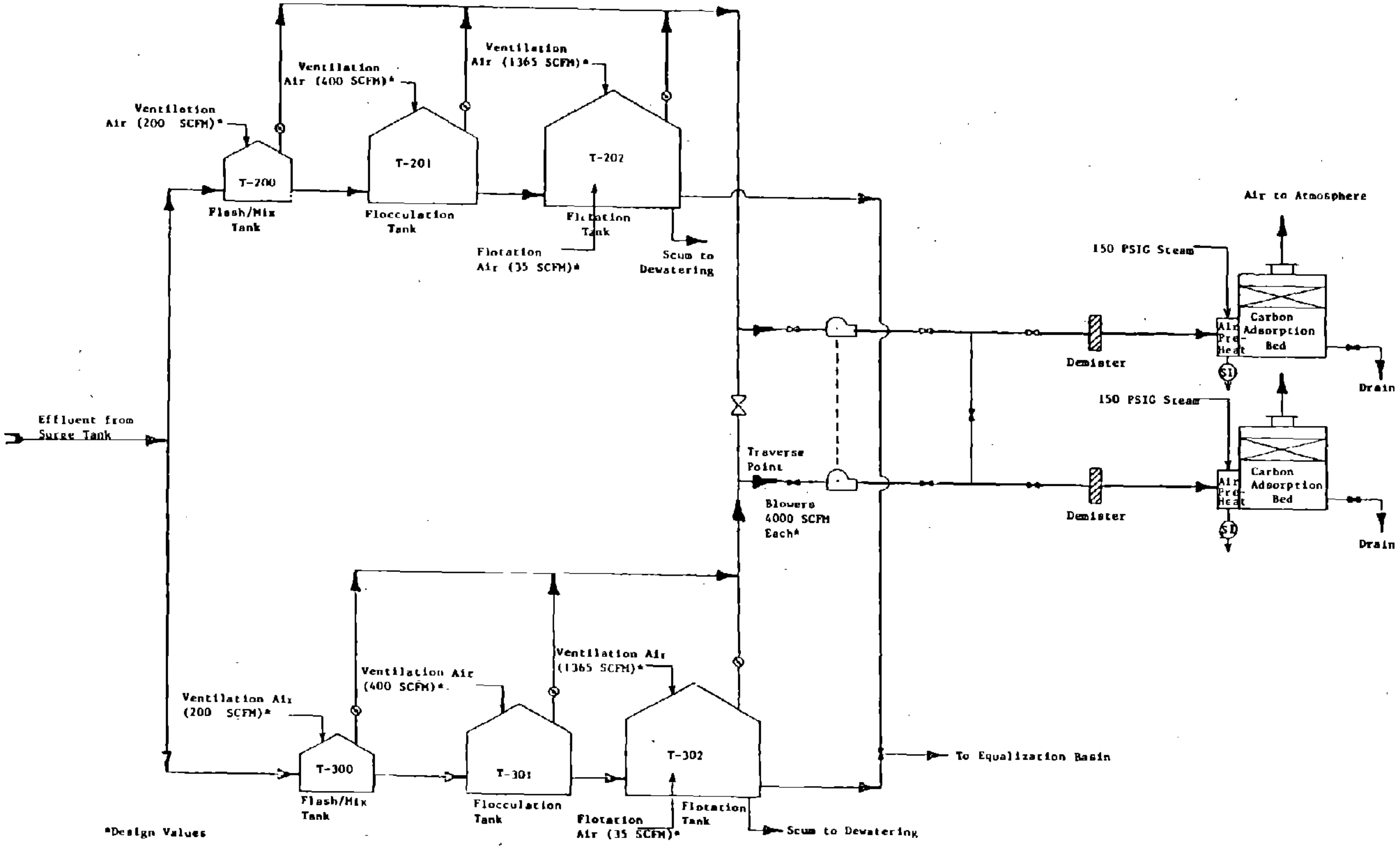


FIGURE 22 - PROCESS FLOW DIAGRAM FOR DAF UNIT

From the flocculation tanks, material is charged to flotation tanks. Here, air is mixed with a portion of recycled clarified DAF effluent. The air dissolved in this slip stream forms small bubbles which float the flocculated oils and solids to the surface of the tank. The floating scum is skimmed off and sent to a dewatering tank. Clarified effluent goes from the flotation tanks to an equalization basin where it is held until sent to secondary wastewater treatment units.

Each of the flash/mix, flocculation and flotation tanks is covered with a permanent steel and fiberglass cover designed and fabricated to the refinery's specifications by Fiberglass Specialty Company in St. Paul, Minnesota. The covered DAF unit is ventilated with a forced draft fan (design capacity = 4000 SCFM) which draws air through 3-inch diameter inlet ports located in the walls of each tank. Air and hydrocarbon emissions are forced through an activated carbon bed with a maximum depth of 5 feet. The hydrocarbons are adsorbed and the clean, odorless air stream is vented to the atmosphere from the top of the carbon bed. Two activated carbon adsorption systems are dedicated to the DAF unit so that one is in operation while the other is shut down for reactivation.

One operator and one head operator per shift are assigned to the refinery effluent treatment plant (excluding the API separators). Operators interviewed during the indepth visit to the refinery reported that a moderate amount of time is spent in the control room. A great deal of operator time is spent out in the refinery checking the DAF unit, the biological treatment units and the sludge disposal facilities.

Routine operator duties at the DAF unit include monitoring performance of pumps and compressors, monitoring the pH adjustment and polymer addition in the flash/mix tanks, and checking the mechanical oil skimmers in the flotation tanks through hatch doors. Like most of the other refinery units, the DAF unit is highly automated, requiring little manual operator adjustment unless an upset occurs.

Hydrocarbon detectors are installed in several locations throughout the DAF unit and monitored in the effluent treatment plant control room. Detectors located in the headspace of each flotation tank indicate hydrocarbon concentration levels with respect to explosive limits. Detectors are also located at the outlet of each carbon adsorption bed. These detectors signal breakthrough of hydrocarbons from the beds, indicating that the carbon should be reactivated.

Each carbon bed is reactivated by an outside contractor every 6 to 8 weeks at a cost of approximately $8500.

Control Evaluation

To document control of operator hydrocarbon exposure by the tank covers, area samples were collected from inside and outside flotation tanks 202 and 302. Low-flow sampling pumps were attached to a brace just inside the hatch of each tank. Outside each tank, pumps were attached to the catwalk near the hatch. Air to be sampled was drawn through a charcoal tube at a nominal rate of 100 cc/minute. Modified NIOSH Method P & CAM 127 was used to analyze the samples for total hydrocarbon content.

Sampling results are shown in Table 10. Amounts for samples were assigned by comparing each sample's total peak chromatogram area to the peak areas of hexane standards. Hexane was used as a reference standard because its molecular weight and carbon number (C-6) were considered representative of the hydrocarbon mix in the separator effluent sent to the DAF unit.

As the table shows, the hydrocarbon concentration inside Tank 302 was measured at more than twice the Permissible Exposure Limit (PEL) of 500 ppm for hexane, the reference standard. Although a lower concentration of 370 ppm was measured in Tank 202, this value is in excess of 100 ppm, the NIOSH-recommended exposure limit and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for hexane.

TABLE 10 TOTAL HYDROCARBON SAMPLING RESULTS

Sample No.	Location	Area Concentration (ppm as hexane)
MD-32	Inside Tank 202	370
MD-2	Outside Tank 202	<1*
MD-1	Inside Tank 302	1100
MD-30	Outside Tank 302	<1*
MD-0	Blank	<1*

*Analytical limit of detection is 1 ppm

Data in the table also show that area hydrocarbon concentrations outside both tanks were measured at less than 1 ppm, the limit of detection for the analytical method used. The very low hydrocarbon level outside the tanks demonstrates the effectiveness of the tank covers and ventilation system in preventing hydrocarbon emissions.

Hydrocarbon concentrations at the face of the flotation tank hatch (when open) were measured with an organic vapor analyzer (OVA). Values ranging from 150 to 180 ppm were detected. Given the relatively low hydrocarbon concentration at the hatch and the short time during which an operator stands with the hatch open, little potential for operator overexposure exists.

Operator exposure to hydrocarbons in the DAF unit is minimal because the tank covers prohibit escape of hydrocarbon vapors to the atmosphere. Although the unit operators spend a large portion of each shift in the unit rather than in the control room, they routinely encounter above-ambient hydrocarbon concentrations only when the flotation tank hatches are opened. Exposure time is minimal (2 to 5 minutes, once or twice per shift).

Additionally, the DAF unit ventilation system draws dilution air through the operator's breathing zone when a tank hatch is opened. Total hydrocarbon concentrations of no more than 180 ppm were detected in the open hatches with the OVA. The efficiency of the DAF unit's ventilation system contributes to the low hatch concentration.

Hydrocarbon monitors located in flotation tank headspace provide an additional employee exposure control. If elevated hydrocarbon concentrations are indicated by the monitors, operators follow established safety procedures in trouble-shooting the unit to locate and solve the problem.

Industry Applicability

As more stringent fugitive emission environmental regulations are imposed on petroleum refinery oil-water separation facilities, the industry trend will continue to move toward covering gravity type and DAF type oil-water separators. Properly designed systems should reduce worker exposure potential to hydrocarbons, H_2S and NH_3. Highly sophisticated systems as described in this section probably are more effective at reducing environmental emissions and worker exposures. However, the degree of system sophistication will probably be a function of the regulations adopted by state agencies. More sophisticated systems are more costly than simple covers, have higher maintenance and operating costs and may create a greater explosion hazard. The system described in this report should be applicable to most any DAF or compact activated sludge treatment facility at any plant processing wastewater containing dissolved gases and volatile liquids.

FUGITIVE EMISSION CONTROLS FOR GRAVITY SEPARATORS

In an attempt to control emissions of hydrogen sulfide (H_2S), ammonia (NH_3), and hydrocarbons, one of the refineries visited initiated an extensive program to modernize and expand its wastewater treatment capabilities. This program included addition of a sour water stripping facility (to remove H_2S and NH_3 from process wastestreams sent to the treatment plant) and the addition of two covered corregated plate impactor (CPI) type separators (to provide improved removal of oil and containment of hydrocarbon vapors from wastewater). Although these and other improvements in the wastewater treatment plant were implemented primarily for environmental compliance purposes, they also provide for reduced employee exposure potential.

The operation of the new sour water stripping facilities has significantly eliminated the amount of H_2S and NH_3 going to the wastewater treating plant. Thus, the chance of operator exposure to these gases has been virtually eliminated under normal operating conditions. The new CPI separators should have improved removal of free oils in covered facilities prior to the wastewater flowing into the WWTP. Thus, less hydrocarbons are available for evaporation from the wastewater in the downstream processing facilities (API separator, DAF unit, biological treating). Both CPI separators are covered reducing the ambient hydrocarbon H_2S and NH_3 concentration 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.

Control Evaluation

Before WWTP modifications were made, 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 11 summarizes the range of results. 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 showed measureable amounts (1-5 ppm) at the API separator and the biotreatment unit.

TABLE 11 SUMMARY OF 1979 HHE SAMPLING RESULTS

	Personal Monitoring (ppm)	Area Monitoring (ppm)	OSHA Standard (ppm)
Substance	8-Hr TWA	8-Hr TWA	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	20

NIOSH concluded from the 1979 Health Hazard Evaluation(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.

In an effort to evaluate the effectiveness of the WWTP modifications as engineering controls to reduce employee exposure, 1-day area and personal sampling was conducted during the indepth visit to the 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. A sodium sulfate tube is used prior to the molecular sieve material to remove moisture. Short-term readings for H_2S were also made using a 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).

As Table 12 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 and well below the OSHA PEL for those substances. All of the higher concentrations were measured at the API separator afterbay.

TABLE 12 SUMMARY OF 1982 SAMPLING RESULTS

Substance	Personal Monitoring (ppm) 8-Hr TWA	Area Monitoring (ppm) 8-Hr TWA	OSHA Standard (ppm) 8-Hr TWA
Benzene	0.1 - 0.2	ND - 2.6	10
Toluene	0.7 - 0.9	0.01 - 9.9	200
Xylene	0.6 - 1.1	0.1 - 16	100

Hydrogen sulfide long term (1-2 hour) samples collected using molecular sieve tubes showed no detectable levels of H_2S (<1 ppm). Spot readings using a MSA direct reading meter showed short term H_2S levels near 1 ppm at the API separator and wet oil separation building.

As was the case for the 2-day HHE sampling effort in 1979, the 1-day sampling effort conducted in 1982 can only provide screening results. No significant drop in BTX levels was observed. However, the BTX levels measured in both studies were low. Hydrogen sulfide sampling results indicate a measurable drop in ambient levels of H_2S.

Industry Applicability

Environmental regulations directed toward reducing the amount of ammonia and sulfides discharged in wastewater have resulted in more efficient removal of hydrogen sulfide (H_2S) and ammonia (NH_3) from refinery wastewater. Generally, the technology used to remove these pollutants is steam stripping whereby the H_2S is separated and subsequently recovered as sulfur and the NH_3 is 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 these compounds in the wastewater collection and treatment systems. They pose potentially acute and chronic health effects problems in refineries processing crudes with significant amounts of sulfur (greater than one percent sulfur by weight).

As environmental and health regulations concerning emissions from wastewater treating facilities become more widespread, the number of petroleum refineries using sour water strippers and covered gravity type separators will continue to grow. Additionally, the trend towards refining more sour crudes will result in wider spread use of sour water strippers. These environmental controls can be very effective at reducing employee exposures to hydrocarbons, H_2S and NH_3. The controls described in this section represent what has become common in the petroleum refining industry.

SECTION 7

EMISSION CONTROLS AT A BENZENE LOADING FACILITY

A potential employee health hazard in areas producing or handling aromatics is overexposure to benzene. A suspect human carcinogen which had been linked to leukemia and similar blood disorders, benzene is currently regulated by OSHA at a Permissible Exposure Limit (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, one refinery visited constructed loading facilities which incorporate several engineered controls. These controls, used in conjunction with personal protective equipment, substantially reduce benzene exposure to workers in the loading area.

DESCRIPTION OF LOADING FACILITIES

In 1980, two loading facilities equipped with engineered controls were constructed at the refinery. One is dedicated to benzene loading; the other is used for loading an aromatic product of mixed xylenes and heavier hydrocarbons but containing less than 0.3 percent benzene. The design of each facility is essentially similar, as described in the following paragraphs.

Figure 23 is a photograph of the refinery's benzene loading facility, located adjacent to the 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 24. An Emco Wheaton 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 25 and 26) 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 grounding connection is made. A visual signal (dual green lights) is displayed on the meter panel when a proper ground connection has been achieved. Also Pacific "canned" pumps are used to move benzene and viton O-rings and gaskets are used on process equipment.

A fugitive emissions collection system was also installed for the benzene loading facility. A simplified diagram of the system at

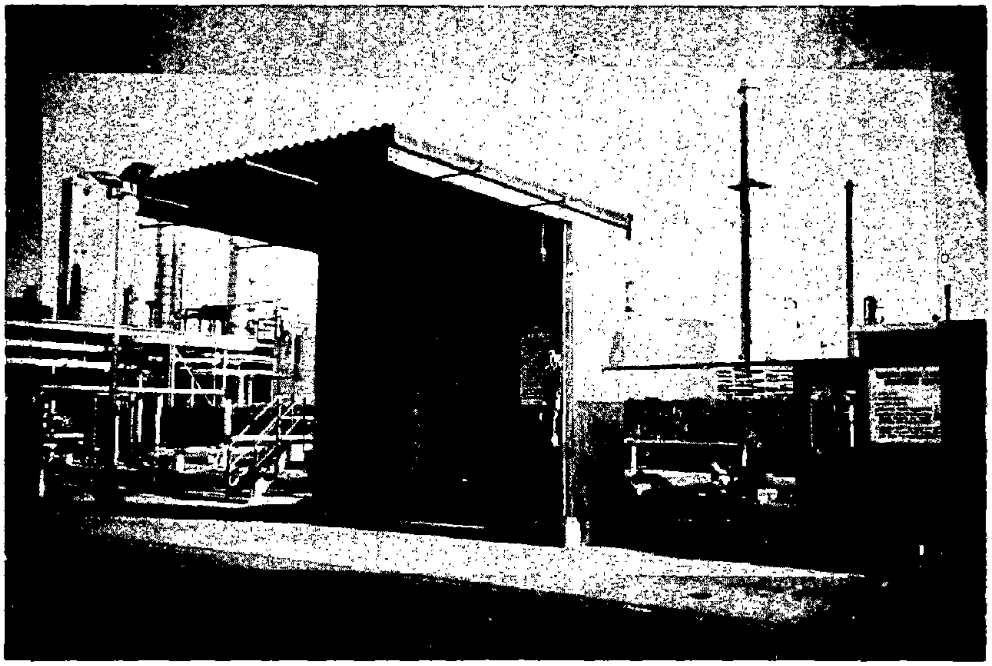


FIGURE 23 - BENZENE LOADING FACILITY

FIGURE 24 - BENZENE LOADING ARM INSIDE CABINET

FIGURE 25 - AUTOMATIC PRODUCT METERING SYSTEM

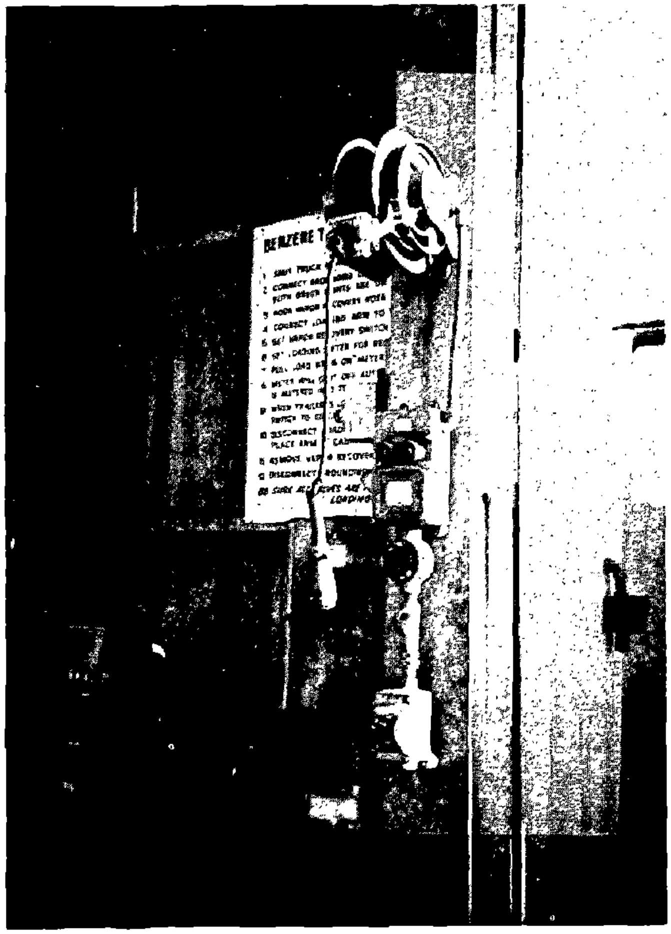


FIGURE 26 - VEHICLE GROUNDING MECHANISM

the benzene loading rack is shown in Figure 27. Fugitive vapors are collected by a flexible hose attached to each tank truck. The system is actuated by the loading facility's delivery meter. Recovered vapor is sent to furnaces where it is incinerated.

During the indepth visit, benzene and aromatics loading activities were observed on what was described by refinery employees as a typical day. On this day, five trucks were loaded with benzene and two were loaded with aromatics product. Based on these 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 8-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 shed is located in the loading area, the loading operator 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.

When a truck arrives at the refinery gate, a guard notifies the loading operator 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. When a truck is positioned at the loading facility, the driver turns off the motor and leaves the vehicle. From this point until the loaded truck is ready to leave the refinery, the operator 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 operator: safety helmet, safety glasses or goggles, rubber gloves, and an organic vapor cartridge respirator.

The operator first connects the vehicle grounding mechanism to the truck, 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. Figure 28 illustrates the next step in the procedure, attaching the loading arm to a corresponding dripless connection on the side of the truck. The operator 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 operator disconnects the loading arm, the vapor recovery hose and the electrical grounding cable, and the truck may leave the refinery.

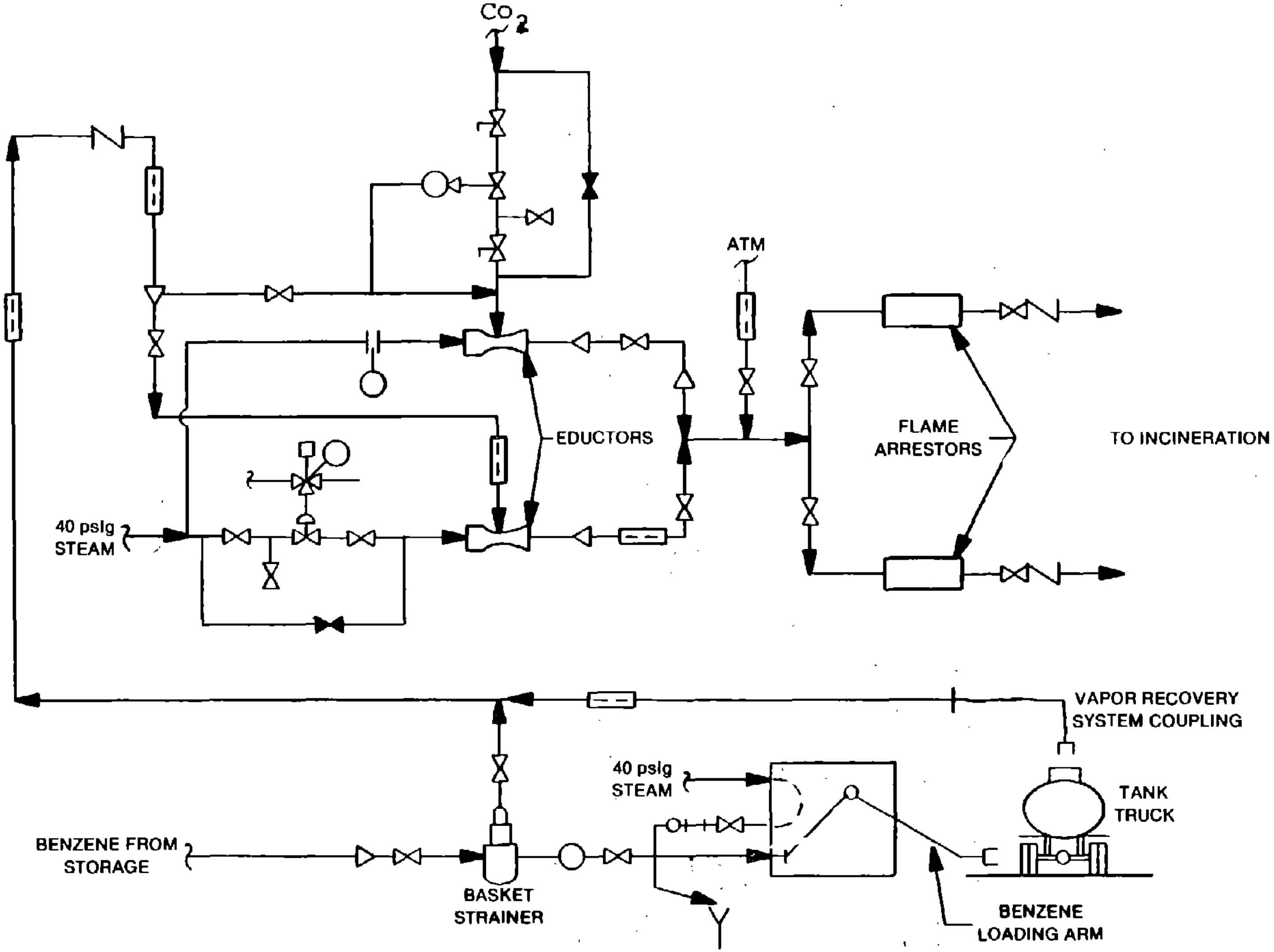


FIGURE 27 - DIAGRAM OF VAPOR RECOVERY SYSTEM

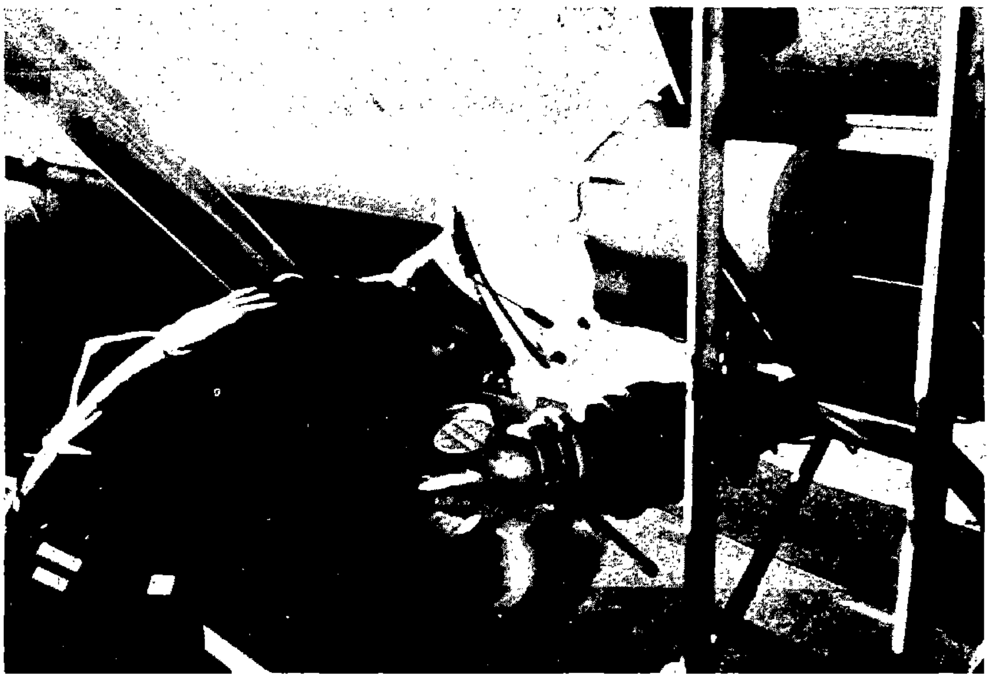


FIGURE 28 - LOADING OPERATOR CONNECTS LOADING ARM TO TRUCK

CONTROL EVALUATION

Long-term personal and area samples were collected around the benzene and aromatics loading facilities during the indepth visit. Low-flow sampling pumps were positioned inside each loading facility. Air to be sampled was drawn through a charcoal tube at a nominal rate of 100 cc/minute. Additionally, a breathing zone full shift sample was collected for the loading operator. This personal sample measured the operator's exposure without respirator. NIOSH Method P & CAM 127 was used to analyze the samples for benzene, toluene, and xylenes.

Sampling results are shown in Table 13. As the table shows, all benzene concentrations are below the current OSHA Permissible Exposure Limit of 10 ppm. However, the area concentration at the benzene loading facility and the loading operator's time-weighted average concentration exceeded the NIOSH-recommended standard of 1 ppm. The operator'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. Parallel personal sampling conducted by the refinery at the same time as the Radian/NIOSH sampling indicated benzene exposure at 1.9 ppm 8-hour TWA. 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.

TABLE 13 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 Loader	5.5*	0.1*	0.04*

*8-hour Time-Weighted Average Concentration

The use of engineered controls and personal protective equipment at the refinery appears 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 the refinery's marketing company. However, other tank trucks observed during the indepth study were not as well maintained. The truck loader had difficulty in establishing a good seal on two trucks in particular, and benzene was spilled as a result. The vast majority of the loading operator's exposure to benzene can be attributed to these spills.

The operator can (and reportedly does) refuse to load trucks with incompatible or poorly maintained connectors. However, in many instances, the operator does not know a connector is bad until he has attempted to initiate loading which is why a respirator is worn during this operation.

INDUSTRY APPLICABILITY

At the time the engineering design was being developed for the benzene loading facility, OSHA's proposed Permissible Exposure Limit was 1 ppm for benzene. The benzene loading facility was specifically designed to reduce the operator exposure to 1-2 ppm without respiratory protection. The estimated cost of the benzene loading facility is approximately $50,000 (1980 dollars). This does not include the cost of the vapor recovery system. The total cost is evenly divided between equipment and installation costs.

This system appears to be very effective at reducing hydrocarbon emissions to below 5 ppm and could be used by any plant loading hazardous chemicals into trucks. Additionally, the systems relatively low cost and simplicity make it a very cost effective approach to reducing worker exposure potential and environmental emissions.

SECTION 8

EQUIPMENT MAINTENANCE CONTROLS

Preventive and routine maintenance procedures can effectively reduce the potential for employee exposure to hazardous substances. Regular preventive maintenance both minimizes the probability of catastrophic failure and reduces the need for unscheduled repairs. Some routine maintenance procedures, such as acoustic testing, may eliminate or substantially reduce situations where reactors or vessels must be opened and entered by maintenance personnel.

MAINTENANCE PROCEDURE DESCRIPTIONS

One of the refineries visited has in place several maintenance programs which contribute to lowered employee exposure potential to hydrocarbons, hydrogen sulfide, superheated steam (noise and heat), and other hazardous materials. These programs, which emphasize controlling equipment leaks and preventing equipment failure, are described in the following paragraphs.

Valve and Flange Leak Detection and Repair

Operations personnel at the refinery check valves and flanges for leaks on a daily basis. During their inspections, operators note leaks by sound, sight, and smell. The monitoring program extends to valves and flanges in hydrocarbon, hydrogen, and steam service. First priority is given to detecting and repairing leaks in hydrocarbon service. The refinery's Maintenance Department is notified daily by Operations as to which valves and flanges are leaking. Maintenance attempts to immediately repair valves which can be repaired while still in service. Typical repair techniques include tightening the packing or adding more rings.

If a valve or flange cannot be repaired by these methods or cannot be blocked out for immediate replacement, an attempt is made to temporarily repair the leak via injection of a thermosetting compound to seal the leak. A number of firms provide this service; this refinery has a separate maintenance contract with Furmanite(R). Examples of flanges sealed with Furmanite(R) are shown in Figure 29.

Leak sealing by means of a thermosetting compound involves injection of the compound directly into the source of the leak with the system operating at normal conditions. The process can seal leaks in flanges, valve glands and bonnets, screwed couplings, heat exchanger joints, unions, turbine casings, weld leaks, holes in pipes, expansion joints, fabricated tank joints, and a wide range of other pressure systems and process plant components. The injected compound fills all of the grooves and pits in the facing of the joint and, once cured, the integrity of

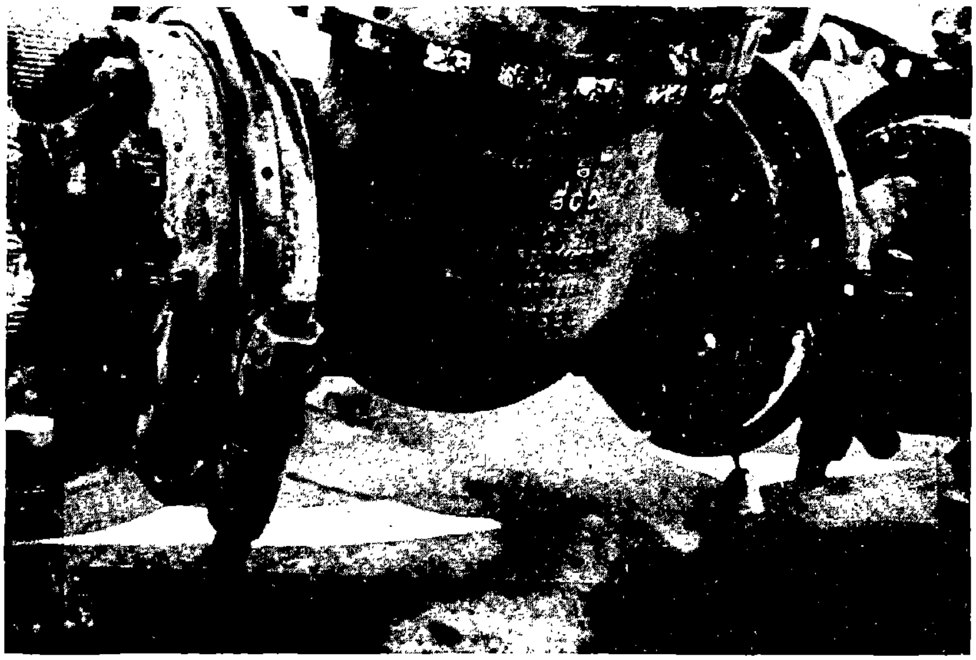


FIGURE 29 - STEAM VALVE FLANGES SEALED WITH FURMANITE (R)

the seal can be equal or better than the original installation. Leaks involving temperatures up to 600°C and pressures up to 5000 psi can be sealed with special thermosetting compounds that are compatible with most fluids.

At each unit turnaround, valves or flanges that leaked or displayed other types of problems are removed, inspected and repaired. Many times the cause of the problem in valves is use of incorrect packing or insufficient packing. All equipment that has been sealed with Furmanite(R) is removed and permanently repaired.

The refinery Operations Department maintains a record of valves and flanges which have caused problems. This record is periodically reviewed by the operations staff to identify valves or flanges with chronic maintenance problems. An effort is made to determine and remedy the cause of these problems.

Exchanger Head Leak Prevention

Heat exchanger heads in high pressure-temperature service are well-known as chronic "leakers." Emissions from exchanger heads are a particular problem in high pressure refinery units servicing hydrogen or light ends (e.g., hydrocracking or reforming units). In many instances, such leaks are caused by exchanger head deformation during bolt tightening.

To prevent this deformation and minimize emissions from heat exchanger heads, the refinery has developed a program which enables it to tighten exchanger heads without undertightening or overtightening. The refinery uses an ultrasonic instrument which measures bolt stretch and a computer program which calculates optimum stretch for each type of bolt.

To determine bolt stretch, an extensometer manufactured by Raymond Engineering, Inc. of Middletown, Connecticut, is used. A pulser within the extensometer shocks a transducer which then delivers a brief, highly damped pulse of ultrasound to one end of the bolt. The pulse travels through the bolt, echoes off the far end and returns to the transducer. The signal's round-trip transit time is measured and recorded in the instrument's microprocessor. When the bolt is tightened (and stretched), the length of the path the signal must travel increases, thereby increasing the transit time.

Refinery engineers said that the extensometer is used primarily to aid in tightening large or critical flanges and exchanger heads such as those in the hydrocracking or reforming units (Figure 30). The instrument has been most useful to control tightening the 3-1/4" diameter bolts used on the hydrocracking unit exchanger heads. The instrument can be used on bolts at temperatures of up to 300°F.

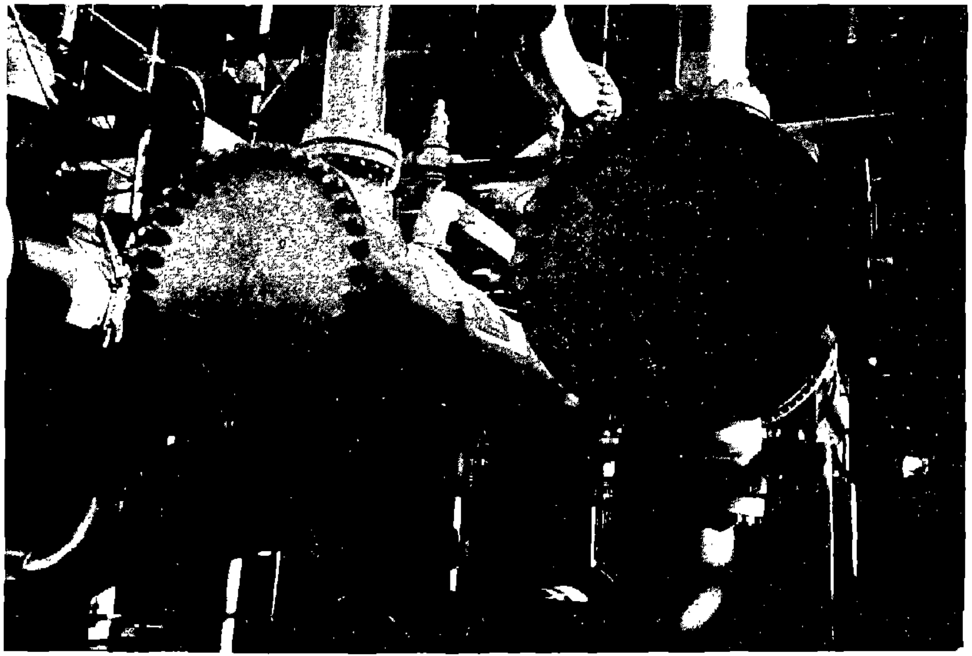


FIGURE 30 - HEAT EXCHANGER HEADS IN HYDROCRACKING UNIT

Refinery operations engineers initially calculated elongation and torque values for each bolt type in each application. Calculations were based on bolt material, gasket material, and yield strength of flange or exchanger head.

Before any bolts are tightened, a reference extensometer reading is taken in the refinery maintenance shop. Glycerine is used to stabilize the interface between the transducer and the surface of the bolt, as shown in Figure 31. As each bolt is being tightened in the field, the extensometer is applied and the degree of stretch is measured.

Bolts for each exchanger head are tightened gradually using a hydraulic torque wrench. During the first tightening sequences, bolts are tightened in a "star" pattern, i.e., bolts opposite each other across the exchanger head surface are tightened. In the final tightening sequence, bolts are tightened in a circular pattern around the exchanger head.

Use of the extensometer is more time-consuming than tightening bolts with a torque wrench alone (5 hours per exchanger head or flange versus 1 hour per head or flange). In some instances, to minimize turnaround time, the refinery monitors the stretch on fewer bolts. However, a majority of bolts must be monitored so that the integrity of the exchanger head seal is maintained. Refinery engineers said that the extra time spent in careful bolt tightening often results in time saved in the long-term; a unit is brought onstream with minimal problems and does not have to be shut down due to leaking exchanger heads or flanges.

In general, refinery engineers were satisfied with the extensometer. One problem existing in an older model such as the one owned by the refinery is its susceptibility to moisture. Newer models being developed are reportedly weather-resistant as well as lighter and easier to carry.

Rotating Equipment Vibration Monitoring

The refinery reports that it has one of the lowest pump seal failure rate of any domestic refineries. It attributes its favorable pump seal maintenance record to the vibration monitoring and alignment/balancing programs.

When the refinery initiated its vibration monitoring program in 1978, the maximum allowable vibration was 0.25 inches per second (IPS). The current maximum allowed is 0.10 IPS. Refinery personnel said that since the program began, the majority of pump failures have been due to worn bearings rather than seal failures. Pumps may run for over two years without major maintenance.

Twenty maintenance personnel permanently assigned to the refinery's machine shop are responsible for analyzing vibration

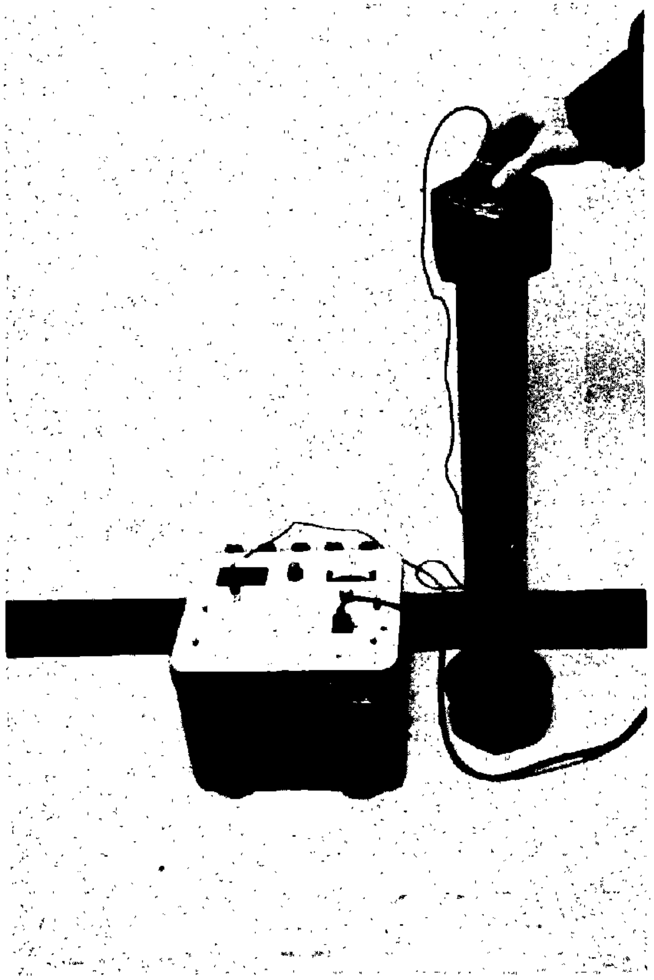


FIGURE 31 - EXTENSOMETER APPLIED TO 3 1/4" - DIAMETER BOLT USED IN HYDROCRACKER EXCHANGER HEAD

monitoring data and aligning or repairing out-of-specification equipment. The refinery has an extensive training program to teach employees how to use vibration monitoring equipment and how to interpret vibration data.

Operators on each refinery unit carry hand-held vibration monitors and check all pumps and compressors in each unit one time per month. Vibration information is sent to the Maintenance Department, which reviews the data and identifies out-of-specification equipment. If a pump has a spare, it is removed from service and repaired immediately. If not spared, it is given high priority for repair during turnaround. Each pump, compressor or turbine is balanced every time it is brought in for maintenance, regardless of its vibration status.

The refinery uses a double indicator alignment method in which both the pump and the motor are aligned simultaneously. The alignment method works equally well for packed or mechanically sealed pumps.

The machine shop maintains detailed records of all pump and other rotating equipment failures. The records are stored in the refinery's computer and are accessed through a CRT terminal located in the machine shop. Spare parts information and repair cost information also are computerized for each equipment item. These records are periodically reviewed by Maintenance and Operations personnel looking for problem trends.

Acoustic Testing

The state in which this refinery operates requires that all pressure vessels receive a biennial inspection. To avoid unnecessary shutdown and start-up of catalyst-containing pressure vessels, the refinery uses acoustic testing to inspect these vessels while still on-stream.

Acoustic testing is used by the refinery in trouble-shooting problems. Such testing locates even small cracks. Tests are usually conducted shortly before a scheduled turnaround. If cracks are found, materials can be ordered and repairs made during turnaround.

The refinery has used acoustic testing to inspect its hydrocracker reactors, reformer reactors, coke drums, and some pipelines and piping systems. The cost of an acoustic inspection varies according to how many vessels are tested. Refinery personnel stated that the overall testing program saves time and money, and provides an effective way to detect and repair potentially serious defects.

MAINTENANCE PROCEDURES EVALUATION

It is well documented that aggressive equipment maintenance programs can significantly reduce emissions from process equipment (e.g., valves, pumps, compressors, flanges, piping). Additionally, these programs generally reduce the number of catastrophic equipment failures (e.g., pump seals); thus reducing fire and safety hazards. The equipment maintenance programs discussed here were studied because the programs appeared to be effective in reducing worker exposures although they were implemented primarily to reduce operating costs through:

- Reduced product and energy losses
- Reduced repair cost for rotating equipment
- Reduced unit down times due to equipment failures and equipment inspections, and
- Reduced safety hazards.

Although no field sampling data were taken during the indepth visit, the positive impact of aggressive good housekeeping and maintenance programs was obvious. Recent data provided by the refinery showed that the rotating equipment balancing program had resulted in a pump seal failure rate 7.7 percent of the industry average. Thus, the potential for worker exposure to large releases of hydrocarbons and toxic gases (H_2S, ammonia, etc.) due to pump seal failures has been significantly reduced.

Repair of leaking valves in hydrocarbon and steam services reduces work exposures to hydrocarbons and noise. It also reduces the risk of major equipment failures which may result in safety hazards (fires and explosions) and acute health effects (burns and asphyxiation).

The heat exchanger head bolt tightening program is said to reduce overall the amount of unit down time and maintenance personnel exposure to leaking exchanger hoods. Hydrocarbon leaks from high temperature and pressure exchangers containing hydrocarbons represents an extreme safety hazard requiring constant vigilance by all petroleum refiners. The refinery visited has been very pleased with the positive results of this program in reducing unit down time and maintenance personnel time near hot, pressurized exchanger heads.

The refinery's acoustic testing program has been effective in reducing the number of in-vessel inspections and in spotting stress cracks in vessels not identifiable by visual inspection. This testing procedure should reduce maintenance worker exposure potential by reducing the need for internal inspections and should reduce the potential for catastrophic equipment failures.

Industry Applicability

All of the equipment maintenance programs discussed here are used by many refineries and can be used by other industries. Many refineries, chemical plants, and gas processing plants are being required to implement equipment maintenance programs, primarily for valve and pump seals, by environmental regulations. This trend will probably continue. However, the unique feature regarding the study of this particular refinery is that its program was implemented for economic and safety reasons. And as such, it has been tailored for the refinery - making it a most effective program. An added advantage of preventive maintenance programs, as described in this section, is the reduction of operator exposure potential.

SECTION 9

CATALYST DUST WET SCRUBBER

Although catalyst handling operations occur infrequently at refineries, they present an occupational health concern because of the high potential for employee overexposure to respirable dust and heavy metals. In an effort to control this exposure, one of the refineries visited uses portable two-stage wet scrubbers to collect catalyst dust from reactor unloading operations. This section provides engineering details about the scrubbers and documents operating experience with them.

SCRUBBER DESCRIPTION

The refinery's catalyst dust scrubbers are constructed using off-the-shelf equipment designed by the W. W. Sly Company of Cleveland, Ohio. Schematics of a scrubber similar to those used are shown in Figures 32 and 33 (courtesy of the W. W. Sly Company). Materials specifications are listed in Table 14.

Catalyst-laden air is drawn into the scrubber at the bottom through a flexible duct. As the air stream travels counter-current through sprays of liquid (a mixture of water and chemical wetting agent), it is cooled and large particles are entrained.

The air stream next flows through two impingement baffle plates. Turbulent interaction of liquid and gas occurs as the air flows through the perforated plates and strikes the impingement surface. As minute liquid droplets containing air and suspended particulate matter mix with liquid flowing across the baffle plates, particles remain with the liquid phase and clean air goes to the mist eliminator before exiting the scrubber.

Each impinger plate has a discharge drain which directs slurry to the bottom of the scrubber. A loop seal and drain is located at the bottom of the scrubber for disposal of catalyst-containing liquid.

Before a reactor vessel is opened for catalyst removal, the catalyst dust scrubber is positioned near the "dump-sock", a canvas chute through which catalyst flows out of the reactor (Figure 34). Water for the scrubber is supplied from a fire hydrant; electricity is obtained from a welding outlet.

When equipment is in place, the "dump sock" is purged with nitrogen and its outlet positioned 6- to 8-inches below the rim of the drum into which catalyst is to be deposited. A nitrogen blanket is maintained over the drum top as a fire-prevention measure when pyrophoric catalyst is handled.

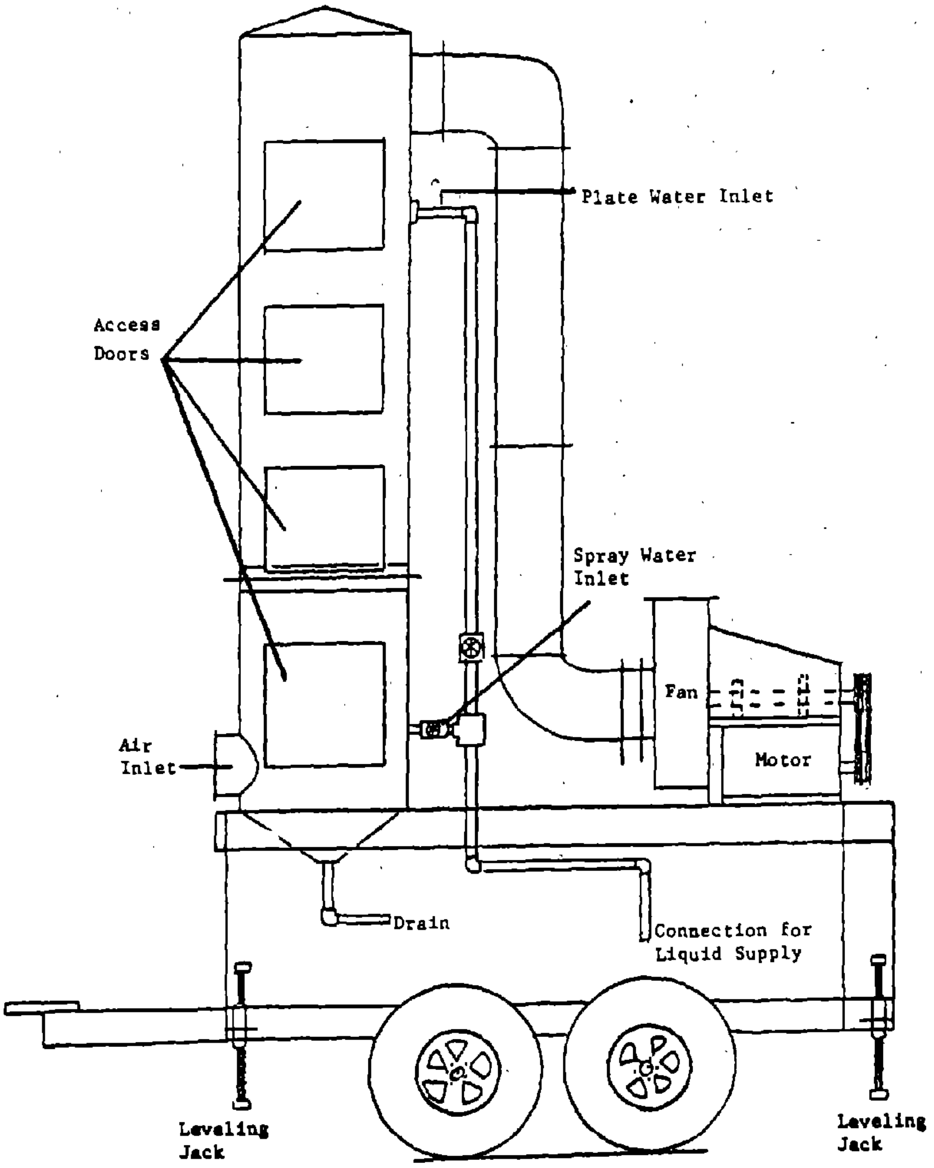


FIGURE 32 - SIDE VIEW OF SLY IMPINGET$^{(R)}$ WET SCRUBBER

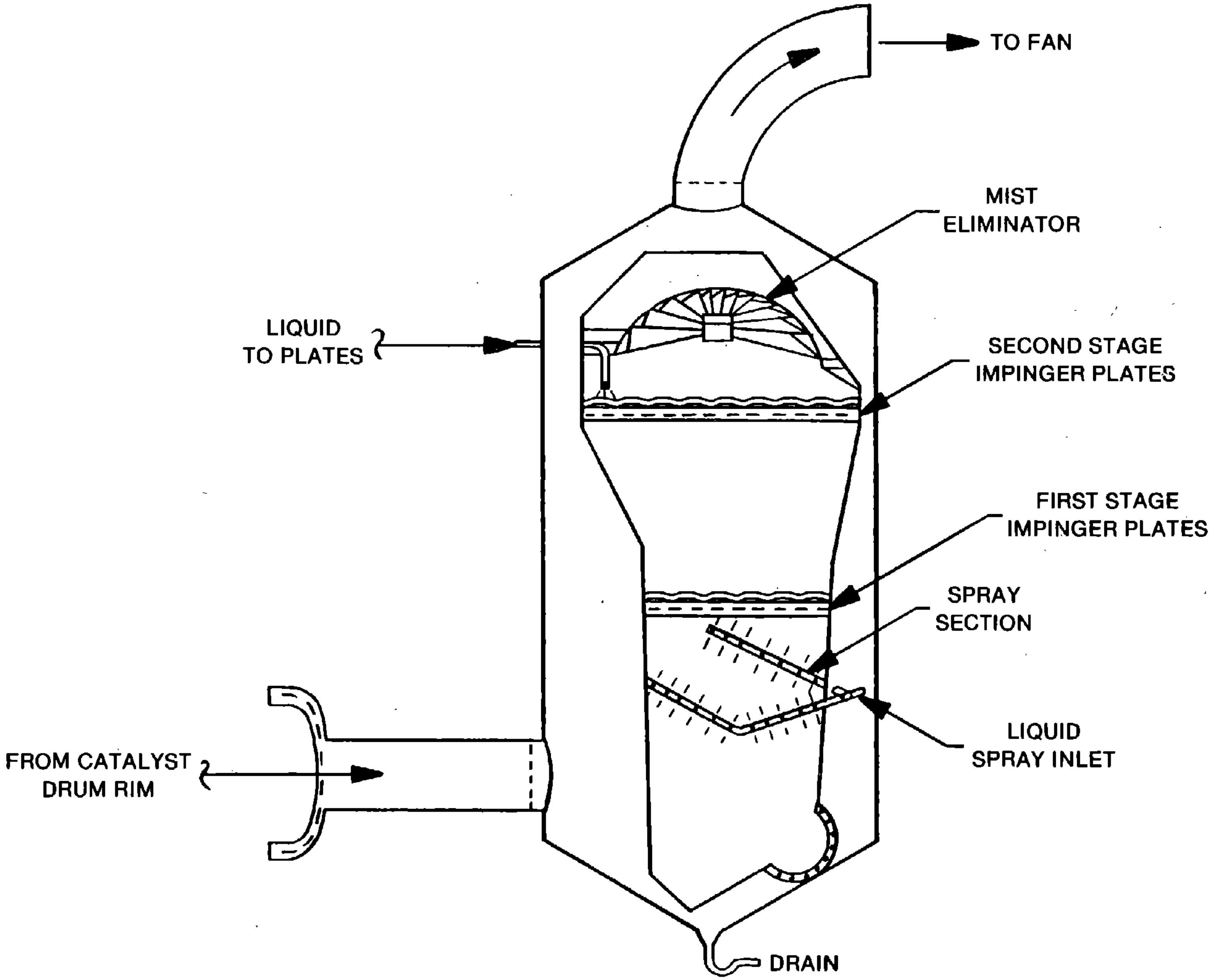


FIGURE 33 - CUTAWAY SCHEMATIC OF SLY TWO-STAGE WET SCRUBBER

TABLE 14 SPECIFICATIONS FOR CATALYST DUST WET SCRUBBER

Valves:
- 1" red valve, series 410, air operated pinch valves with aluminum bodies and gum rubber sleeves.

Ductwork
- 10 feet of 8" interior diameter duct, No. 18 gauge galvanized iron; variable length duct pieces of same material.
- 90° elbow, 8" interior diameter, 20 radius, No. 24 gauge galvanized iron.
- Variable-length flexible duct for intake nozzle.

Shell:
- No. 14 gauge stainless steel, type 304.

Fixed Blade Mist Eliminator:
- No. 16 gauge stainless steel, type 304.

Internal Parts:
- Variable gauge stainless steel, type 304.

Fan:
- Chicago Blower radial blade No. 9LS SQF, Arrangement ME1; 1546 CFM, 10" SP, 2803 RPM, 4-01 BHP.

Motor:
- Explosion-proof, Class 1, V-belt drive; 5 HP, 1800 RPM for 3Y; 60/460 volts.

Pressure regulators:
- Design for 5 GPM at 20 psig or equal.

Inlet/Outlet:
- Stainless steel and 1/4" mild steel flanges.

Water Requirements: 5 GPM at 20 psig.

Pressure Drop: 5" w.g. at outlet, saturated.

Air Flow Through Impinger Plates: 1270 CFM.

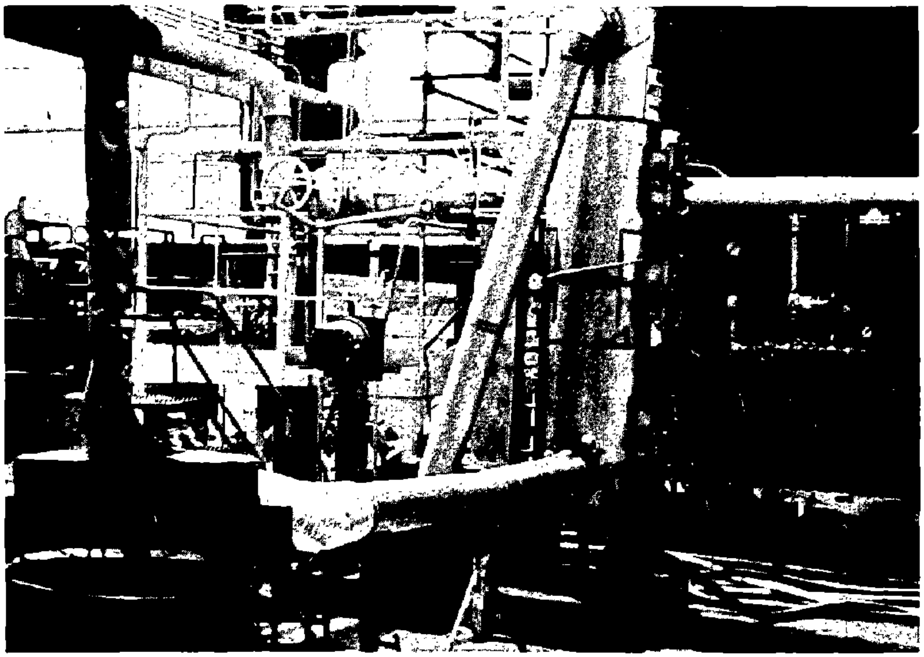


FIGURE 34 - POSITIONING DUST SCRUBBER

A semicircular slotted ventilation hood, shown in Figures 35 and 36, is attached to the drum rim and connected to the scrubber via an 8-inch flexible duct (Figure 37). After the scrubber is activated, catalyst dumping may begin.

The catalyst dust is scrubbed from the air collected by the drum hood. Catalyst-containing liquid drains from the bottom of the scrubber to a storage tank. Periodically, the tank is drained into a vacuum truck, and the liquid sent to disposal with hazardous waste from other refinery processes. The catalyst/liquid slurry must be disposed of under EPA hazardous waste disposal regulations because of its heavy metal content.

In the past, scrubbers have been mounted on a wooden platform leveled by shims. Plans are underway to install leveling jacks on the platform to make the leveling process faster and easier.

The refinery uses a wetting agent which is introduced to the scrubber through a hose in the lower scrubber door. Plans exist to modify each scrubber so that the wetting agent is introduced directly to the water injection line. Refinery safety personnel feel that wetting action will be enhanced if such a modification is made.

Reactor turnaround operations, including catalyst dumping and replacement, are performed by contractor personnel under refinery supervision. The time required for a dump varies with the type of catalyst, size of reactor, and extent to which problems are encountered. The operation typically continues for 8 to 14 hours.

CONTROL EVALUATION

Because no catalyst dumping operations were scheduled during site visits to the refinery, no sampling data could be obtained. However, refinery safety personnel provided information and photographs which could be used to evaluate the scrubber and its effectiveness.

Overexposure to catalyst dust is hazardous because a large portion of the dust particles fall within the respirable size range (1 - 10 microns in diameter). Additionally, a large portion of catalyst dust is comprised of heavy metals such as nickel, rhenium, molybdenum, or platinum, which can cause deleterious effects if introduced to the body through the respiratory tract.

The catalyst dust wet scrubber substantially reduces the quantity of dust generated when catalytic reactors are emptied, but does not completely remove the respirable dust generated. Sampling data collected by the refinery indicate that breathing zone respirable dust levels have decreased for all workers involved in the dump operation so that supplied air respiratory protective

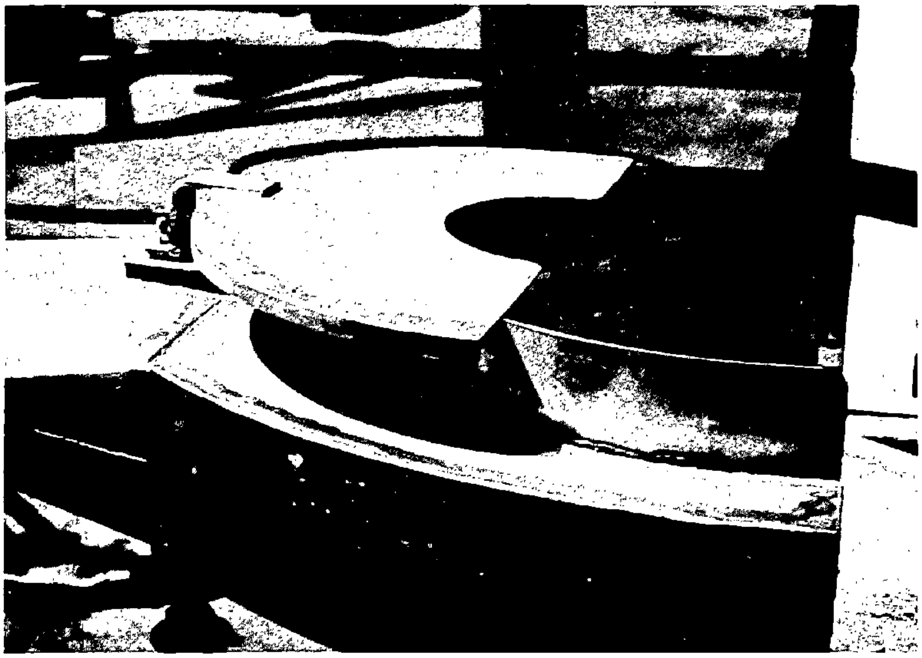


FIGURE 35 - SLOTTED VENTILATION HOOD

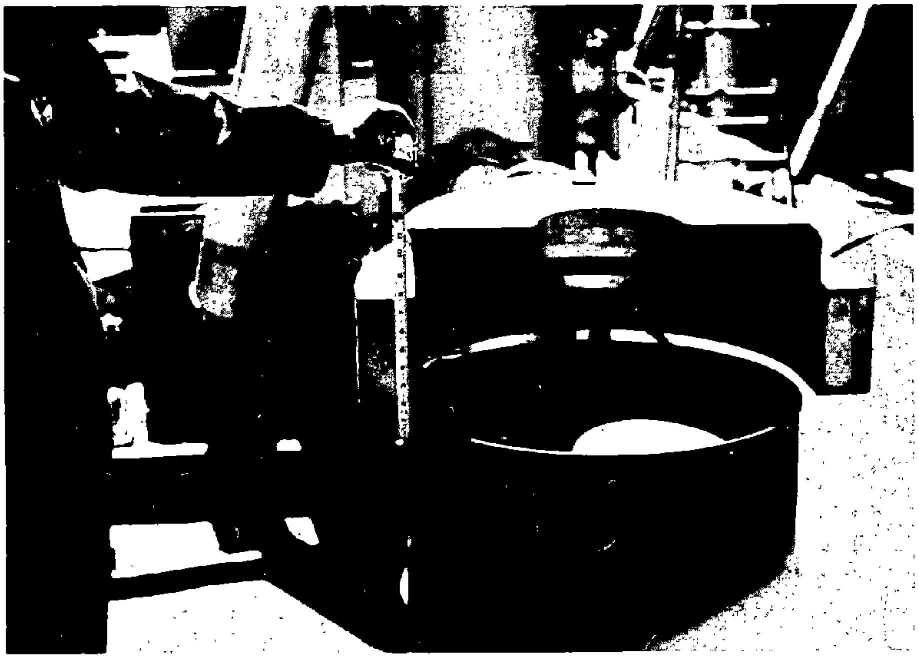


FIGURE 36 - SLOTTED HOOD POSITIONED OVER DRUM RIM

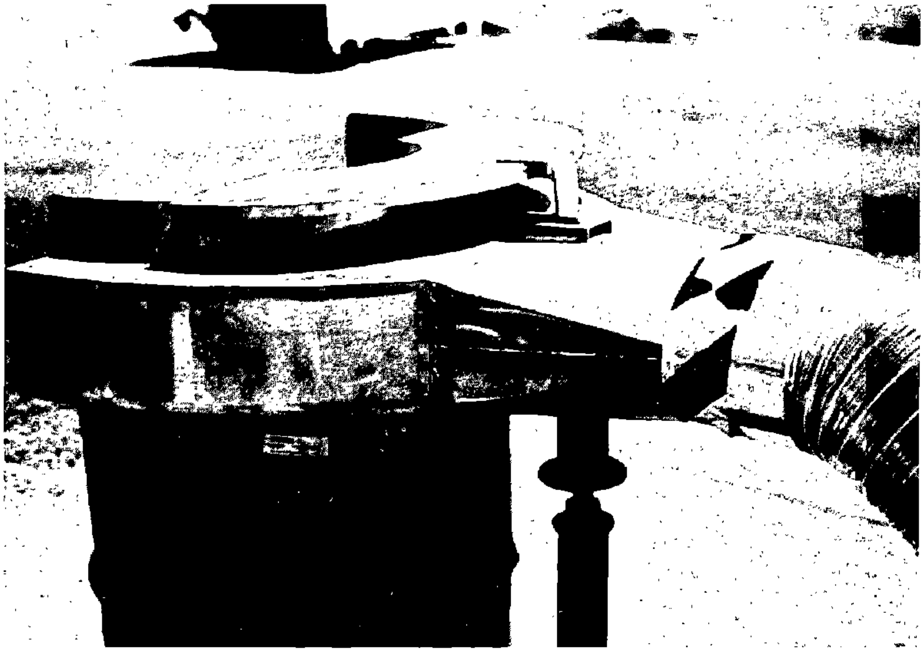


FIGURE 37 - HOOD ATTACHED TO FLEXIBLE DUCT

equipment, used prior to scrubber construction, is no longer required. Employees still must wear full face or half-mask dust respirators, depending on the job performed. This protection is required because the scrubber does not remove 100 percent of the respirable dust evolved during catalyst dumping. A matrix of personal protective equipment and clothing required during catalyst handling activities is shown in Table 15.

Refinery safety personnel estimate that the catalyst dust scrubber's efficiency is greater than 98 percent (calculated on a mass basis). Its efficiency is not affected by catalyst type; the scrubber works equally well with powdery catalysts such as those used in the refinery's fluid catalytic cracking reactors or with pelletized catalyst. No corrosion or plugging problems have occurred with any catalyst type. The scrubber's effectiveness is due largely to its ease of operation and its capability for use on a drum rim, in close proximity to the dust source.

The older of the two scrubbers used by the refinery has logged over 200 hours of service. During this time, no major problems have been encountered. Minor problems have been encountered in leveling the scrubber and in adding wetting agent.

Although the system does not entirely reduce the need for respiratory protection, it can eliminate the need to use supplied air respirators. Thus, drum loading time can be reduced and the elimination of supplied air hoses and air cylinders reduces the chance of worker injury due to impaired mobility.

INDUSTRY APPLICABILITY

The described catalyst dust wet scrubber could effectively be used by any plant where drum loading of a solid material generates a dust problem at the drum. Because the system has low capital and operating costs, is easy to use, and is portable, it can be cost effective for both intermittent and continuous operations.

TABLE 15 CATALYST HANDLING PROTECTIVE EQUIPMENT

Employee		Dumper	Empty Barrel Handler	Bag Tier	Pallet Loader	Forklift Driver		Visitor
Sanitation	Shower Trailer	●	●	●	●	●		
	Work Area Kept Dust Free	●	●	●	●	●		
	Regulated Area	●	●	●	●	●		
	Hands/Face Wash-Up Area	●	●	●	●	●		
Respiratory Protection	Scott Air Paks							
	Air Line Respirators							
	Full Face Piece Dust Resp.	●		●				
	Comfo II Half Mask Resp.		●		●			
	3M 8710 Dust Resp.					●		●
Head Protection	Hard Hats	●	●	●	●	●		●
	Safety Glasses							
	Face Shields							
	Chemical Goggles							
Clothing	Ebony Cloth/Gralite Suits							
	Neoprene/Rubber Boots	●		●				
	Chemical Gloves	●	●	●				
	Byrd Cloth Coveralls	●						
	Coveralls		●	●	●	●		
	Underwear	●						
	Socks	●						

SECTION 10

LUBE OIL AND WAX PROCESSING AND CONSTRUCTION CHANGES

Indepth visits were made to two refineries producing essentially the same products from equivalent feedstocks. Both plants emphasize good housekeeping practices and proper equipment maintenance. The refineries differ in their age and the type of processes used to upgrade lube oil stocks. It was decided that the two refineries offer a unique opportunity to study employee exposure potentials associated with differences in process technology and physical plant design. The refinery processes studied indepth and discussed following are:

- Lube Oil Upgrading
  - new refinery using hydrofinishing
  - older refinery using furfural extraction and clay filtering
- Lube Oil Dewaxing (modern plant design and traditional plant design).

COMPARISON OF EXPOSURE POTENTIAL FOR LUBE OIL HYDROFINISHING, FURFURAL EXTRACTION, AND CLAY FILTERING

A variety of technologies are currently used by refineries to upgrade their lube oil stocks. One of the newer upgrading technologies is lube oil hydrogenation. From a processing viewpoint, hydrogenation offers several advantages, including the capability to upgrade high sulfur stocks. From an employee exposure viewpoint, hydrogenation appears desirable because there is little potential for exposure during routine operations due to the enclosed nature of the process. All of the potentially hazardous substances are normally contained in the unit process equipment (pumps, compressors, valves, pipes, vessels, etc). Only substances released from equipment leaks, from process waters in open sewers and from maintenance operations would expose workers to potentially hazardous components (hydrocarbons, hydrogen sulfide, ammonia). When equipment leaks occur, the exposure potential is relatively low due to the openness of the unit (no equipment enclosed in building).

The refinery visited processes a light and heavy waxy distillate through parallel trains of reactors. High pressures and temperatures cause the distillate to react with hydrogen over a fixed catalyst bed converting sulfur, nitrogen and oxygen to H_2S, NH_3 and H_2O. Additionally, the heavy distillate is cracked to reduce the distillate viscosity index. Light gases and hydrocarbons are flashed from the hydrotreated distillates prior to the distillates being block treated through an MEK dewaxing unit.

The traditional processes used by refineries to upgrade lube oil quality are extraction using furfural or phenol followed by filtration typically using bauxite as the filtration media. The extraction process contains all process streams within vessels, pipes, valves, pumps, etc. Employee exposures to heavy hydrocarbons and furfural or phenol occur due to process leaks and equipment maintenance. The filtration process is a batch operation requiring frequent opening of the filter vessels to remove clay/bauxite for regeneration. Operator exposures to heavy hydrocarbons, naphtha and clay particulates occur during the clay dumping and regeneration operations.

Furfural extraction is used by the refinery visited to improve the lube oil viscosity index, color and carbon residue content. In operation, neutral and bright stocks from the solvent dewaxing unit are block treated through the furfural unit. The untreated oil is contacted with furfural in a packed column. The treated lube stock leaves the top of the contacting tower and is pumped to a fractionation and steam stripping tower where residual furfural is stripped from the lube oil for recovery. The steam stripped lube stock goes to storage before clay filtering and blending/packaging.

The refinery visited uses a 20-60 mesh bauxite for finishing lube oil stocks (neutral and bright) and some wax products. The lube stock and waxes are heated and passed through beds of bauxite. The bauxite retains the undesirable color and chemically reactive compounds. Once the adsorption/filtering capacity of the bauxite is used up, the bauxite is washed with naphtha, steam stripped to remove the naphtha wash, and dumped from the filter bed. The dumped bauxite is then regenerated by burning off adsorbed hydrocarbons in an open hearth furnace. The regenerated bauxite is placed back in the filter bed and is ready again for finishing lube oils and waxes.

Employee Exposure Evaluation

Both area and personal exposure monitoring were conducted for each of the lube oil upgrading processes to characterize employee exposure potential. Table 16 summarizes the contaminant concentrations that were measured. The following paragraphs describe the monitoring methods that were used.

Polynuclear Aromatic Hydrocarbons --

Full-shift personal monitoring for polynuclear aromatic hydrocarbons (PAH) was conducted for the hydrogenation unit helper, the furfural extraction unit helper, and the clay filter unit helper. Full-shift area samples were collected near one of the heat exchangers in the hydrogenation unit, near the vacuum drain in the furfural extraction unit, and near the unloading chute in the clay filter unit. Samples were collected and analyzed according to current methods recommended (although not

TABLE 16 SUMMARY OF EMPLOYEE EXPOSURES AT HYDROFINISHING, FURFURAL EXTRACTION, AND CLAY FILTERING UNITS

Process	Substance or Agent	OSHA PEL	Exposure Range	Potential Effects of Overexposure
Hydrogenation	hydrogen sulfide	20 ppm (ceiling) 50 ppm (maximum)	none detected	eye and respiratory tract irritation; pulmonary edema; respiratory failure.
	ammonia	50 ppm (8-hr, TWA)	none detected	eye, skin, and mucous membrane irritation; nausea; vomiting; pulmonary edema; respiratory failure.
	PAH*	none established	0.25-0.54 ug/m^3 (phenanthrene)	eye, skin, and respiratory tract irritation; carcinogenic potential.
	noise	90 dBA, 8-hr (= 100% exposure)	49% of allowable	loss of hearing.
Furfural Extraction	furfural	5 ppm	1.2-1.8 ppm	eye, skin, and mucous membrane irritation; upper respiratory tract irritation; headache, fatigue; dermatitis.
	PAH*	none established	0.26-0.30 ug/m^3 (phenanthrene)	eye, skin, and respiratory tract irritation; carcinogenic potential.
	noise	90 dBA, 8-hr (=100% exposure)	15-56%	loss of hearing.
Clay Filtering	PAH*	none established	0.71 ug/m^3 (phenanthrene)	eye, skin, and respiratory tract irritation; carcinogenic potential.
	respirable dust	5 mg/m^3	none detected to 0.28 mg/m^3	bronchitis.

*Polynuclear Aromatic Hydrocarbons

yet published) by NIOSH. Personal sampling pumps were used to draw air through the sampling train shown in Figure 38 at a flow rate of 1.5 liters per minute. Filters and sorbent tubes were extracted and desorbed with acetonitrile and then analyzed by high-pressure liquid chromatographic technique. Analysis consisted of a qualitative identification for 17 standard PAH's.

Only phenanthrene was found to be present in significant quantity. Subsequent quantitative analysis showed quantifiable amounts of phenanthrene on the sorbent tubes but not on the prefilters. There are currently no legal or recommended exposure limits for individual PAH's.

Hydrogen Sulfide --

Full-shift area monitoring for hydrogen sulfide was conducted on both days of the visit at the hydrogenation unit. One sample was collected above the drain under the cold flash drum, and one sample was collected on the compressor platform near recycle and make-up compressors. Samples were collected using low-flow sampling pumps and sorbent tubes which were analyzed for hydrogen sulfide according to NIOSH Method P & CAM 296. Grab-sample concentration measurements were made with colorimetric indicator tubes. No hydrogen sulfide was detected by either sampling method.

Ammonia --

Grab-sample concentration measurements for ammonia were made in the hydrogenation unit using colorimetric indicator tubes. No ammonia was detected.

Respirable Dust --

Full-shift personal sampling for respirable dust was conducted for the clay filter unit operator and helper on both days of the survey. Full-shift area samples were collected in the operating control room, the belt loading area, the upper level filter area, and the lower kiln area. Samples were collected using a personal sampling pump to draw air through a 5-micron pore-sized PVC filter preceded by a cyclone size selector to remove non-respirable particulate. A flow rate of 1.7 liters per minute was maintained throughout the sampling period.

All samples were well below the OSHA PEL for nuisance dust. Since a variety of operational problems were experienced in the clay filter unit during the days monitored, sampling results may underestimate dust levels considerably. The clay filter unit operated at a level substantially below capacity on both days. It is likely that dust levels during normal operations are somewhat higher.

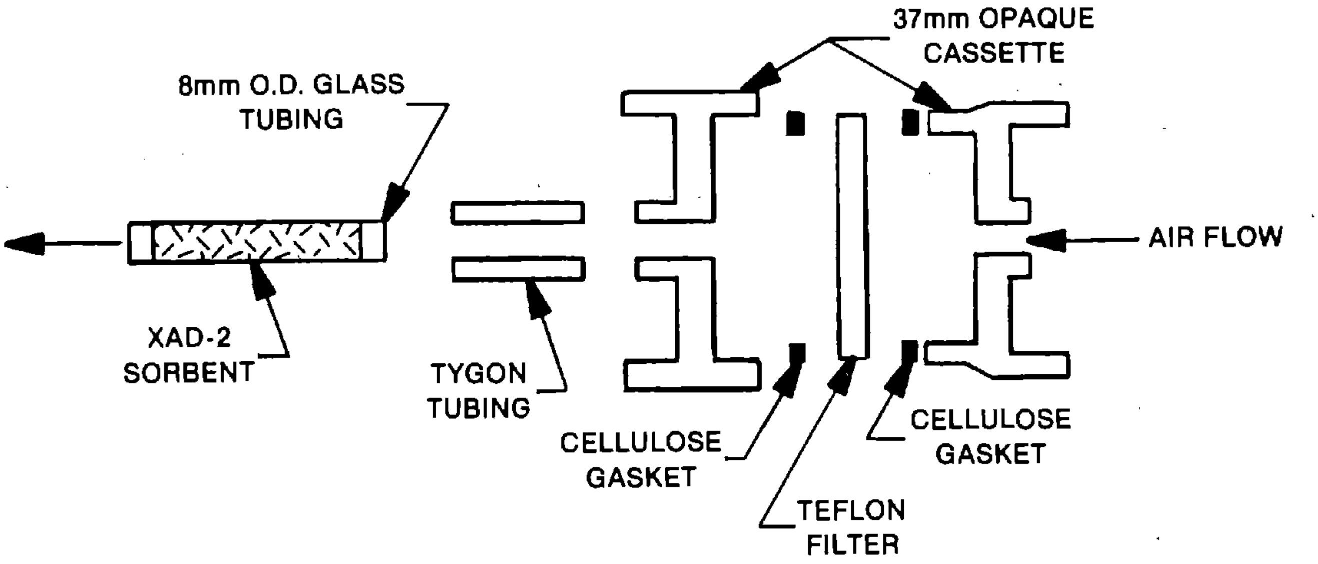


FIGURE 38 - MONITORING DEVICE FOR PAH'S

Noise --

Sound level measurements were taken near various pieces of equipment and operator locations in the hydrogenation unit and the furfural extraction and clay filter units. A sound level meter was used to measure sound levels on the A-weighted, slow-response scale. Noise levels above 90 dBA were recorded near heaters in the hydrogenation unit and near furnaces in the furfural extraction unit.

Personal noise exposure measurements were taken for operators in the hydrogenation unit and the furfural extraction unit. Dosimeters were set to respond in accordance with permissible OSHA noise exposure limits (100% = 90 dBA for 8 hours). All noise exposure measurements were below 56 percent of the OSHA PEL.

Industry Applicability

The use of hydrogenation processes to upgrade lube stocks is becoming more popular with the refining industry due to its processing advantages over the more conventional extraction and filtering processes. Based on the brief sampling effort conducted under this program, it appears that the hydrogenation process for upgrading lube oils and waxes presents minimal exposure potential for operators and eliminates potential exposure to furfural and clay particulates. Additionally, the replacement of two processing units (extraction and filtration) by one unit (hydrogenation) can result in fewer operating and maintenance employees with potential for exposure.

COMPARISON OF OLD AND NEW SOLVENT DEWAXING FACILITIES

The current industry practice of open-air construction and centrally located control rooms has some inherent advantages with respect to reducing employee exposures. Emissions from equipment that is housed in buildings tend to concentrate because of the restricted movement of dilution air. Employees who work in these buildings may then be exposed to higher concentrations than employees who work in areas where air movement is less restricted. Central control rooms are generally located away from the operating units. Exposure potential is reduced for employees who spend a large portion of the workshift in central control rooms which are relatively free of airborne contaminants.

One of the newer lube oil refineries visited uses the central control room concept and "open-air" construction practices in locating pump and compressor banks. In contrast, the older lube oil refinery studied employs a more traditional concept of unit-centered control rooms and enclosing structures for pump and compressor banks.

Area and personal monitoring were conducted in the solvent dewaxing units at the two lube oil refineries visited. The dewaxing units are essentially the same except for location of control room, use of enclosure buildings, and type of refrigerant. Maintenance and housekeeping receive high priority at both refineries. The paragraphs that follow contain process descriptions and descriptions of employee exposures measured during the two indepth visits.

Solvent Dewaxing Process Description and Associated Exposure Potentials

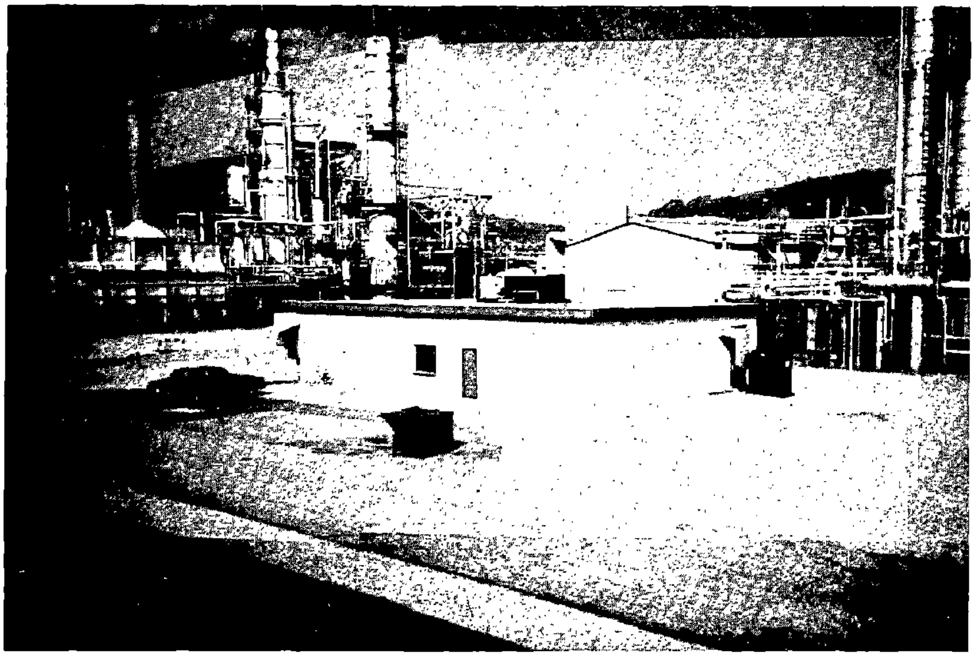
Dewaxing is the most difficult part of lube oil manufacture. The dewaxing process removes wax from lube oils to improve the low temperature fluidity characteristics of the oil. The oil is contacted with solvent and chilled, causing the wax to crystallize. The crystallized wax is separated from the mixture by vacuum filtration. The dewaxed oil and solvent are separated by distillation and steam stripping. The solvent is recycled. The wax, usually containing at least 10 percent oil, is solvent treated again under different conditions to obtain a deoiled wax product of the desired specifications. Refrigeration, filtration, and distillation are used to recover the wax and solvent.

A MEK (methyl ethyl ketone) and toluene mixture is used as the dewaxing solvent at both refineries. At one time, benzene was also a component in the solvent mixture. Its use was discontinued years ago as an exposure and cost reduction measure. Since most of the solvent used in the units is recycled continuously, benzene is still present in small, residual concentrations.

Employees may be exposed to MEK, toluene, and benzene during routine plant operation and maintenance as a result of emissions from process equipment or sample collection procedures. At the newer refinery, operators use a central control room which is located away from the unit. Solvent pumps are located in an open-air area beneath the filter building. At the older refinery, unit control areas are located in the unit itself. Figure 39 shows photographs of the newer central control room and older unit-centered control room.

Figure 40 shows photographs of the new and old refineries' vacuum filter buildings. The newer facility only encloses the vacuum filters located on the second floor. The vacuum filter pumps are located under the building but open to the air on all sides. The older facility has both floors enclosed.

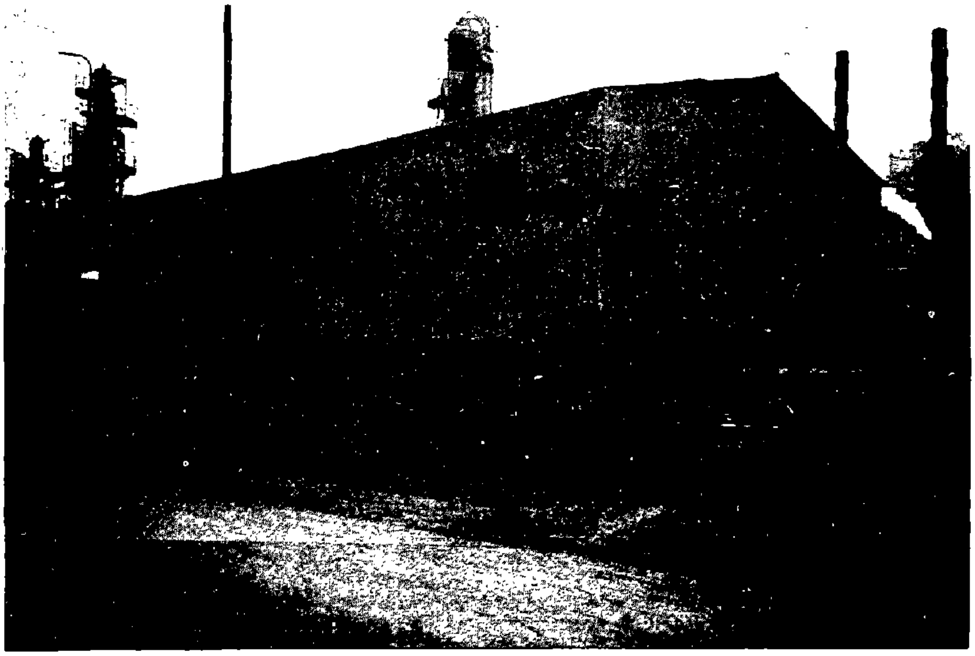
At the newer refinery, propane is used as the refrigerant gas. Ammonia is used at the older refinery. Exposure to either of these gases may occur as a result of process leaks. Propane is less toxic than ammonia and is less likely to concentrate because of the open-air construction for compressors at the newer refinery. Compressors and controls for the ammonia refrigeration



The central control room at the newer refinery houses operating controls for nearby units.

The unit control area for the solvent dewaxing operation is housed in the unit itself at the older refinery.

FIGURE 39 - COMPARISON OF CONTROL ROOM LOCATION



At the newer refinery, solvent pumps are located in an open-air area beneath the filter building.

At the older refinery, solvent pumps are located inside an enclosed brick building.

FIGURE 40 - COMPARISON OF SOLVENT PUMP LOCATION

unit at the older refinery are located in a brick building. See Figure 41.

Inert gas is produced for use in wax filter cake removal. Exposure to these gases is not considered hazardous except in the case of a major uncontrolled release.

Process equipment may present noise exposure hazards to workers. In the solvent dewaxing units, gas compressors (particularly the centrifugal compressors used at the newer refinery) and solvent pumps are equipment items that operate at elevated noise levels.

Employee Exposure Evaluation

Both area and personal monitoring were conducted in the solvent dewaxing units at the newer and older refineries to characterize employee exposure potential. Table 17 and this section summarize workplace monitoring methods and reports the results of workplace monitoring.

MEK, Benzene, and Toluene --

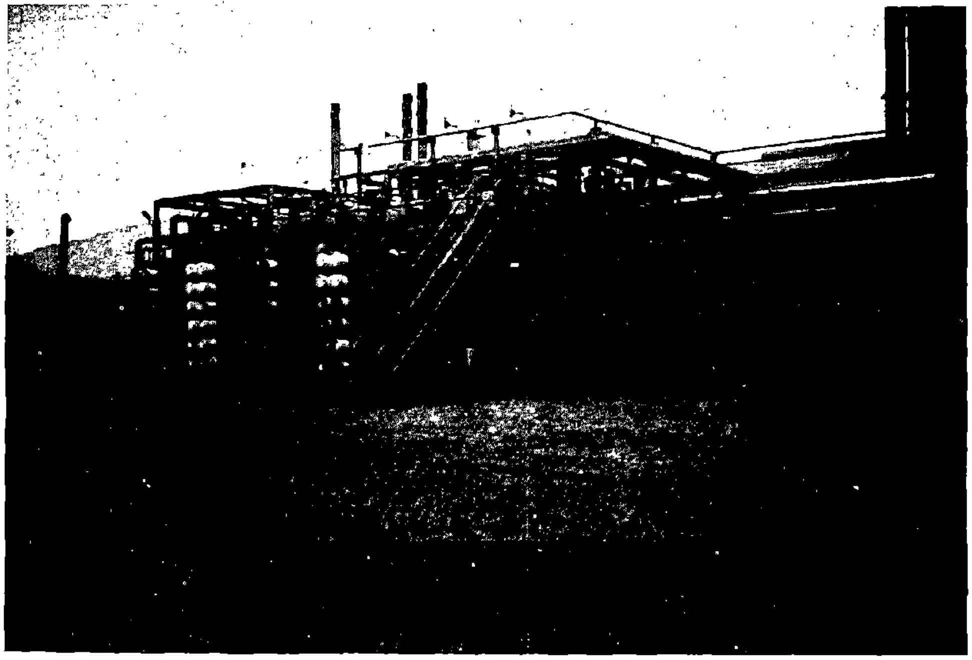
Full-shift area and personal monitoring were conducted over a 2-day period at each of the refineries studied. Personal monitoring was conducted for the unit operator, refrigeration man, filterman, and helper at each refinery. Area samples were collected in control rooms, pump banks, solvent recovery areas, chiller areas, and in the filter buildings at each plant. Sampling times ranged from 302 minutes to 446 minutes. All sampling results were well below the OSHA, ACGIH, and NIOSH-recommended exposure limits.

Samples were collected using low-flow sampling pumps and charcoal tubes. After exposure, charcoal tubes were desorbed using carbon disulfide as a solvent. Samples were analyzed by gas chromatography using a flame ionization detector. No overexposures were noted, however, concentrations measured for the dewaxing process at the older refinery were substantially higher than those measured at the newer refinery.

Grab sample concentration measurements were made using colorimetric indicator tubes for benzene, toluene, and MEK. No excess concentrations were noted.

Ammonia --

Full shift area and personal monitoring for ammonia were conducted in the chiller bay and compressor building at the older refinery. Average concentrations of ammonia were estimated using colorimetric passive dosimeter monitors. All concentrations were below the OSHA PEL of 50 ppm.



At the newer refinery, chillers and compressors are located in an unenclosed area.

At the older refinery, the compressors are located in a brick building (left) and the chillers are housed in a partially-enclosed metal housing (right).

FIGURE 41 - COMPARISON OF REFRIGERATION UNIT HOUSING

TABLE 17 SUMMARY OF EMPLOYEE EXPOSURES AT OLD AND NEW DEWAXING UNITS

Exposure Agent	OSHA PEL	Potential Effects of Overexposure		Exposure Range - PPM	
				Newer Dewaxing Unit	Older Dewaxing Unit
Methyl Ethyl Ketone	200 ppm	dermatitis, eye and mucous membrane irritation; narcosis; nausea, vomiting; lack of coordination	Processing Areas	ND to 0.26	0.046 to 27
			Control Room	ND	0.095 to 0.12
			Personal	ND to 0.19	0.14 to 9.1
Toluene	200 ppm	eye, respiratory tract, and skin irritation; dermatitis; headache; dizziness; drowsiness, lack of coordination; coma	Processing Areas	0.62 to 1.2	0.47 to 27
			Control Room	0.013 to 0.014	0.029 to 0.57
			Personal	0.022 to 0.68	0.57 to 15
Benzene	10 ppm	eye, skin and upper respiratory tract irritation; dermatitis; headache; dizziness; nausea; convulsions; heart arrythmia; blood diseases	Processing Areas	0.0001 to 0.01	0.0031-0.023
			Control Room	0.0086 to 0.01	ND to 0.011
			Personal	0.0021 to 0.017	ND to 0.0084
Ammonia	50 ppm	eye, skin, and mucous membrane irritation; nausea; vomiting; pulmonary edema; respiratory failure	- Chiller Area -	NA	<10
			- Compressor Building -	NA	17 to 40
			- Personal -	NA	<10
Noise	90 dBA, 8-hr	loss of hearing	Unit Areas	80 to 102 dBA	50 to 95 dBA
			Personal	6 to 24% of Allowable	25 to 44% of Allowable

ND - None Detected
NA - Not Applicable

Noise --

Sound level measurements were taken near compressors, pumps, and chillers, and in the solvent recovery unit, filter building, and operator's shelter at each refinery. A sound level meter was used to measure sound levels on the A-weighted, slow-response scale. Sound levels above 90 dBA were recorded near refrigeration compressors at both refineries and near solvent pumps at the newer refinery. The centrifugal propane pumps used at the newer refinery produced a substantially higher level of noise (102 dBA) than did the reciprocating ammonia compressors used at the older refinery (94 dBA). Since the compressors in the older refinery are housed in a brick building, noise levels in the nearby chiller area are relatively low. The chiller area at the newer refinery is near the unenclosed compressors and the noise level there is relatively higher.

Personal noise exposure measurements were taken for workers in the solvent dewaxing unit at both refineries using personal dosimeters. Dosimeters were set to respond in accordance with permissible OSHA noise exposure limits (100% = 90 dBA for 8-hrs). All noise exposure measurements were below 44% of the OSHA PEL.

Sampling Results Discussion --

Employee exposures to MEK, toluene, and benzene in the lube oil dewaxing operation at the newer refinery are substantially lower than those at a comparable operation at the older refinery. Plant design features that are typical of new refinery construction practices (i.e., central control rooms, open-air construction) contribute to reduced employee exposure concentrations.

Although monitoring results generally show higher personal exposures and higher average area concentrations at the older refinery than at the newer refinery, it should be noted that all exposures are extremely low when compared to recommended and legal standards. Even during upset conditions at the older refinery, the highest personal exposure measured was less than 8% of the OSHA PEL for toluene. The highest average area concentration (also during upset conditions) was less than 14% of the OSHA PEL for toluene.

Industry Applicability

Since 1950, almost all units constructed by the petroleum refining industry employ open air construction. Older processing units were typically constructed inside brick or metal buildings. Because of this construction philosophy, the industry has trended towards reducing employee exposure potential by not confining emissions inside buildings. Whenever possible, this philosophy should be followed by all industries.

Another industry trend has been toward building process control rooms located away from the process unit. Many "grass roots" refineries and new processing complexes put all unit process controls in a centrally located control room. This remotely located control room can significantly reduce operator exposure potential because:

- Central control rooms not located in the units usually have lower ambient concentrations of fugitive emissions; especially if they use positive pressure and filtered ventilation.
- More sophisticated remote controls are employed thus reducing the amount of operator time required in the unit, and
- Frequently fewer operators are required to run the units, thus reducing the number of employees potentially exposed.

This trend is expected to continue in the petroleum refinery industry because it is also more economical. However, whenever possible, any industry should evaluate the positive health and safety impacts of remotely locating process control rooms. In some instances, retrofit of a remotely located control room may be the best approach to reducing operator exposure to particularly hazardous chemicals (e.g., benzene and vinyl chloride).

SECTION 11

RECOMMENDATIONS AND CONCLUSIONS

The recommendations and conclusions that follow are directed at fostering continued government/industry efforts toward facilitating the implementation of employee exposure controls within the petroleum refining industry.

RECOMMENDATIONS FOR FUTURE STUDIES

Because of the scope of the program, long-term (several months to a year) evaluation of each exposure control technology studied was not possible. Area and personal sampling were typically conducted for only one or two time periods (e.g., shifts or job functions). Consequently, many of the recommendations suggest follow-up studies to improve the evaluation data base.

HF Alkylation Unit Exposure Control Programs

The HF alkylation unit exposure controls studied represent the most recent facilities and procedures developed by the petroleum refining industry to date. The unit and exposure control facilities came on line in 1982 and incorporate over 40 years of industry experience in handling HF. Although the refinery reported no problems after 6 months of operation, a follow-up visit to this refinery in future years would be of interest to see how effective the three exposure controls studied have been over an extended period of time. Also, a better description of the separate maintenance facility could be accomplished. This facility was still being constructed at the time of the indepth visit.

Discussions with refinery personnel and HF alkylation unit process licensors indicate that improvements in employee exposure controls are not disseminated on a regular basis but by word of mouth, through licensor training programs and through training just after installation of process modifications. No formal regular communication procedure such as a newsletter is used to ensure quick information transfer. Annual discussions with refiners and process licensors by NIOSH and/or industry organizations followed by publication of a refinery employee exposure control publication would ensure quicker access to new exposure control ideas.

Process Sampling Systems

Under this program a brief evalation was conducted on the effectiveness of enclosure systems around conventional valve and spigot sampling facilities and unit acid density measuring (gravimetric) facilities. The enclosures appear to be effective engineering control which reduce the potential for dermal and inhalation exposures to unit operators. Other types of closed sampling systems can be used to reduce employee exposures:

- o Collecting samples under pressure in a metal cylinder (bomb)
- o On-line sampling instruments (gas chromatograph).

A more comprehensive study, evaluating the sampling exposure potential and exposure reductions which can be obtained by using these systems would be most informative. Problems exist in using any of these systems and, if not appropriately addressed, can lead to higher overall employee exposure potential.

For example, the use of pressurized bomb samples may reduce unit operator exposure potential but may increase laboratory personnel exposure potential due to leaking valves on the bomb and during bomb depressurization prior to analysis. Indepth evaluation of sample collection strategies would provide useful information to determine in what situations a particular sampling system should be used. Additionally, useful guidelines towards operator and laboratory personal protective clothing and work practices could also be provided.

Area Monitoring Systems

The advent of new technology contaminant detector, controller, and data handling systems, have made area monitors for many substances a reliable, cost efficient and effective employee exposure control. Although NIOSH has recently funded work assessing area monitors as engineering controls, the rapid advancements in this area should be continuously tracked and disseminated to the appropriate industries. Also, additional emphasis should be directed at the proper handling of the monitoring data. This includes both during emergencies (alarms, panel board displays, computerized warning systems, etc.) and as an effective tool to document long term employee exposure potential.

Evaluation of Fugitive Emission Controls

Probably one of the most significant trends in the petroleum refining industry which will reduce low-level, long-term employee exposures to hydrocarbons is the implementation of equipment inspection and maintenance programs. These programs, whether implemented to reduce product losses and maintenance costs or to comply with environmental regulations, can be very effective employee exposure controls.

However, insufficient data are available regarding the effectiveness of these controls. Additionally, secondary employee exposure impacts should be explored. For example, do these programs result in increased exposures to maintenance employees and, if so, under what conditions can this be prevented. This work could be coupled with present NIOSH programs which are focusing on maintenance exposures and process equipment which reduce emissions from leaking seals or other equipment failures.

Evaluation of Industry Process and Construction Trends

The petroleum refining industry expends substantial effort in developing new and improving existing processing technologies. Some examples of this include:

- Use of new alloys and non-metal materials of construction
- Use of remotely and centrally located control rooms
- Use of process control computers
- Use of lube oil hydrogenation processes
- Use of fluid catalytic cracking and
- The increased use of sour crudes resulting in the increased need for sulfur handling processes.

Some of these trends have positive effects toward reducing occupational exposures and others increase the potential for serious occupational exposure.

Process developments and construction trends usually occur because of economic factors. Frequently the impact on worker health is not adequately addressed. It is important that NIOSH work closely with industry in evaluating the pros and cons of each development and provide industry with the necessary information to mitigate any increase in employee exposure potential.

CONCLUSION

Due to a number of considerations, this study was developed within the following framework:

- Six refinery processing areas
- Participation of seven refineries and one refinery process licensing firm
- Fourteen employee exposure control applications.

All of the controls studied indepth and presented in this report were developed by refining companies and process licensing firms. As such, they represent proven technologies which are effective in reducing employee exposure. Many of the controls described were implemented for other reasons than health and safety control: economic, environmental, and fire or explosion. In most cases, the controls are already in use by many other petroleum refineries. The purpose of this report is to encourage other refiners and industries to implement similar controls by information transfer.

All of the refineries visited were extremely supportive of this program; the success of the program is due to this support. Because these refineries had good health and safety programs, a wide range of employee exposure controls were identified. Those that were selected for indepth study were considered to be most widely applicable to other petroleum refineries. Additionally, a good mix of engineered and administrative controls were selected within the processing areas of focus.

There are, no doubt, many other employee exposure controls of considerable merit that were not studied under this program. Future programs similar to this, whether funded by government and/or industry, would benefit industry by facilitating the implementation of proven employee exposure controls. The many industry contacts made during this program and the support received is indicative of the industries' commitment to improved health and safety programs for refinery workers. It is hoped that this program has furthered this effort and fostered healthy government/industry interaction.

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