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PPG INDUSTRIES, INC.

CHEMICAL DIVISION

LAKE CHARLES, LOUISIANA

VINYL CHLORIDE MONOMER II
OPERATIONS MANUAL

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CONFIDENTIAL

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Subject to Protective Order
of 14th Judicial District Court
No. 91-1145

CPC
~~VCM-II~~ OPERATING MANUAL

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Revisions to this Operations Manual should be recorded on the next page. The date and reasons for any changes should also be recorded, along with the originator of changes.

VCM II OPERATING MANUAL

RECORD OF CHANGES

Date	Change No.	Description	Originator

NOTES ON PAGE NUMBERING

This manual is designed to permit revision or additions without disturbing the order of page numbers or the figure designations of illustrations and tables other than in the particular section affected by the changes. Pages are numbered using a combination of two numbers, the first being the section number while the second represents a page, illustration, or table in that section. Thus, page 4-6 represents page 6 in section IV; Figure 8.7 represents Figure 7 in section VIII.

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II. OVERVIEW OF THE LAKE CHARLES COMPLEX

The Lake Charles Plant started with chlorine/caustic and has grown into a major producer of industrial chemicals. Vinyl chloride, ethyl chloride, chlorinated solvents and silica products are among these chemicals.

The VCM II Plant produces ethylene dichloride and vinyl chloride. An incinerator is included to consume plant vents. This incinerator can also consume vents from other Plant B-I and Plant B-II Production units.

The following general overview of Plants B-I and B-II discusses other ways the VCM II Plant is tied to other operating units in Plants B-I and B-II, and with the rest of the Lake Charles complex.

OVERVIEW OF PLANTS B-I AND B-II

The Chlorinated Organics Area is divided into two production management areas. These are known as Plant B-I and Plant B-II. The VCM II Plant is a part of Plant B-II.

Plant B-I consists of the following units, or systems:

1. OHC I
2. Tetra
3. Bottoms Recovery
4. Incinerators
5. Effluent Treatment

6. Sodium Formate Destruction
7. VCM I
8. EC/HCl
9. Per/Tri

Plant B-II consists of:

1. EDC
2. VDCM
3. Tri-Ethane II
4. VCM II

The VCM Storage areas in B-I and B-II are operated by VCM II personnel. Even though Plants B-I and B-II are different production/management areas, they are very closely tied together by such things as chlorine feed systems, ethylene feed systems, steam systems, nitrogen systems, oxygen systems, production storage systems, vent systems, pollution prevention systems, hydrogen chloride distribution systems, electrical systems, and many other ways.

Not only are Plants B-I and B-II closely tied together; both are tied closely with the rest of the Lake Charles Chemical complex. Electrical power, steam, chlorine, and caustic, for example, are produced in Plants A and C, but used throughout the whole chemical complex.

Communications between operating units throughout the whole chemical complex is a must because of the very close ties mentioned above. Each operating unit must communicate with all other units that are tied together concerning such things as rate changes, emergencies, shut-downs, etc., so the plants can be operated in as safe, efficient, and nonpolluting a manner as possible. Every activity in each operating unit throughout the complex demands some sort of activity in other operating units.

III. COMPOUND ABBREVIATIONS

Abbreviation	Name	Formula
C_2H_2	Acetylene	C_2H_2
BD	Butadiene (1,3)	C_4H_6
$CaCl_2$	Calcium Chloride	$CaCl_2$
CO_2	Carbon Dioxide	CO_2
CO	Carbon Monoxide	CO
CCl_4	Carbon Tetrachloride	CCl_4
NaOH	Caustic Soda (Cell Liquor)	NaOH
Chloral	Chloral	CCl_3CHO
Cl_2	Chlorine	Cl_2
$CHCl_3$	Chloroform	$CHCl_3$
CLP	Chloroprene	C_4H_5Cl
Cis	Cis-1,2-Dichloroethylene	$C_2H_2Cl_2$
DCE	1,1 Dichloroethane	$C_2H_4Cl_2$
EDC	1,2 Dichloroethane	$C_2H_4Cl_2$
Dowtherm	Dowtherm LF	———
C_2H_6	Ethane	C_2H_6
EC	Ethyl Chloride	C_2H_5Cl
C_2H_4	Ethylene	C_2H_4
$FeCl_3$	Ferric Chloride	$FeCl_3$
HCl	Hydrogen Chlorde	HCl
CH_4	Methane (Natural Gas)	CH_4
ME Cl	Methyl Chloride	CH_3Cl
F-22	Monochlorodifluoromethane	$CHClF_2$

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Abbreviation	Name	Formula
MVA	Monovinyl Acetylene	C_4H_4
N_2	Nitrogen	N_2
O_2	Oxygen	O_2
PENTA	Pentachloroethane	C_2HCl_5
PER	Perchloroethylene	C_2Cl_4
Phosgene	Phosgene	$COCl_2$
Formate	Sodium Formate	$NaHCO_2$
H_2SO_4	Sulfuric Acid	H_2SO_4
SYM-TETRA	Sym-tetrachloroethane	$C_2H_2Cl_4$
TRANS	Trans-1,2-Dichloroethylene	$C_2H_2Cl_2$
TARS	Any Heavy Chlorinated Compounds	—
TCE	1,1,2-Trichloroethane	$C_2H_3Cl_3$
TRI	Trichloroethylene	C_2HCl_3
UNSYM-TETRA	Unsym-tetrachloroethane	$C_2H_2Cl_4$
VC (VCM)	Vinyl Chloride	C_2H_3Cl
VDC	Vinylidene Chloride	$C_2H_2Cl_2$
H_2O	Water	H_2O

IV. GENERAL DESCRIPTION OF VCM II PROCESS

A. USES OF PRODUCT

The chief uses of vinyl chloride monomer are in the production of polymers (PVC) and copolymers. A wide range of properties have made their uses possible in many applications. One example of a copolymer which utilizes vinyl chloride is the Saran(R) Line of plastics; this is a copolymer of vinyl chloride and vinylidene chloride. Polyvinyl chloride (PVC) is widely used in electrical products (wire and cable insulation, fixtures), construction products (siding, pipe), packaging films, floor and wall coverings, and consumer products (wearing apparel, credit cards, phonograph records).

B. OVERVIEWS OF PROCESS

There are several different processes, or sections within the VCM II Plant. These are:

1. OHC - EDC Section
2. Liquid Phase - EDC Section
3. EDC Purification and Storage Section
4. VCM Section
5. VCM Shift Storage Section
6. Incineration Section
7. Plant Effluent Collection Section

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All of these different processes, or sections, are meshed together to form the VCM II Plant. The VCM II Plant is designed to operate in a "BALANCED" fashion. This means that all of the above systems are tied together and each must function as designed in order for production of vinyl chloride monomer to occur as intended. Because of the need to operate balanced, the fact that all systems within the VCM II Plant are closely tied together, and for safety and pollution reasons, it is very important that <u>all</u> operations personnel understand that each person's actions and/or non-actions have a very real effect on VCM II Plant operations. A brief overview of the VCM II Plant is presented below for a better understanding of these statements.

EDC is manufactured in the OHC unit by feeding ethylene, HCl (from VCM unit) and oxygen into fluid bed reactors. Heat of reaction is removed by circulating liquid Dowtherm through cooling coils in the reactor. The reaction products flow to graphite condensers where essentially all of the crude EDC and water formed in the reaction is condensed. The uncondensed ethylene and inerts stream passing through the condensers is returned to the reactor feed system, except for a small purge stream, via recycle jet.

The condensed reactor crude EDC is phase separated for phase water removal, caustic treated for removal of chloral and finally dried in an azeotropic drying still. The dry neutral crude is then fed to the DH bottoms tanks. After qualification, the crude EDC is sent to the EDC purification system.

EDC is manufactured in the LP-EDC section of the plant by direct chlorination of ethylene in a reactor filled with boiling liquid EDC. Vaporized chlorine and ethylene are sparged into the liquid within the reactor and go into solution. The reaction takes place between dissolved chlorine and ethylene, and the exothermic heat of reaction boils EDC out of the reactor. The EDC vapor leaving the reactor is condensed and a portion of the condensate is recycled to the reactor in order to maintain a constant liquid level. The remaining condensate is LP-EDC crude product and is fed to EDC Purification. The vent from the LP-EDC unit is fed along with the HCl feed from the VCM section to OHC to recover the ethylene.

The EDC Purification unit consists of a light ends column and a heavy ends column. Small amounts of both higher and lower boiling compounds than EDC are formed in both EDC manufacturing sections and also in the cracking operation. Crude EDC from the LP-EDC and OHC-EDC units is combined with the unreacted EDC (recycle) from the VCM unit and processed through the EDC Purification unit for removal of these impurities prior to being fed to the EDC cracking furnaces. The high purity EDC stream is fed to cracking furnaces where a portion is converted to VCM and HCl, and the rest passes through unchanged. The gaseous mixture of VCM-EDC-HCl leaving the furnaces is quench cooled and then partially condensed. The vapor and liquid is fed to the absorber/stripper system. HCl is separated overhead and fed to the OHC-EDC unit. The VCM-EDC mixture flows to the VCM product still where VCM is separated overhead. It is then neutralized and sent to product storage. Part of the EDC fraction is recirculated to the absorber/stripper system as lean oil and the remainder is recycled through EDC Purification to the cracking furnaces. After laboratory clearance, the pure VCM product is transferred to storage facilities from where it will be loaded in railcars, barges, or ships for shipment to customers.

Within the VCM II Plant is an incinerator. The purpose of the incinerator is to burn vents from the different sections in the VCM II Plant. These vents contain chlorinated organic wastes which cannot be allowed to get into the atmosphere for health reasons. The chlorinated organic wastes are oxidized to carbon dioxide, water, and hydrogen chloride. These combustion gases are chemically treated for the removal of HCl before being emitted to the atmosphere.

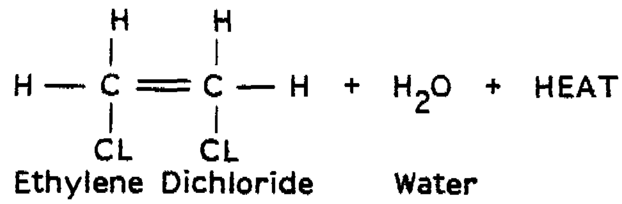
Water is made during the formation of EDC in the OHC process. It is also used as a scrubbing agent for various vent streams in the VCM II Plant. Process water discharged from the VCM II Plant which contains small amounts of chlorinated organics cannot be allowed to be discharged into the waterways while containing chlorinated organics because of health reasons. This water is transferred directly to the Plant B waste treatment area. Process pad run-off which may contain organics is collected in separator basins and allowed to phase separate. The water phase is sent to Plant B to be steam-stripped. The recovered organic phase is sent back to VCM II OHC for reprocessing.

C. GENERAL CHEMISTRY

1. <u>OHC Section</u>

The OHC process utilizes C_2H_4, O_2, and HCl to form EDC. The controlled general chemical reaction is as follows:

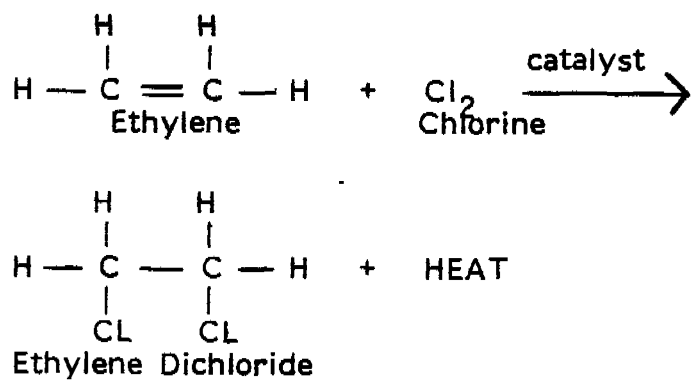
$$\underset{\text{Ethylene}}{H-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H} + \underset{\text{Hydrogen Chloride}}{2\,HCl} + \underset{\text{Oxygen}}{\tfrac{1}{2}\,O_2} \xrightarrow{\text{catalyst}}$$



The catalyst used in this reaction is a clay carrier coated with cupric chloride and potassium chloride.

2. Liquid Phase EDC Section

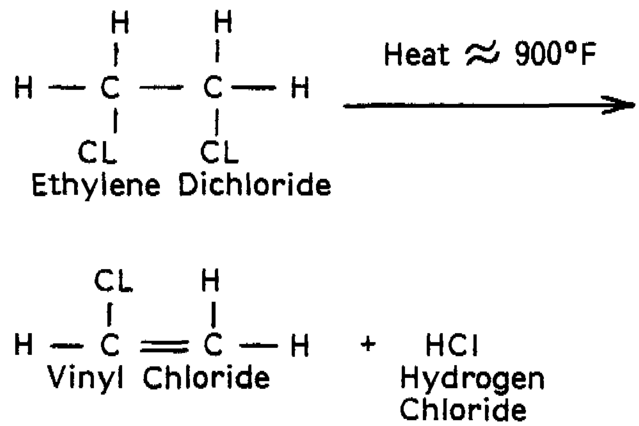
EDC is produced in the LP-EDC section by reacting Cl_2 and C_2H_4 gases in a liquid EDC bed containing $FeCl_3$ catalyst. The general chemical reaction is as follows:



In both the OHC and LP-EDC sections, the reactions are exothermic. An exothermic reaction is one that gives off heat.

3. Vinyl Chloride Monomer Section

VCM is produced in natural gas-fired vaporizing/cracking furnaces. In these furnaces, EDC is cracked by heating it to around 900° to form VCM and HCl. The general chemical reaction is:



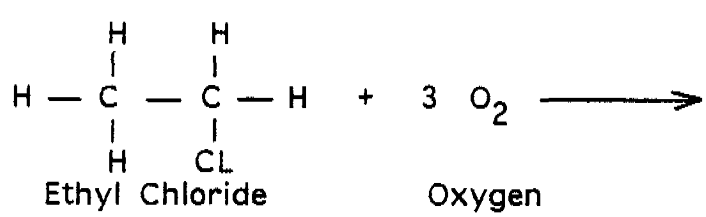
Excessive temperatures in the EDC cracking process must be avoided because of the formation of coke which will deposit out on the tube walls in the furnaces. Coke formation will result in a reduction of VCM production capacity.

The cracking process is an endothermic chemical reaction. This means that heat is absorbed into the reaction in the cracking process.

4. Incinerator Section

The incinerator is designed to oxidize chlorinated organic wastes that are present in VCM II vent streams to CO_2, H_2O, and HCl. The chlorinated organic wastes are oxidized according to the following examples of general chemical reactions:

Reaction No. 1 Example ---



$$2\ CO_2 \quad + \quad HCl \quad + \quad 2\ H_2O$$

Carbon Dioxide	Hydrogen Chloride	Water

This is an exothermic chemical reaction.

Reaction No. 2 Example ---

$$\begin{array}{ccccccc} & & CL & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & CL & & CL & & \end{array} \quad + \quad 2\ O_2 \xrightarrow{\text{HEAT}}$$

1,1,2 Trichloroethane   Oxygen

$$2\ CO_2 \quad + \quad 3\ HCl$$

Carbon Dioxide	Hydrogen Chloride

This is an endothermic chemical reaction.

Reaction No. 3 Example ---

$$\begin{array}{ccc} CL & & CL \\ | & & | \\ C & = & C \\ | & & | \\ CL & & CL \end{array} \quad + \quad 2\ H_2O \quad + \quad O_2 \xrightarrow{\text{HEAT}} 2\ CO_2 \quad + \quad 4\ HCl$$

Perchloro-ethylene	Atomizing Steam	Oxygen	Carbon Dioxide	Hydrogen Chloride

This is an endothermic chemical reaction.

When "Light" chlorinated compounds are burned, as shown in Reaction No. 1, a large amount of heat is released. Heat is consumed when "Heavy" chlorinated compounds are burned, as shown in Reaction No. 2 and No. 3. This heat is supplied by burning lightly chlorinated compounds such as ethyl chloride, or by burning hydrocarbons such as methane and ethylene.

When chlorinated compounds which contain fewer hydrogen atoms than chlorine atoms are burned, hydrogen must be supplied from some other source in order for the chlorine to form hydrogen chloride. Atomized steam is normally used to supply hydrogen for this type reaction, as indicated by Reaction No. 3.

Oxygen for these reactions is supplied by air. An excess of oxygen should be maintained at all times. Insufficient oxygen will cause carbon (smoke) and carbon monoxide to be formed as combustion products. However, too much oxygen causes free chlorine and oxides of nitrogen to be formed. Control of oxygen is very important because of these problems.

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DETAILED CLEARING PROCEDURES

VINYL CHLORIDE

The general procedures for clearing equipment or lines which contain some or all VCM are given below in the section on VCM Precautions. Proper respiratory protection must also be used.

Hazards of Vinyl Chloride:

1. Very highly flammable.
2. Irritant to skin or eyes.
3. Vinyl Chloride is a cancer suspect agent.
4. ~~May cause frost bite if liquid comes into contact with skin.~~
5. Exposure to vapors can cause a narcotic/anesthetic effect.

Treatment if Contact with Body:

1. Wash thoroughly and remove contaminated clothing.
2. Apply skin cream to the affected area.
3. Report the incident promptly to your supervisor.

Protective Clothing Required:

Normally none required. Special clothing may be specified by supervision. Special clothing may be required for vessel entry.

Other Safety Precautions:

1. Proper respiratory protection must be used.
2. Clearing should not be done when maintenance workers are in the area.
3. Hoses and connections should be checked thoroughly.
4. Purging should be to the vent collection system only.

Clearing Procedure:

1. Isolate vessels or line.
2. Push (with N_2) all possible liquid out and into other vessels or pipe.
3. Vent (through a Teflon-lined hose) the line or equipment at a slow rate (to collection system). Frost on the outside of piping or equipment indicates VC is still present.
4. Nitrogen purge the equipment after venting has stopped.
5. Check all bleeds and drains to make sure they are not plugged.
6. Tag out.

Special Maintenance Worker Precautions:

1. Respiratory protection should be worn when the first break is made.
2. Double-check drains (for pumps especially) and vents by sticking a wire through an open valve.
3. Break loose bolts of a flange first on the side away from the worker.

SULFURIC ACID

Hazards of H_2SO_4:

1. Causes very rapid destruction of tissue (is the most hazardous chemical in the plant).
2. May splatter and produce heat when mixed with water.
3. Treat as a flammable material (because of hydrogen generation).

Treatment if Contact with the Body

Flush quickly with large quantities of water and remove contaminated clothing during washing.

Protective Clothing Required:

Complete slicker suit, high top rubber boots, rubber gloves, and full face shield.

Other Safety Precaution:

1. Water hose should be available and in service.
2. Safety showers should be located, and a route to them planned.
3. Someone else should know what you are doing.

Clearing Procedure:

1. Isolate equipment or line.
2. Drain equipment or line.
3. Flush the area very well.
4. Wash the line or equipment with a large amount of water, if possible.
5. Vessels should be filled with water and drained repeatedly until cleaned.
6. Purge to dry.
7. Check all bleeds and drains to make sure a purge is coming out.
8. Tag out.

Special Maintenance Worker Precautions:

1. Normally the same protective clothing and safety precaution requirements as for operators.
2. Break loose bolts of a flange first on the side away from the worker.

VOLATILE ORGANICS

Hazards of Volatile Organics:

1. Very highly flammable.
2. Irritant to skin or eyes.
3. Vapors are toxic.
4. May cause frost bite if liquid comes into contact with skin.

Treatment if Contact with Body:

1. Wash thoroughly and remove contaminated clothing.
2. Apply skin cream to the affected area.
3. Take other measures as specified by production supervisors.

Protective Clothing Required:

Normally none required. Special clothing may be specified by supervision. Overalls will be required for vessel entry.

Other Safety Precautions:

1. Clearing should not be done when maintenance workers are in the area, if at all possible.
2. Hoses and connections should be checked thoroughly.

Clearing Procedure:

1. Isolate equipment or line.
2. Push (with N_2) all possible liquid out and into other vessels or pipe.
3. Vent (through a Teflon-lined hose) the line or equipment at a slow rate (to vent collection system). Frost on the outside of piping or equipment indicates organics are still present.
4. Nitrogen purge the equipment after venting has stopped.
5. Check all bleeds and drains to make sure they are not plugged.
6. Tag out.

Special Maintenance Worker Precautions:

1. Double-check drains (for pumps especially) and vents by sticking a wire through an open valve.
2. Break loose bolts of flange first on the side away from the worker.

EDC, BOTTOMS

Hazards of Non-volatile Organics:

1. Flammable.
2. Vapors are toxic.
3. Strong irritant to skin and eyes.
4. Will cause severe skin dryness.

Treatment if Contact with Body:

1. Wash thoroughly and remove contaminated clothing.
2. If shoes, belts, billfolds, or any other leather goods are soaked with organics, they should be thoroughly washed and allowed to dry before being used again.
3. Apply skin cream to the affected area.

Protective Clothing Required:

None required.

Other Safety Precautions:

1. Clearing should not be done when maintenance workers are in the area if at all possible.
2. Only organic hoses in good condition should be used.

Clearing Procedures:

1. Isolate equipment or line.
2. Push (with N_2) all liquid into other process equipment, if possible. Use Teflon-lined hoses. Drain to a liquid dump box if the liquid cannot be pushed into other process equipment. Do not drain any quantities of organics to the sewer.
3. Check all bleeds and drains to make sure a purge is coming out.
4. Tag out.

Special Maintenance Worker Precautions:

Break loose bolts of flange first on the side away from the worker.

HCl GAS

Hazards of HCl Gas:

1. Causes irritation of the skin or membranes of the respiratory system.
2. Treat as a flammable material (because of hydrogen generation).

Treatment if Contact with the Body:

Flush quickly with a large amount of water and remove contaminated clothing during flushing.

Protective Clothing Required:

Rubber gloves.

Other Safety Precautions:

1. Safety showers should be located, and a route to them planned.
2. Make sure respirator cartridge is fresh.

Clearing Procedure:

1. Isolate equipment or line.
2. Vent equipment to a scrubber or into a container of water until the pressure is down to 5-10 psi (to prevent water from sucking back into the line after all pressure bleeds off). The water in the container will become muriatic acid and should be handled carefully.
3. Purge (with air or nitrogen) through the equipment and into the scrubber until all HCl is removed.
4. Take precautions to prevent water from entering the cleared equipment.
5. Tag out.

Special Maintenance Worker Precautions:

Break loose bolts of a flange first on the side away from the worker. Some organic liquid or acid may be left in the line.

HYDROCHLORIC ACID

Hazards of Hydrochloric Acid:

1. Causes irritation of the skin.
2. Treat as a flammable material (because of hydrogen generation).

Treatment if Contact with the Body:

Flush quickly with a large amount of water and remove contaminated clothing during flushing.

Protective Clothing Required:

Rubber gloves, rubber shoes.

Other Safety Precautions:

1. Water hose should be available and in service.
2. Safety showers should be located, and a route to them planned.

Clearing Procedure:

1. Isolate equipment or line.
2. Drain equipment or line.
3. Flush the area very well.
4. Wash the line or equipment.
5. Check all bleeds and drains to make sure they are open.
6. Tag out.

Special Maintenance Worker Precautions:

1. Goggles should be worn.
2. Break loose bolts of a flange first on the side away from the worker.

CHLORINE (GAS OR LIQUID)

Hazards of Chlorine:

1. Causes irritation of the respiratory system.
2. Skin contact may cause skin irritation and blistering.

Treatment:

1. Clothing contaminated with liquid Cl_2 should be removed.
2. If respiratory problems are severe, injured person should go to First Aid for breathing of oxygen.

Protection Clothing Required:

Rubber gloves.

Other Safety Precautions:

1. Make sure respirator cartridge is fresh.
2. Do not allow grease or oil to get into Cl_2 lines.

Clearing Procedure:

1. Isolate equipment or line.
2. Vent equipment into a solution of soda ash or caustic until the pressure is down to 5-10 psi (to prevent the solution from sucking back into the line after all pressure bleeds off).

3. Purge (with air or nitrogen) through the equipment and into the solution until all Cl_2 is removed.
4. Take precautions to prevent water or other contaminants from entering the clearing equipment.
5. Tag out.

Special Maintenance Worker Precautions:

Break loose bolts of a flange first on the side away from the worker.

CAUSTIC SODA

Hazards of Caustic:

1. Causes very rapid destruction of tissue.
2. Will react with water to produce heat.
3. Reacts violently with many organic chemicals.
4. Will ruin wool or leather goods.

Treatment if Contact with Body:

Flush quickly with large quantities of water and remove contaminated clothing during washing.

Protective Clothing Required:

Rubber gloves, rubber shoes, and full face shield.

Other Safety Precautions:

1. Water hose should be available and in service.
2. Safety showers should be located, and a route to them planned.

Clearing Procedure:

1. Isolate equipment or line.
2. Drain equipment or line.
3. Flush the line or equipment with a large flow of water.
4. Fill vessels with water and overflow until all caustic is removed.
5. Flush the area very well.
6. Check all bleeds and drains to make sure they are unplugged.
7. Tag out.

Special Maintenance Worker Precautions:

1. Goggles and full face shield should be worn.
2. Break loose bolts of a flange first on the side away from the worker.

NAME	CHEMICAL FORMULA OR ABBREVIATION	PAGE
BETZ 2040	________	
BETZ Slimicide C-30	________	
BETZ Slimicide J-12	________	
BETZ Slimicide 242	________	
Calcium Chloride	$CaCl_2$	
Caustic Soda (Lye, Sodium Hydroxide)	NaOH	
Cell Liquor (Sodium Hydroxide, Caustic)	NaOH	
Chlorine	Cl_2	
Chloroform	$CHCl_3$	
Dowtherm LF		
Ethylene	C_2H_4	
Ethylene Dichloride	EDC	
Ferric Chloride	$FeCl_3$	
Freon 22 (Monochlorodifluoromethane)	F-22	
Halon 1301	$CBrF_3$	
Hydrogen Chloride	HCl	
Methane (Natural Gas)	CH_4	
Nitrogen	N_2	
Oxygen	O_2	
Sulfuric Acid	H_2SO_4	
Tetrachloroethane (Sym. and Unsym.)	TECL	
Trichloroethane (1,1,2)	TCE	
Vinyl Chloride	VC or VCM	

SL 003019

OCCURRENCE:

Used as antifoulant in the Heavies Still Reboiler

NAME: Aftol

FORMULA: n/a

FLASH POINT: 100°F

EXPLOSIVE LIMITS: None

MAXIMUM ALLOWABLE CONCENTRATION: n/a

HAZARDOUS PROPERTIES: Aftol may cause an allergic skin reaction. Contact should be avoided with eyes, skin and clothing.

TREATMENT: Wash contaminated area with soap and water. Remove contaminated clothing. Flush eyes with water for a minimum of 15 minutes.

DESCRIPTION: Aftol AP-5518 is a solution of acylated polyamines and acrylic type polymer and an aromatic schiff's base. The solvent is aromatic.

OCCURRENCE:

Cooling Tower Water Treatment Chemical

NAME: BETZ 2020

FORMULA: n/a
FLASH POINT: Closed Cup > 200°F

EXPLOSIVE LIMITS: n/a

MAXIMUM ALLOWABLE CONCENTRATION: n/a

SAFETY PRECAUTIONS: Do not take internally. Concentrated form may cause eye and skin irritation on contact. Do not get into eyes, skin, or clothing. Wear gloves and goggles or face shield when handling.

TREATMENT: In case of contact with skin, wash well with soap and water. In case of contact with eyes, flush promptly with clear water for 15 minutes. In case of ingestion or contact with eyes, secure immediate medical attention.

In all cases, report to First Aid.

OCCURRENCE:

Cooling Tower Water Treatment Chemical

NAME: BETZ 2040

FORMULA: n/a

FLASH POINT: Closed Cup > 200°F

EXPLOSIVE LIMITS: n/a

MAXIMUM ALLOWABLE CONCENTRATION: n/a

SAFETY PRECAUTIONS: Do not take internally. This product contains potassium hydroxide and, accordingly, is alkaline. May cause eye irritations and skin burns. Do not get into eyes, on skin or clothing. Do not inhale fumes. Wear rubber gloves and goggles or face shield when handling.

TREATMENT: In case of contact with skin, wash well with soap and water. In case of contact with eyes, flush promptly and thoroughly with clear water. In case of ingestion or contact with eyes, secure immediate medical attention.

In all cases, report to First Aid.

NOTE: Do Not mix with acidic materials.

Do Not store liquid-side components in steel containers.

OCCURRENCE:

Cooling Tower Water Treatment Chemical

NAME: BETZ Slimicide C-30

FORMULA: n/a

FLASH POINT: Open Cup 169°F

EXPLOSIVE LIMITS: n/a

MAXIMUM ALLOWABLE CONCENTRATION: n/a

SAFETY PRECAUTIONS: Combustible

WARNING - TOXIC - Harmful or fatal if swallowed or absorbed through skin. Causes skin irritations. Avoid breathing vapor or mist. Use with adequate ventilation. Do not get into eyes, on skin or clothing. Wear rubber gloves and goggles or face shield when handling.

TREATMENT: In case of contact with skin, wash well with soap and water. In case of contact with eyes, flush promptly and thoroughly with clear water. In case of ingestion or contact with eyes, secure immediate medical attention.

In all cases, report to First Aid.

NOTE: Do Not reuse empty container.

Do Not use, pour, or store near heat or open flame. Keep container closed when not in use.

OCCURRENCE:

Cooling Tower Water Treatment Chemical

NAME: BETZ Slimicide J-12

FORMULA: n/a

FLASH POINT: Open Cup 175°F

EXPLOSIVE LIMITS: n/a

MAXIMUM ALLOWABLE CONCENTRATION: n/a

SAFETY PRECAUTIONS: May be fatal if swallowed. May be absorbed through skin. Causes severe eye and skin damage. Avoid breathing spray mist. Do not get into eyes, on skin or clothing. Wear rubber gloves, and goggles or face shield when handling.

TREATMENT: Wash thoroughly after handling. Remove and wash clothing before reuse.

In case of swallowing, take patient immediately to a hospital or physician.

In case of contact with skin, wash thoroughly with soap and water. If irritation persists, get medical attention. In case of contact with eyes, flush promptly and thoroughly with clear water. In case of ingestion or contact with eyes, secure immediate medical attention.

In all cases, report to First Aid.

NOTE: Do Not store near food stuffs.

This product is toxic to fish and wildlife. Do Not allow product to enter streams, lakes, etc.

Do Not reuse container.

OCCURRENCE:

Cooling Tower Water Treatment Chemical

NAME: BETZ Slimicide 242

FORMULA: n/a

FLASH POINT: Open Cup 122°F

EXPLOSIVE LIMITS: n/a

MAXIMUM ALLOWABLE CONCENTRATION n/a

SAFETY PRECAUTIONS: Combustible

Harmful if swallowed. Causes eye and skin irritations. Do Not get into eyes, on skin or clothing. Wear rubber gloves, goggles or face shield when handling.

TREATMENT: Wash thoroughly after handling. In case of contact with skin, wash well with soap and water. In case of contact with eyes, flush promptly and thoroughly with clear water. In case of ingestion or contact with eyes, secure immediate medical attention.

In all cases, report to First Aid.

NOTE: Do Not store near food stuffs.

Do Not reuse container.

Keep away from heat or open flame.

This product is toxic to fish and wildlife. Do Not allow product to enter streams, lakes, etc.

OCCURRENCE:

VCM Neutralizers
Condensate Treatment
Brine Treatment

NAME: Caustic Soda (Sodium Hydroxide) (Lye)

FORMULA: $NaOH$

FLASH POINT: None

EXPLOSIVE LIMITS: None

MAXIMUM ALLOWABLE CONCENTRATION: 1.2 ppm by volume

HAZARDOUS PROPERTIES: This material, both solid and solution, has markedly corrosive action upon all body tissue. Caustic solution is detectable by the slippery feeling of soapy water. Its corrosive action on tissue causes burns and frequently deep ulceration, with ultimate scarring. Prolonged contact with dilute solutions has a destructive effect upon tissue. Mists, vapors, and dusts of this compound cause small burns, and contact with the eyes, either in the solid or solution form, rapidly causes severe damage. Ingestion either in the solid or solution form causes very serious damage to the mucous membranes or other tissues with which contact is made. It can cause perforation and scarring. Effects of inhalation vary from mild irritation of the mucous membranes to a severe pneumonitis. It can cause an irritant dermatitis of skin. Caustic soda will react with water or steam to produce heat and will attack organic tissue. Where large quantities are handled, the area should be well ventilated and face masks should be worn.

TREATMENT: Skin - Speed in removing the caustic from contact with the skin is important. Remove all contaminated clothing at once. Then flush the skin with large quantities of cool or cold water thoroughly. The use of small portions of water, such as by sponging, may cause more serious injury due to heat liberated on dilution.

Eyes - If any caustic soda contacts the eyes, they should be irrigated immediately with an abundant amount of water for at least 15 minutes. The eyelids should be held apart during irrigation. A physician should be seen immediately after the eye is thoroughly washed.

SL 003027

OCCURRENCE:
Present as an impurity in all of the EDC streams except the lights still bottoms product. The lights still overhead stream will have the highest percentage of chloroform.

NAME: Chloroform

FORMULA: $CHCl_3$

FLASH POINT: None

EXPLOSIVE LIMITS: Will not burn in air.

MAXIMUM ALLOWABLE CONCENTRATION: 50 ppm for 8 hrs.

HAZARDOUS PROPERTIES: The most important hazard of chloroform arises from the fact that repeated exposure to low atmospheric concentrations may result in damage to the liver and kidneys. In high concentrations it has narcotic properties and is an effective surgical anesthetic. Contact with skin and mucous membranes may produce irritation.

In the presence of excess water or at very high temperatures, such as occur in open flames, chloroform decomposes to give phosgene, hydrogen chloride, and other products.

In the presence of strong alkalis and water, chloroform may become violently explosive.

On exposure to air and sunlight, chloroform slowly oxidizes to phosgene.

TREATMENT: If substantial quantities are spilled upon a person, the contaminated clothing should be removed promptly and the affected skin area should be flushed with plenty of water. The contaminated clothing should not be worn until free of the material.

If the eyes are contaminated, they should be flushed with plenty of flowing water. Medical attention should be obtained if any irritation persists.

If chloroform has been swallowed, vomiting should be induced as soon as possible by tickling the throat with a finger or by giving an emetic, such as two tablespoonsful of common salt in a glass of warm water. CALL A PHYSICIAN.

Anyone showing signs of ill effects from breathing the vapor of chloroform should be removed to fresh air, kept warm and quiet and be made to rest. If breathing stops, artificial resuscitation should be given. Get medical attention promptly.

OCCURRENCE:

As a circulating cooling liquid used to control OHC Reactor temperature.

NAME: Dowtherm LF

FORMULA: Mixture of Diphenyloxide and Methylated Biphenyl

PROPERTIES: Heavier than air.
Dowtherm LF is used in our process as a liquid and is a mixture of two chemicals. It is not normally toxic or otherwise hazardous, except that at the temperatures we will use it, safeguards must be provided. It has a very distinctive odor.

HEALTH HAZARDS: Unless the fumes are so strong as to cause oxygen deficiency, there is no hazard. The odor is irritating to intolerable below the safe toxic limit.

Skin irritation is of minor consequence; however, contact should be avoided. Dowtherm LF fluid in both the liquid and vapor form is mildly irritating to the eyes. If the eyes are accidentally contaminated with fluid, they should be thoroughly washed with water at least 5 minutes and medical attention obtained.

FIRE HAZARD: The temperatures of use are above the flash point (260°F), so precautions must be taken as if it were highly flammable. Inert gas (N_2) purge and "no burning and welding" procedures must be used. The best fire extinguisher is water, because its vapor concentration is very low at water temperatures.

SL 003028

OCCURRENCE:

Raw Material Feed to OHC and LP-EDC reactors.

NAME: Ethylene

FORMULA: C_2H_4

EXPLOSIVE LIMITS: 2.75 to 28.60% by volume with air.

HAZARDOUS PROPERTIES: A simple asphyxiant. A dangerous fire and explosion hazard.

TREATMENT: Fire should be fought with carbon dioxide or dry chemicals.

SL 003029

OCCURRENCE:

Main OHC-LP
EDC Product
Feed to EDC Cracking Furnaces and Main Process Liquor in VCM Section.

NAME: Ethylene Dichloride (EDC) (1,2-Dichloroethane)

FORMULA: CH_2ClCH_2Cl

FLASH POINT: 64.9°F open cup, 55.4°F closed cup

EXPLOSIVE LIMITS: 6.2 to 15.9% by volume

MAXIMUM ALLOWABLE CONCENTRATION: 50 ppm., 200 mg/m^3

HAZARDOUS PROPERTIES: Ethylene Dichloride has a distinctive odor and strong local irritating effects, which give warning of its presence in relatively safe concentrations. There is irritation of the eyes and upper respiratory passages. Ethylene Dichloride has a specific effect on the cornea. Exposure to the vapor, or, in animals, injection under the skin, produces a clouding which may progress to endothelial necrosis and infiltration of the corn a by lumphocytes and connective tissue cells. The narcotic action of the compound is strong, probably of the same order as chloroform. Its toxic effect upon the liver and kidneys are less than that of carbon tetrachloride, but animal experiments indicate that these organs may show congestion and fatty degeneration. Edema of the lungs has also been reported in animals. Dermatitis in man has been observed.

In short exposures to high concentrations, the picture is one of irritation of the eyes, nose and throat, followed by dizziness, nausea, vomiting, increasing stupor, cyanosis, rapid pulse, and loss of consciousness.

Chronic poisoning, where exposure has occurred over a period of several months, may cause loss of appetite, nausea and vomiting, epigastric distress, tremors, nystagmus, leucocytosis, low blood sugar levels, and possibly dermatitis if there has been skin contact.

Employees exposed regularly to ethylene dichloride should be examined at least semiannually, by a physician acquainted with the occupational hazards involved. Physical examinations should be required also when any symptoms of poisoning occur.

Employees who may be subjected to severe exposures of ethylene dichloride vapor as in tank cleaning and repairs in intermittent operations where general ventilation is not practical, in cases of failure of piping or equipment, and in cleaning up spills, should be provided when indicated with proper eye and respiratory protection as follows:

(a) Suitable gastight chemical safety goggles.

(b) Rescue harness and life line for those entering a tank or enclosed storage space. An outside attendant should maintain constant observation.

(c) Positive pressure hose masks with hose inlet in a vapor-free atmosphere.

Air-line masks with reducing valve and filter suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply, or self-contained breathing apparatus with stored oxygen or air, which allows greater mobility but usually requires more highly trained men. In tank work small manholes may make this apparatus unsuitable because of its bulk, although the type known as self-generating is specially designed for entrance and egress through small openings.

Masks and breathing apparatus should be approved by the United States Bureau of Mines and should be equipped with full face pieces.

(d) Industrial gas masks, approved by the United States Bureau of Mines with canisters approved for use in ethylene dichloride vapor should be used only when it is certain that the concentration of vapor is less than 2 per cent by volume (20,000 parts per million) and the atmospheric oxygen is not lower than 16 per cent, and then only for exposures not exceeding one-half hour.

TREATMENT: All contaminated clothing should be removed at once. Clothing, including shoes, soaked in ethylene dichloride should be removed and not worn again until thoroughly dry. All affected areas should be washed thoroughly with warm water and soap. After this, an ointment containing lanolin should be applied in order to replace the natural skin oils. For serious or persistent cases of skin trouble and for signs of symptoms of generalized poisoning, a physician should be consulted.

If liquid ethylene dichloride has entered the eyes, they should be washed promptly with copious quantities of water for at least 15 minutes. It is advisable to irrigate the eyes gently with water at room temperature in order to minimize additional pain or discomfort. Ethylene dichloride vapor can produce injury to the eyes if the exposure is intense or in the same manner as for the liquid. Medical attention should be obtained in all these contacts with the eyes.

OCCURRENCE:

Used as catalyst in LP-EDC section

NAME: Ferric Chloride

FORMULA: $FeCl_3$

FLASH POINT: None

EXPLOSIVE LIMITS: None

HAZARDOUS PROPERTIES: Ferric chloride presents no particular problem in handling. Hoever, in the anhydrous form, it may be injurious to clothing, and all contamination of both skin and clothing should be washed off immediately. In the case of eye contact, flush immediately and thoroughly with water and then rinse with a weak solution of sodium bicarbonate or boric acid. A physician should always be consulted in such cases.

Ferric chloride will seriously stain clothing and skin when it is contacted so it is advisable to wear gloves and aprons when handling it.

Ferric chloride is extremely hygroscopic (absorbs water), and when this takes place, heat realease occurs. * When taking material from a drum, remove the desired quantity as quickly as possible and immediately seal the drum to prevent it from absorbing moisture from the air.

*Remove the drum lid carefully to relieve any pressure that may be built up inside.

OCCURRENCE:

Used as a refrigerant in refrigeration units.

NAME: Freon-22 (Monochlorodifluoromethane)

FORMULA: $CHCF_2$

FLASH POINT: None

EXPLOSIVE LIMITS: None

MAXIMUM ALLOWABLE CONCENTRATION: Unknown

HAZARDOUS PROPERTIES: Freon-22 is very dangerous when heated to decomposition. It emits highly toxic fumes of chlorides and fluorides. Never allow any open flames to come in contact with Freon-22 or any vessels containing it.

OCCURRENCE:

Is the main constituent of the fuel gas burned in the Dowtherm heater, cracking furnaces and incinerator. Added to LP-EDC Reactor Vent.

NAME: Methane (Natural Gas)

FORMULA: CH_4

FLASH POINT: None

EXPLOSIVE LIMITS: 5.3% to 14.0% by volume

HAZARDOUS PROPERTIES: A simple asphyxiant. A dangerous fire and explosion hazard.

TREATMENT: Fire should be fought with carbon dioxide or dry chemicals.

NOTE: Methane used in the VCM II Plant is odorless. It does not have the "typical" natural gas smell you may be used to, as no mercaptans are added.

OCCURRENCE:

Raw material feed to the OHC Reactors.

NAME: Oxygen

FORMULA: O_2

HAZARDOUS PROPERTIES: Too high a percentage of O_2 in the air we breathe will cause the person to pass out. Therefore, O_2 lines on a vessel should be isolated before man entry.

Pure O_2 will cause many things to burn spontaneously at a much lower temperature level than air. Normal hydrocarbon oils and greases, for example, should never be exposed to O_2. Never use a gasket or valve, etc., for O_2 service unless you are sure it is acceptable.

At higher temperatures, O_2 will burn steel, stainless steel, or other alloy pipe and equipment. Therefore, should a fire occur at or near an O_2 line, play water on the line to keep it cool. The normal "air" explosive ranges are considerably widened with hydrocarbon or chlorinated hydrocarbons in the presence of high O_2.

TREATMENT: If a pass out should occur, remove the man from the area, apply artificial respiration if necessary, and get first aid help.

SL 003035

OCCURRENCE:

Chemical for cooling tower water treatment

NAME: Sulfuric Acid

FORMULA: H_2SO_4

FLASH POINT: None

EXPLOSIVE LIMITS: None

MAXIMUM ALLOWABLE CONCENTRATION: 1 mg/m of Air

HAZARDOUS PROPERTIES: THIS IS ONE OF THE MOST TREACHEROUS CHEMICALS TO HUMAN FLESH. The greatest hazard of sulfuric acid is physical contact. Because of its affinity for water, it dries tissue, creating heat, and resulting in a painful slow healing burn. Repeated skin contact with diluted sulfuric acid solution can cause dermatitis.

Sulfuric acid reacts with water to produce heat. The acid should always be added to water upon dilution, never vice versa.

TREATMENT: Skin - Immediately remove all contaminated clothing and equipment. FLush the exposed area with an abundance of water. After thorough irrigation with water, applications of mild alkaline solutions may be used. Do not apply oils or ointments to burned area without instructions from a physician.

Eyes - Flush with water for 15 minutes holding eyelids open. An eye anesthetic may be used for pain. Never use ointment. Call a specialist. Report to First Aid.

Swallowing - If conscious, have patient wash mouth with water. Give at least 1 oz. of milk of magnesia or aluminum hydroxide gel well diluted in water. If these are not available, drink milk mixed with whites of eggs. Do not induce vomiting or pass a stomach tube. Call a physician. Report to First Aid.

Inhalation - Remove patient from contaminated area. Give artificial respiration and oxygen if necessary. Report to First Aid.

SL 003037

OCCURRENCE:

Present in significant quantities in EDC section streams, particularly Heavies Still Bottoms.

NAME: Symmetrical and Assymmetrical Tetrachloroethane (S. TeCE & A. TeCE)

FORMULA: $CHCl_2$ $CHCl_2$ and CCl_3CH_2Cl

FLASH POINT: None

EXPLOSIVE LIMITS: None

MAXIMUM ALLOWABLE CONCENTRATION: 5 ppm for 8 hour exposure

HAZARDOUS PROPERTIES: The tetrachloroethanes are not flammable or explosive but are the most toxic of the chlorinated ethanes that will be handled in the plant.

The tetrachloroethanes are toxic by inhalation, by prolonged and repeated contact with skin or mucous membranes or by oral intake. Although toxic, tetrachloroethanes may be handled safely if proper precautions are constantly observed. Prolonged or repeated exposures to the product in any form are hazardous.

The signs and symptoms of excessive absorption usually appear gradually and only after repeated exposures. In order of appearance they commonly are unusual fatigue, loss of appetite and weight, sick stomach and vomiting, constipation, abdominal pain, jaundice, drowsiness, going on in severe cases to unconsciousness and death. Some cases show marked involvement of the nervous system with headache, numbness and tingling in fingers and toes, trembling and twitching of muscles and even paralysis of some muscles.

The signs and symptoms of tetrachloroethane poisoning given above are due to systematic poisoning characterized by marked damage to the liver, kidneys, heart, blood cells, and nervous system. The clinical picture varies with the type of exposure and the amount of the material which has been absorbed either at one time or at repeated times. Most serious effects are usually on the liver and the blood. The principal route of absorption is by breathing the vapor, although it may be absorbed by the skin. Tetrachloroethane is currently considered the most toxic of the chlorinated hydrocarbon solvents in industrial use.

Continued exposure to high concentrations of the tetrachloroethanes leads to local irritation of the eyes and nose. There may be sick stomach and vomiting, but since tetrachloroethane is less volatile than other hydrocarbon solvents, it does not often have an anesthetic effect.

Subacute tetrachloroethane poisoning is the form usually encountered. This develops gradually as a result of prolonged o repeated work in an atmosphere containing more than 5 parts of tetrachloroethane per million parts of air but under conditions where the amount absorbed causes no immediate reaction. Repeated exposure even to low concentrations seems to increase sensitivity, and may lead to subacute poisoning.

For some time, workers with subacute poisoning may show only such signs and symptoms as unusual fatigue, loss of appetite and weight, constipation and abdominal distress or pain. At any time they may develop more severe evidence of absorption such as vomiting, dizziness, tenderness and pain over the liver and jaundice. Even if removed from further exposure, the illness may persist and grow worse over a period of days, weeks or even months and may finally even end in death. However, if after a few months there has been steady improvement, complete recovery is the rule.

Some conditions under which subacute poisoning may occur in employees are as follows:

(a) Where the ventilation is inadequate, resulting in high concentrations of more than 5 parts of tetrachloroethane per million of air.

(b) Where the vapor concentrations are high intermittently, due to faulty handling of the liquid.

(c) Failure of the individual to observe precautionary measures.

Tetrachloroethane is absorbed through the skin so that systemic poisoning can occur by this route with the same signs and symptoms as described above.

Tetrachloroethane may cause dermatitis after repeated or prolonged contact with the skin, such as that which might occur in the handling of rags wet with the chemical product, dipping hands into the liquid, or wearing clothing saturated with it. Reddening, burning and rarely, blisters may follow such exposure. In certain rare cases, the dermatitis may be caused by hypersensitivity to tetrachloroethane. The skin becomes rough, red and dry due to the removal of skin oils. It cracks easily and is readily susceptible to infection. The skin has a chapped appearance.

Tetrachloroethane may enter the eyes either as a vapor or as a liquid (spray or splash). The resultant irritation produces lacrimation, burning and other symptoms of inflammation. It can cause serious eye damage if immediate care is neglected.

The first symptoms after toxic amounts of tetrachloroethane are taken by mouth are those of irritation of stomach and bowels, such as sick stomach, vomiting and diarrhea with bloody stools. It is absorbed very rapidly and even a small amount may go on to produce unconsciousness and a deep flushing of the skin. Death is apt to occur before such systemic changes as liver and kidney damage occur.

TREATMENT: Most important in the case of any poisoning is quick removal from exposure. In the case of tetrachloroethane poisoning, this means first removing the patient from the contaminated atmosphere and insofar as possible, removing the tetrachloroethane from the patient's skin, or gastrointestinal tract, if those areas are involved.

The patient should be kept quiet and comfortably warm, but not hot.

A physician should be called immediately. He should be told briefly and clearly what has happened and the exact location of the patient.

A person showing symptoms of tetrachloroethane vapor poisoning should be removed promptly from the contaminated area. In case breathing has stopped, effective artificial respiration, such as that obtained by the prone pressure method or the Eve rocking method should be started immediately. If oxygen inhalation apparatus is available, oxygen should be administered, but only if one familiar with the operation of the apparatus is present to administer it. If the patient is conscious, hot tea or coffee may be given as a stimulant. A physician should be called at once.

All contaminated clothing should be removed at once. Clothing, including shoes, soaked in tetrachloroethane should be removed and not worn again until thoroughly free from tetrachloroethane. All affected areas should be washed thoroughly with warm water and soap. After this, an ointment containing lanolin should be applied in order to help in replacing the natural skin oils. For serious or persistent cases of skin trouble, and for signs and symptoms of generalized poisoning, a physician should be consulted.

If liquid tetrachloroethane has entered the eyes, they should be washed promptly with copious quantities of water for at least 15 minutes. (It is advisable to irrigate the eyes gently with water at room temperature in order to minimize additional pain or discomfort.) Medical attention should be obtained in all cases involving contact with the eyes.

If a person has swallowed tetrachloroethane, he should be made to vomit, if conscious, by having him drink a glassful or more of lukewarm water in which a teaspoonful of salt to the glassful has been dissolved; a similar amount of warm soapy water may be used. If necessary, the patient should be encouraged to stick his finger down his throat to induce vomiting. When possible, vomiting should be induced at least three times. Following this a tablespoon of Epsom Salt dissolved in a glass of water should be given. A physician should be called immediately.

OCCURRENCE:

Major product of VCM units.

NAME: Vinyl Chloride (Chloroethylene) (VCM or VC)

FORMULA: CH_2CHCl

FLASH POINT: -108.4°F - open cup, -162°F - closed cup

EXPLOSIVE LIMITS: 4 to 22% by volume

MAXIMUM ALLOWABLE CONCENTRATION: 1 ppm for 8 hours/5ppm for 15 minute ceiling.

HAZARDOUS PROPERTIES: Vinyl chloride is not very poisonous; it is extremely flammable and it has a narcotic effect. Continued exposures may cause some kidney deterioration. Inhalation of vapors greater than 500 ppm may produce a slight narcotic effect. At concentrations of 4% or greater, VCM vapors may produce a deep or fatal anesthesia. The Department of Labor has declared Vinyl Chloride to be a carcinogenic (cancer-causing) compound.

The main danger of VCM is the extreme flammability of the vapors. VCM, when burning, will form HCl and possibly phosgene; so, never approach a fire without a gas mask.

Any spill of VCM will result in an explosive mixture being formed, and because of the high density of the VCM gas, the mixture will tend to stay near ground. It will take very little to explode the VCM vapors --static electricity spark, friction spark, or an arcing device are all dangerous when VCM is spilled.

TREATMENT: Remove the injured person from the contaminated area; if breathing has stopped, perform artificial respiration. In any case, make sure the person injured is reported to First Aid immediately. If any liquid enters the eye, wash the eye continuously with a large amount of water for at least 15 minutes; then get the person to First Aid. All exposed persons should be referred to the Medical Department.

SL 003041

SL 003042

The cell liquor distribution system from Battery Limits is shown beginning on P & ID 56A-10035.

B. OHC-EDC Section

1. Dowtherm System

The purpose of the Dowtherm System is to:

a. Control the catalyst bed temperature by removing the heat of reaction from the reactor.

b. Recover the heat of reaction by generating 45 psig steam in the Dowtherm cooler.

c. Heat the reactor and catalyst for startup.

The Dowtherm System consists of a storage drum and a storage pump which are common to both reactors. There are two recirculation pumps, one surge drum and one dowtherm cooler for each reactor. The Dowtherm Heater System is described in the following section of this manual.

Normal flow for the dowtherm is from the discharge of the circulation pumps to the distribution header inside the reactor, through the 30-tube passes inside the reactor, to the outlet header, through the dowtherm cooler and back to the circulation pump suction.

The catalyst bed temperature is controlled by adjusting the temperature of the dowtherm being circulated to the reactor. At full reactor rates essentially all of the dowtherm must go through the cooler to get enough cooling on the reactor. But at lower rates some of the dowtherm is allowed to bypass the cooler through TIC-9652/9752 to keep from getting too much cooling on the reactor. At minimum rates, too much dowtherm would go through the cooler even if the cooler bypass (TIC 9652/9752) was wide open. The cooler throttle valve (HIC 9653/9753) is used to throttle flow through the cooler at low rates.

Dowtherm flow is kept relatively constant to the reactor at about 4000 GPM. The cooler throttle valve should not be left throttled enough for dowtherm flow to the reactor to be restricted.

Dowtherm expands and contracts as it is heated and cooled. The dowtherm surge drum is to provide enough volume to accomodate this expansion and contraction. The surge drum should have a low level when the system is cold which will allow for expansion to a high level when the reactor is heated for start-up. The surge drums are equipped with a nitrogen pad and vent system to maintain approximately 10-15 psig on the dowtherm system.

The dowtherm surge drum is tied into the suction of the circulation pumps to be sure the pump suction is flooded with dowtherm at all times. This is done to eliminate one cause of loss of dowtherm circulation. It is very important to maintain good dowtherm circulation at all times. Loss of circulation for periods as short as one minute can cause severe reactor overheating and large dowtherm releases through the SRV on the surge drum. The stuffing box and bearing housing on the circulation pumps are jacketed and cooled with cooling tower water. The quench gland is purged with 45 psig steam to keep the outside of the seal faces clean.

Water introduced to a hot dowtherm system (by starting flow through a wet section of piping or by having water in dowtherm that is being added to raise the level in an operating system) will flash and if the quantity is sufficient it will cause pump cavitation, vapor locking in some passes and a release of dowtherm or steam through the SRV on the surge drum. Vapor locking can be cured by bleeding the steam vapors out of the bleed valves on the outlet of each pass.

Dowtherm must be cooled to about 310°F to get maximum rates on an OHC reactor. Two problems can prevent adequate cooling of dowtherm:

a) high steam pressure on the steam side of the dowtherm cooler and

b) leakage through the dowtherm temperature control valve (TIC-9652 & 9752).

Dowtherm that is too cold promotes corrosion/erosion on the tubes inside the reactor, therefore dowtherm should always be 300°F or greater.

The volume of dowtherm required to fill the system is about 6500 gallons excluding any dowtherm for the surge drum.

Protection against dowtherm spills caused by circulation pump's seal failures is provided for by remote stop switches for these pumps. These switches are located in the control room on the OIP-2 panel. HS-9853 A/B will trip dowtherm circulation pumps one and two, HS-9953 A/B will trip dowtherm circulation pumps three and four. These pumps can only be started in the field.

If a seal leak occurs, the leaking pump should not be shut down until the spare pump is running or until the reactor shutdown system has been activated.

Dowtherm leaks should be reported to supervision immediately so repairs can be made. There have been fires in our plant as a result of insulation becoming soaked with dowtherm.

The Dowtherm system is shown on P & ID's 56A-10025, 56A-20026, 56A-10027 and 56A-10038.

2. Dowtherm Heater

The purpose of the dowtherm heater is to heat dowtherm so that the catalyst bed in the reactor can be heated to the startup temperature of 500°F. The dowtherm temperature required will be from 520 to 550°F.

The dowtherm heater is needed only for reactor heatup prior to start-up. The piping and valving arrangement allow dowtherm from either reactor system to be circulated through the heater. Early in the reactor start-up procedure, the heater is shut down, bypassed and then isolated from the system.

The dowtherm heater is a direct-fired radiant heater utilizing three natural gas-fired burners to heat dowtherm. Each burner is designed to release a maximum of 3.45 MM Btu/hr and a minimum of 1.15 MM Btu/hr. Air is supplied to the burners by natural draft through primary and secondary air registers. After start-up, the primary and secondary air must be adjusted to give the minimum sized stable flame and the proper flame characteristics. Secondary air should be adjusted each time the firing rate is changed.

Lighting of burners is accomplished with electronic ignition pilots. Natural gas pressure downstream of the pilot regulator should be adjusted to between 2 and 5 psig. Pilots should not be lit under any circumstances until the atmosphere inside the heater has been checked with an explosion meter. The majority of fired heater explosions occur as a result of improper light-off procedures. The start-up procedure is detailed in the S.O.P. Manual.

Burner adjustment is critical to safe furnace operation. A burner that has not been properly adjusted can cause flame impingement on the dowtherm tubes. Flame impingement causes the tube metal to overheat, weaken and erode. Overheating of the tube metal causes brittleness and dowtherm decomposition, and could result in a tube rupture. When dowtherm decomposes, it leaves a carbon film on the inside of the tube which makes it easier to overheat a tube.

Dowtherm is split into four parallel passes before going into the heater. Each pass has six tubes. The temperature and flow from each pass is measured. There is also a tube metal temperature measured on each pass. Overheating and rupture of tubes is a very real fire hazard in the OHC unit. The heater is located away from other process equipment and provided with remote isolation valves to minimize this hazard. Snuffing steam with a manually operated, remotely located valve is provided in the event that there is a tube rupture within the furnace.

Proper flame pattern, clean dowtherm tubes and sufficient dowtherm flow are all necessary to prevent high tube metal temperature and fires caused by tube failure.

The furnace is equipped with a shutdown system. The dowtherm furnace shutdown system is activated by the following:

a) Low dowtherm flow through any one of the four tube passes.

b) High tube wall temperature on any one of the four tube passes.

c) High stack temperature.

d) High dowtherm temperature in any one pass out of the heater.

e) Vapor detector shutdown system.

f) Two remote manual trips.

g) Flame failure within the heater.

h) Low fuel supply pressure.

i) High fuel supply pressure.

Features a) through d) are to help prevent overheating of tube metal, decomposition of dowtherm and to decrease the possibility of a tube failure. Features e) and f) are provided to prevent ignition of a vapor cloud by the dowtherm furnace. Features g) through i) are to help prevent an explosion inside the combustion chamber of the dowtherm heater. The shutdown and control system instrumentation are described in the Safety Control System Manual. The Dowtherm Heater is shown on P & ID 56A-10027.

3. OHC Reactor System

The purpose of the OHC reactor system is to consume VCM byproduct HCl and produce crude EDC, thereby recovering Cl so that it can end up in VCM product. The HCl is reacted with ethylene, oxygen, and recycled reactor vent gases to form crude EDC. The crude EDC is processed and used as feed stock to the furnaces at VCM II and possibly to other units within the Lake Charles Plant.

Proper operation of the OHC reactor system is necessary to assure an efficient and productive plant. Any stoppages or reductions of reactor rates will have an adverse effect on the HCl-producing and crude EDC-consuming units. The crude EDC will be readily depleted. The HCl is a byproduct of the HCl-producing units and cannot be stored. (See the HCl Distribution System section of this manual). Any large rate changes or shutdowns must be communicated to units involved.

The OHC reactor system begins with the upstream block valve of the individual feed header's pressure control valves. The system ends at the downstream block valves of the reactor degasser level control valve and the system pressure control stations.

The OHC reactor system consists of two identical reactor trains. Included in the trains are feed, cooling, condensing, catalyst charging,

OHC REACTOR AND FEED SYSTEM

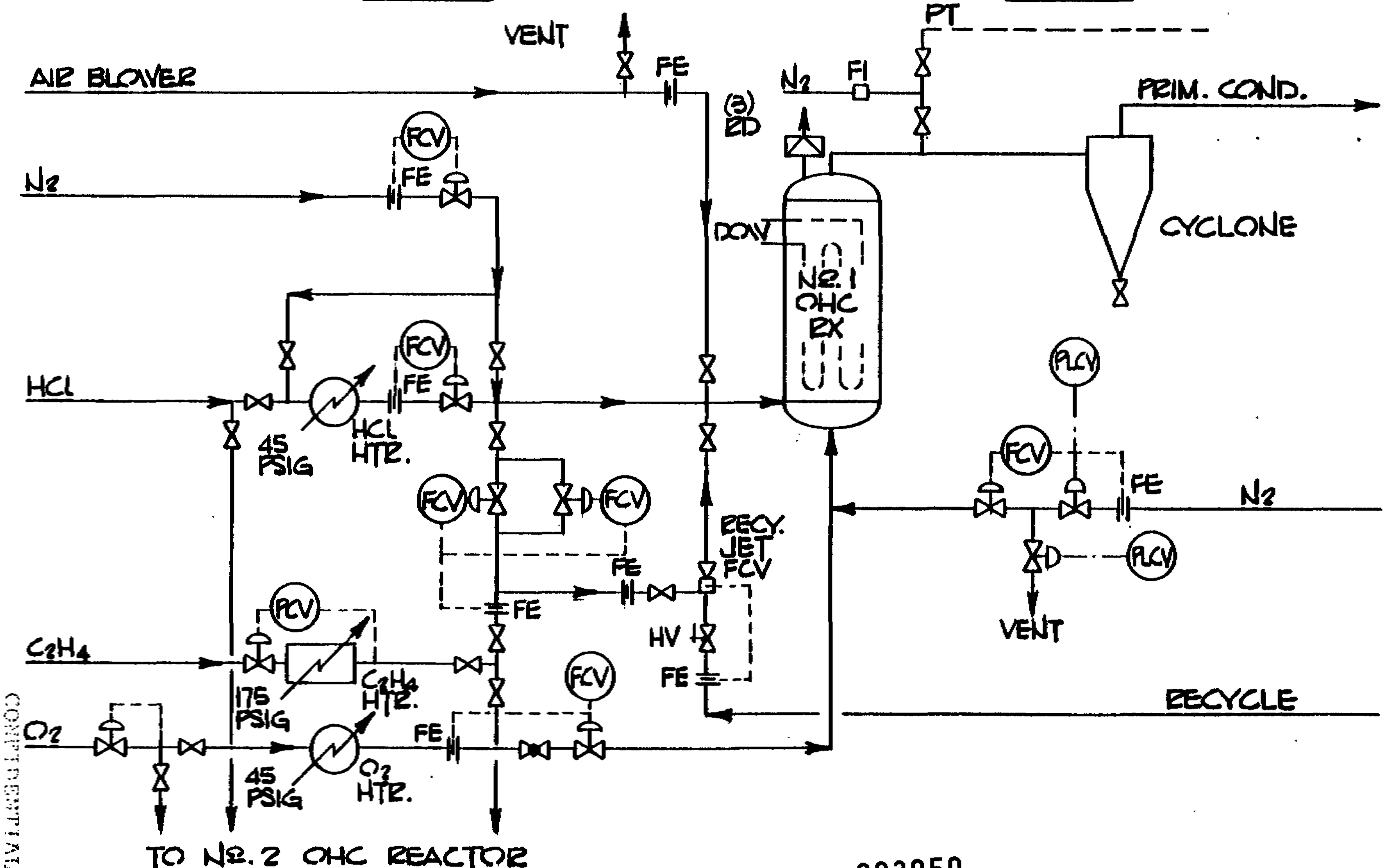

FIG. VII-2

OHC REACTOR HCL FEED SYSTEM

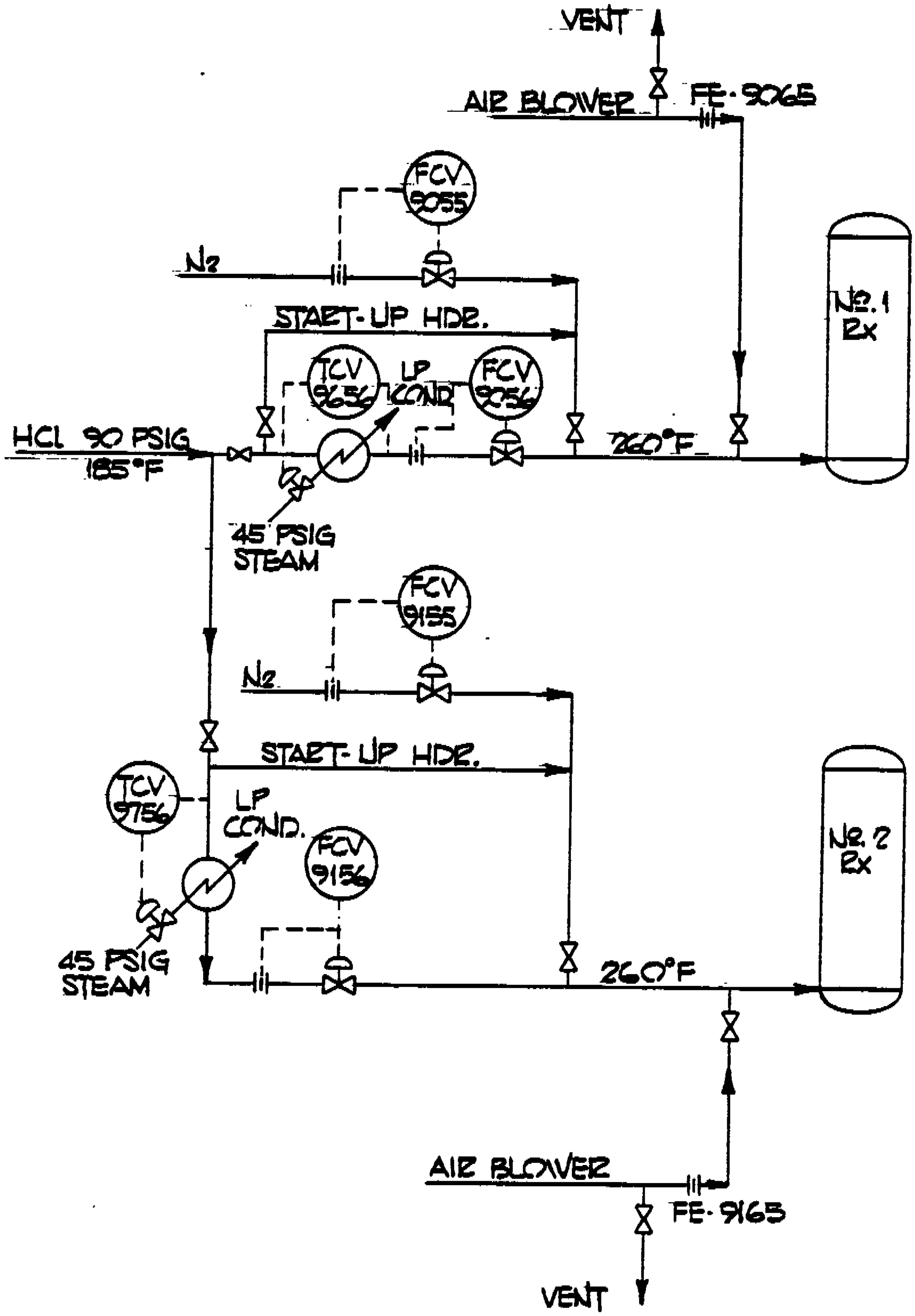

FIG. VII-3

The HCl, ethylene, and recycle are premixed in a nickel feed header. The HCl, ethylene, and recycle mixture is called the mixed feed, and the header is the mixed feed header.

The HCl, ethylene and oxygen are metered through orifice runs that have dual flow transmitters and a pressure transmitter. The flows are computed from the average of the two flow transmitters compensated by pressure. The computer provides temperature compensated flow indications and alarms on the CRT's.

b. HCl Feed

The HCl feed pressure will depend on the HCl distribution head pressure. This pressure must be at least 5 PSIG above the mixed feed header pressure to get the HCl into the system.

The HCl flows through a spiral-type heat exchanger, heated by 45 PSIG steam. The steam is supplied through a temperature-control valve which is controlled by the HCl outlet temperature.

The HCl flows through the orifice run and then through a flow-control valve designed to maintain the flow through the orifice within a set range. The HCl is then fed into the mixed feed header.

c. Ethylene Feed

The ethylee feed supply pressure is controlled at a metering station in plant B-1, managed by the EDC-1 unit. (See the Ethylene System section in this manual.)

OHC REACTOR
C_2H_4 FEED SYSTEM

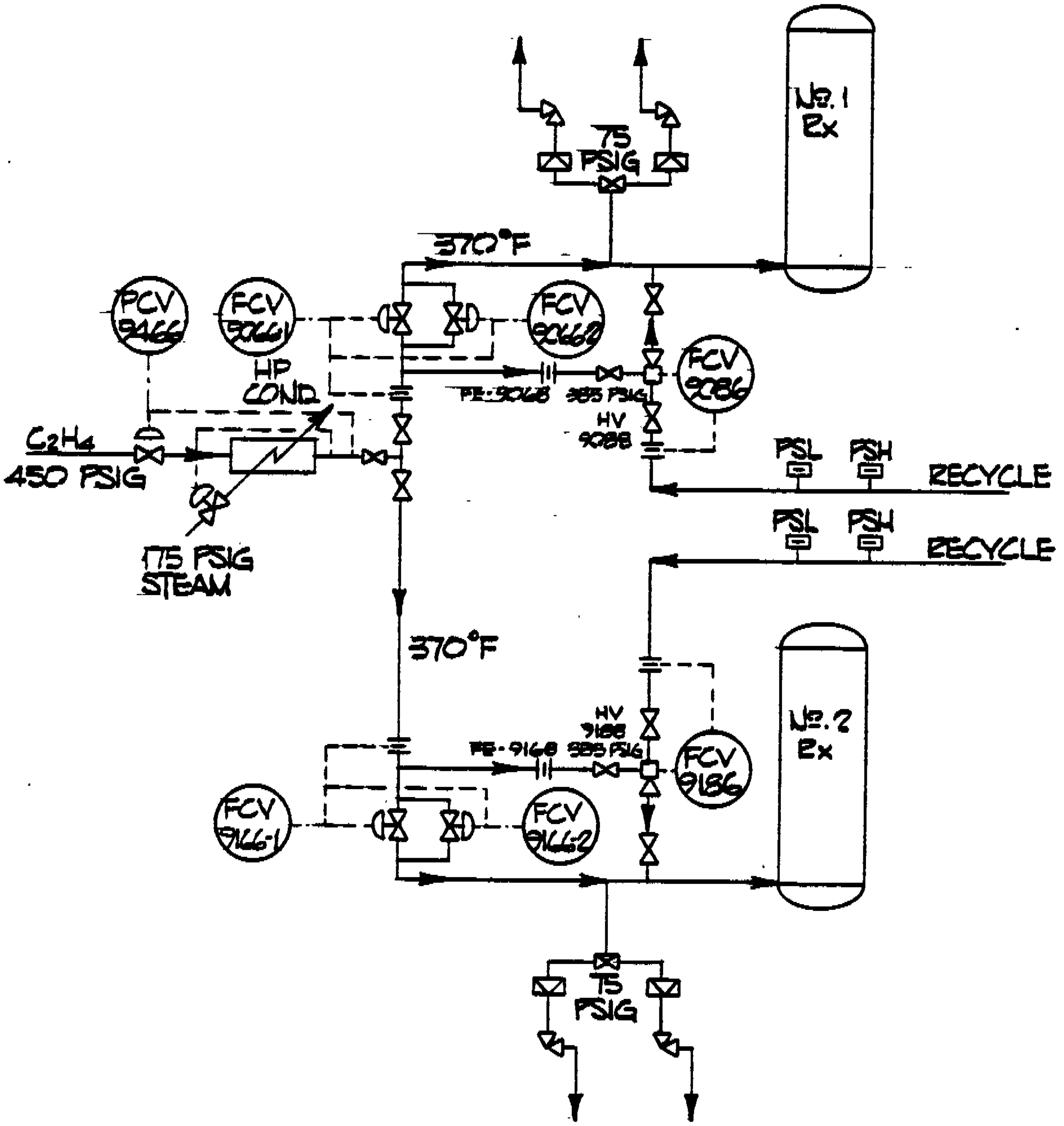

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FIG. VII-4

The ethylene line pressure is reduced in the VCM II unit by a pressure-control valve set to maintain the pressure downstream of the pre-heater.

The ethylene flows through a multitube-type heat exchanger. The pre-heater is actually two shell and tube heat exchangers in parallel. Ethylene flows through the tube side and 175 PSIG steam flows through the shell side. The steam is supplied by a temperature-control valve which is controlled by the ethylene outlet temperature.

The ethylene flow is then split to each reactor feed system. The ethylene flow to each reactor is metered through an orifice run with dual flow transmitters and a pressure transmitter. The flow through this orifice is called the total ethylene feed flow.

The ethylene flows through an on-off automatic block valve. The flow is then split; one flow is ethylene make-up; the other is motive gas for the recycle jet.

The make-up ethylene flow goes to two parallel flow-control valves, one large and one small. The total flow input to the flow-control valves is split such that the small valve opens initially, and as flow is increased, the large valve opens. The make-up ethylene then enters the mixed feed header.

The ethylene motive gas flows through an orifice run that meters the flow. The motive gas flow transmitter provides an input for the recycle jet flow controller. The motive gas is flow-controlled at a rate that will maintain the desired recycle flow.

When motive gas is started to the recycle jet, the total ethylene flow must remain the same. The large ethylene make-up flow control valve will cut back to maintain total flow. The recycle jet compressor requires a minimum of 385 PSIG motive gas supply pressure.

d. Recycle Feed

The recycle vent gas feed pressure will depend on the reactor system pressure. The recycle stream is the vent from the entrainment separator. The recycle is fed to the reactor feed system through a teflon-lined pipe. The recycle flow indication to the reactor is also pressure and temperature compensated, managed by the computer and displayed on the CRT.

The recycle flows through an on-off automatic isolation valve and then to the jet compressor.

The recycle is fed into the mixed feed header. All parts of the jet compressor in contact with the recycle stream are constructed of monel.

The mixed feed is fed into a chamber in the bottom head of the reactor.

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e. Oxygen Feed

The oxygen feed supply pressure is controlled at a metering station in Plant B-1, managed by the Per-Tri unit. (See Nitrogen-Oxygen-Air Metering Station system section in this manual.)

OHC REACTOR
OXYGEN FEED SYSTEM

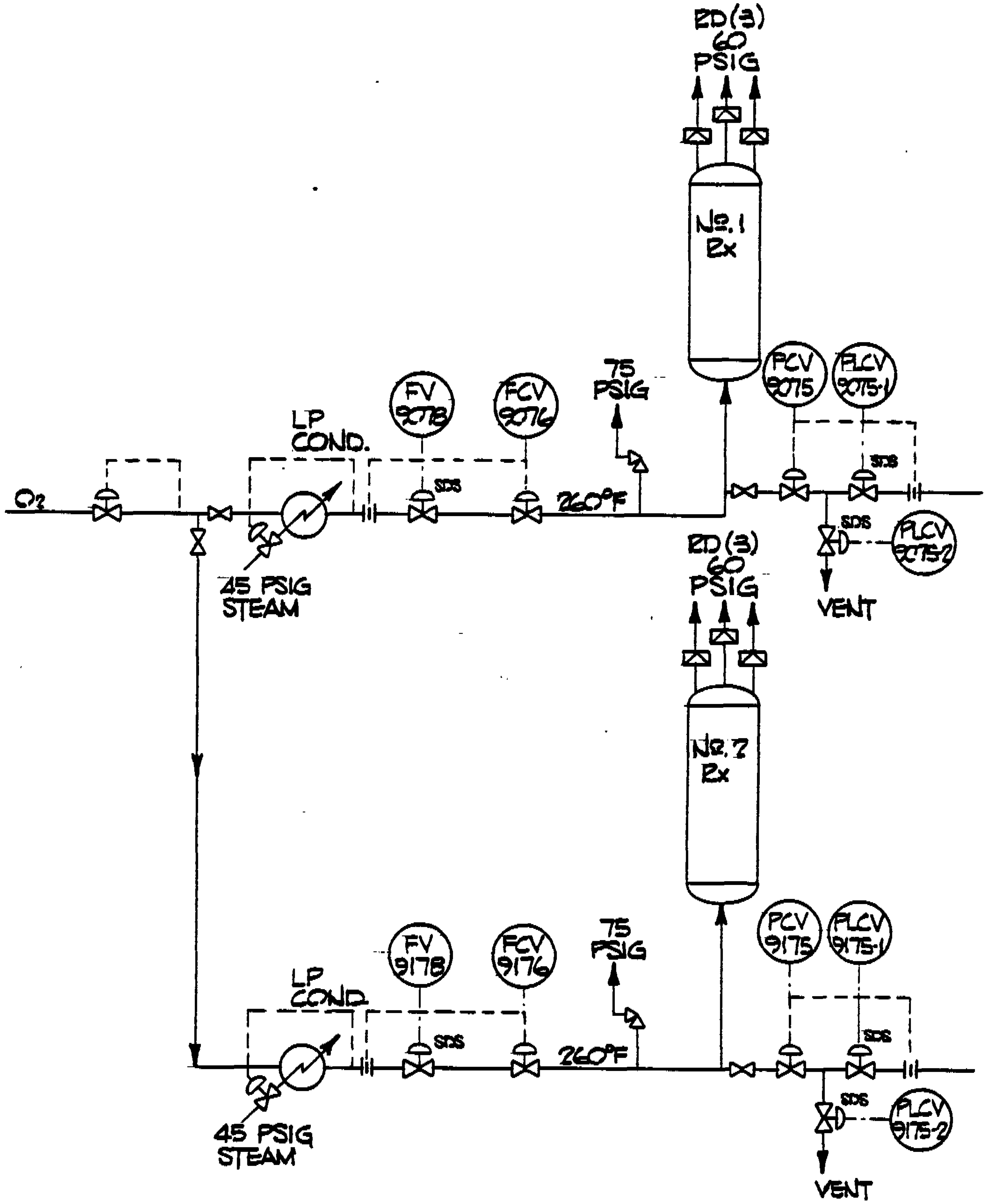

FIG. VII-5

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The oxygen line pressure is reduced in the VCM II OHC unit by a pressure-control valve. The oxygen flow is then split to each reactor feed system.

The oxygen to each reactor flows through a spiral-type heat exchanger, heated by 45 PSIG steam. The steam is supplied through a temperature-control valve which is controlled by the oxygen outlet temperature. The piping out of the pre-heater is constructed from stainless steel because oxygen at high temperatures attacks carbon steel.

The oxygen flow is metered and flow-controlled in the same manner as the HCl--dual flow transmitters and pressure compensated. The oxygen header also has an on-off automatic isolation valve.

Oxygen is fed into the bottom reactor head through a separate feed inlet. The oxygen is not premixed with the mixed feed, because an uncontrolled reaction could occur if the streams come in contact before reaching the catalyst inside the reactor.

Safety relief valves are provided in the reactor feed system. Two are located on the HCl feed header, downstream of the flow-control valve. They are set to relieve at 75 PSIG. The two safety relief valves are mounted together with a three-way transflow ball valve for switching from one to another for maintenance.

A safety relief valve is located on the ethylene header, upstream of the preheater. It is set to relieve at 600 PSIG.

The 175 PSIG steam supply to the ethylene has a safety relief valve located downstream of the temperature-control valve. It is set to relieve at 300 PSIG.

The recycle feed header has a safety relief valve located downstream of the automatic isolation valve. It is set to relieve at 75 PSIG.

The oxygen feed header has a safety relief valve set for 75 PSIG located downstream of the flow-control valve.

f. Reactor System

The reactor is a vertical vessel constructed from Inconel. The bottom reactor head is stainless steel. The bottom head serves as the feed manifold. Mixed feed enters the head directly through four 6" nozzles on the sides of the bottom head.

The mixed feed is distributed across the reactor by a distribution plate fitted with 844 mixed feed nozzles. The oxygen enters the bottom reactor head through a 4" nozzle. The oxygen is distributed into the reactor by 241 oxygen-feed nozzles which sparge the oxygen into the reactor 19" above the distributor plate (just above the 180° ells of the cooling tubes). The distribution plate, mixed feed nozzles and oxygen nozzles are Inconel. The mixed-feed and oxygen nozzles are designed so that a minimum of 25% of the total pressure drop across the reactor will occur across the distributor plate and feed nozzles; this pressure drop is necessary in order to insure that the feeds are distributed evenly across the reactor.

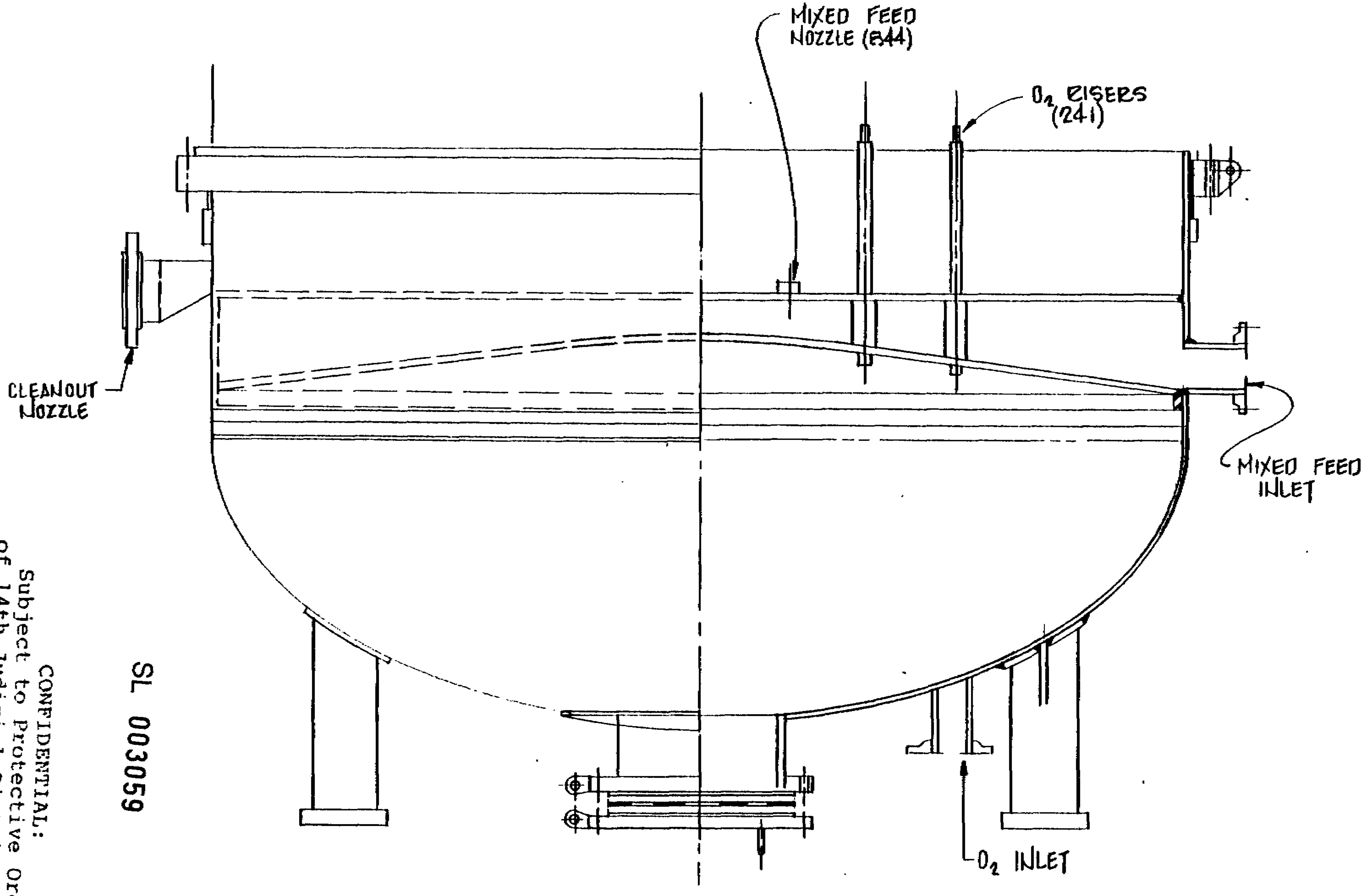

Fig
OHC REACTOR HEAD

FIG. VII-6

g. Reactor Pressure/Velocity Control

The OHC reaction is catalyzed by an 7.5-8% copper, 5.0-5.5% potassium catalyst. The copper and potassium compounds are applied as a coating to a clay carrier. The catalyst is fluidized in the reactor by the reacting gases. A superficial fluid velocity of 1.0 ft./sec. is required in the reactor in order to maintain fluidization with a minimum catalyst carry-over. This minimum velocity must be maintained at all production rates. A velocity of less than 1.0 ft/sec. would result in slow catalyst movement, resulting in clinkering and loss of fluidization. Loss of fluidization would result in plugging of the feed orifices and require complete reactor shutdown, catalyst removal, cleaning and recharging. Velocities greater than 1.3 ft/ sec. will result in increased catalyst carry-over and a higher attrition rate of catalyst due to more fines generation. Since varying production rates require varying feed rates, the velocity must be maintained constant by changing the reactor conditions so as to maintain a constant volume flow of gases in the reactor. This is accomplished by changing the reactor pressure (temperature will be essentially constant) with varying production rates. Thus, the reactor pressure will be decreased as the production rate is decreased.

h. Reactor Temperature Control

The reactions that take place within the OHC reactor are highly exothermic (give off heat) which make heat removal from the reactor necessary. This is accomplished by circulating liquid Dowtherm through 30 parallel banks of 3" pipe hairpin loops suspended in the fluidized bed. The pipe loops are suspended from a level 25 feet above the distributor and extended down to 1 - 1/2' above the distributor plate. The reactor temperature is controlled by varying the inlet Dowtherm temperature (with approximately constant Dowtherm flow rates for all production rates). The hot liquid Dowtherm is circulated to a Dowtherm cooler. The cooler is a U-Tube kettle-type reboiler with the Dowtherm acting as the heat source in the tubes while steam is formed in the shell. (See the Steam and Condensate Collection System section of this manual.)

The outlet Dowtherm temperature from the cooling system is maintained at the desired setpoint by automatically bypassing Dowtherm around the cooler at the rate necessary to maintain this temperature. An MLS is also provided to control flow through the cooler. The Dowtherm then flows to Dowtherm circulation pumps (which also can pull from a Dowtherm surge tank), which pump the Dowtherm to the reactor. (See the Dowtherm System section of this manual.)

Thermocouples are provided to monitor the reactor temperature profile. Reactor temperature profile thermocouples are located at the following reactor levels: 4 at 2 ft.; 2 at 8 ft. (bed); 2 at 20 ft.; 2 at 26 ft.; 2 at 27 ft.; 2 at 28 ft; and 2 in the reactor dome.

i. Catalyst Addition/Removal

Since the reactor is continuously discharging catalyst overhead, make-up catalyst must be added. Located at the top of the reactor is a catalyst charge pot and an Inconel catalyst addition valve. The charge pot is filled with catalyst, pressurized with nitrogen, and the catalyst is blown through the addition valve.

The catalyst charge pot has a safety relief valve set to relieve at 150 PSIG.

The gases flowing through the reactor leave the reactor through an inconel overhead vapor line. These gases carry catalyst dust with them that must be removed. Before leaving the reactor, the gases pass through about 20 feet of vapor space where most of the catalyst drops out. The remaining dust is removed by an inconel cyclone that causes a centrifugal action of the gases, and the catalyst particles drop out. The lower section of the cyclone is steam-jacketed to prevent condensation of reactor gases, with subsequent corrosion taking place.

The catalyst that drops out in the cyclone is blown down to a replaceable blowdown drum. The drum is vented to a furan scrubber packed with ceramic saddles. The dust in this vent stream is scrubbed with water. The blowdown header is a steel pipe.

The cyclone blowdown operation must be carefully done, since the gases in the cyclone are flammable upon air exposure. The blowdown of entrained catalyst particles can set up static electricity generation. During operation, a metered ethylene purge is maintained on the header to fluidize the catalyst. The blowdown header is purged with nitrogen prior to dumping. The procedure for removing this catalyst is discussed in the "Standard Operating Procedure Manual."

j. Reactor Condensing System

The hot gases from the cyclone overhead flow through an inconel header to the primary condenser.

The primary condenser is a vertical upflow shell and tube exchanger with cooling tower water in the shell. All surfaces in contact with the reactor vent gases are graphite or tantalum, while the rest is steel. Graphite cannot withstand temperatures above 338°F; therefore, care must be taken to prevent damage to the exchangers from over-temperature. The bottom tee under the primary condenser is carbon steel lined with tantalum. Tantalum is also heat-sensitive and requires a quenching fluid to keep it cool. The condensed reactor vent flows down through the tee providing the quenching fluid. Whenever there is too little condensate flowing out of the primary, a water flush is provided.

High pressure well water is put into the process side of the primary condenser top head. The top tube sheet of the exchanger has teflon weirs on the top of each tube. The well water is distributed across the entire tube sheet before it flows down through the tubes. This provides an evenly distributed flush down through all the tubes.

The well water flow is remotely controlled by a manual loading station; however, if the gas temperature in the bottom head exceeds a preset temperature, the remote valve is automatically opened wide open. To assure that high pressure well water is available to the flush water valves, a well water booster pump will be running at all times. Remote start switches are provided to start these pumps. These switches are located on the operator interface panel No. 2.

OHC REACTOR CONDENSING SYSTEM

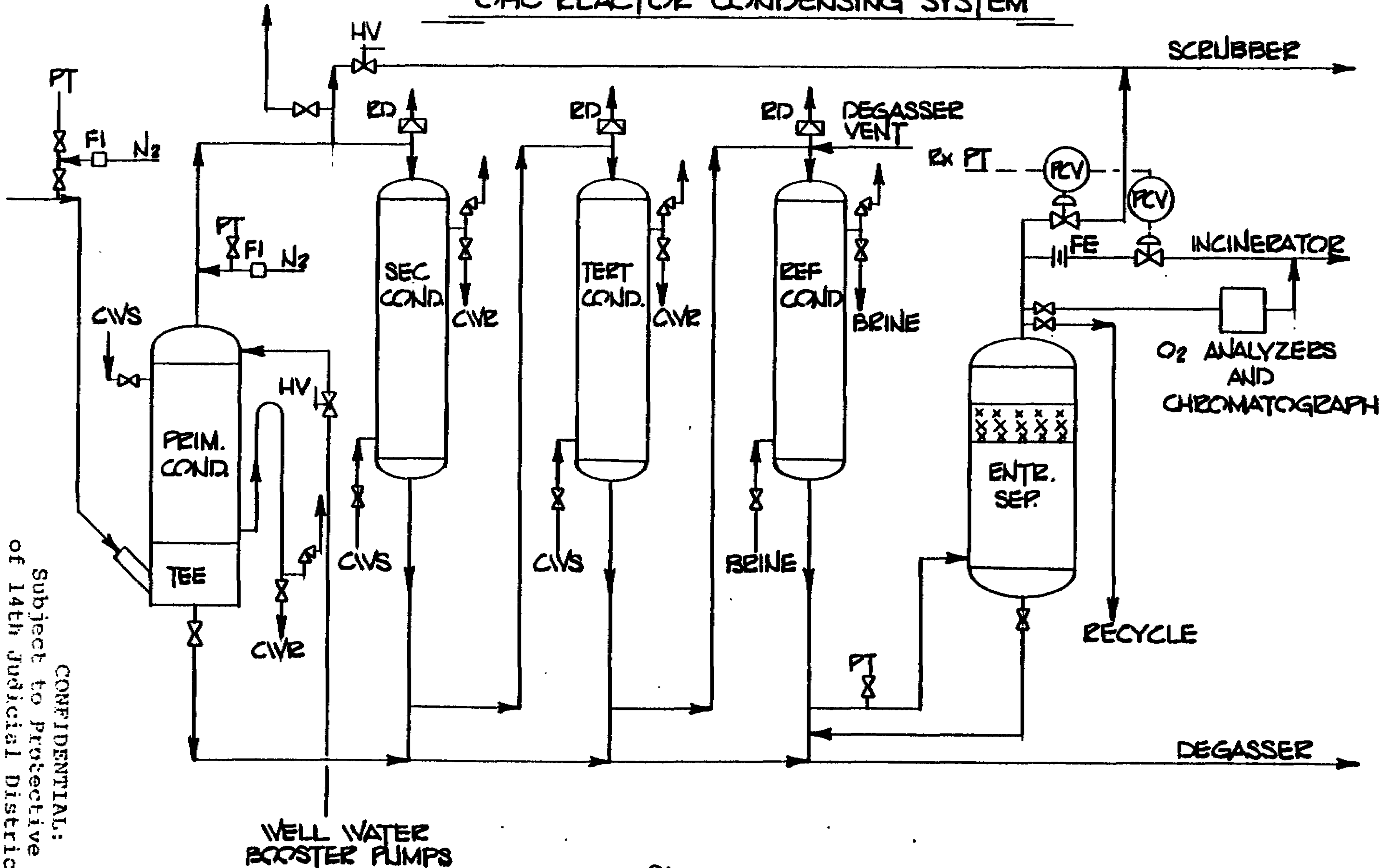

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FIG. VII-7

There are annubar-type flow indicators on the cooling water headers to each graphite heat exchanger in the OHC reactor system. These indicators are used to adjust the cooling water or brine flow through the exchanger. The flow will be adjusted to the design velocity to prevent setting up vibration of the graphite tubes that would cause tube failures.

Pressure transmitters located on the primary condenser inlet and overhead vent headers are provided to detect any restriction that could develop in the condenser or tee. A metered nitrogen purge is maintained on the impulse lines to prevent plugging.

Gases exit the primary condenser through a teflon-lined header, then go to the secondary condenser. A remotely operated automatic vent valve is located on this header to vent the reactor off-gas during reactor heat-up and initial feed addition. The gases are vented to a large "start-up" atmospheric scrubber.

During start-up, when a high inert load exists, an excessive pressure drop will take place in the condensers. An 8" ball valve is also provided to vent the system to the atmosphere while charging catalyst to the reactor from hoppers.

The secondary condenser is a vertical downflow exchanger very similar in construction to the primary condenser, and has graphite tubes cooled by cooling tower water. The condensate and uncondensed reactor vent flow out the bottom of the secondary condenser. The uncondensed vent gases flow to the top of the tertiary condenser through a teflon-lined header.

The tertiary condenser is also a vertical downflow exchanger with graphite tubes cooled by cooling tower water. The condensate and uncondensed reactor vent flow out the bottom of the tertiary condenser. The uncondensed vent gases flow to the top of the refrigerated condenser.

The refrigerated condenser is a vertical downflow exchanger with graphite tubes cooled by refrigerated brine. The condensate and uncondensed reactor vent gases flow out the bottom of the condenser.

k. Condensate Collection

The condensed crude out of each condenser is collected in a common teflon-lined header and is fed to a teflon-lined reactor degasser. Some dissolved gases are vented from the degasser and are equalized into the inlet of the refrigerated condenser. Condensed crude flows from the degasser through a level-control valve to the flasher and then to the condensed crude processing system.

The uncondensed reactor vent gases exiting the bottom of the refrigerated condenser are essentially free of EDC, but contain both ethylene and oxygen. The gas flows to a teflon-lined entrainment separator where entrained liquid is removed. Most of this gas goes back as recycle to the feed system. Part of the gas is vented to the incinerator and is called the normal purge vent. The amount of vented gas is controlled automatically so as to maintain a set back pressure on the reactor. The pressure controller for the pressure-control valve receives its pressure indication from a transmitter located on the reactor vent header upstream of the cyclone. The impulse line to the transmitter is purged with nitrogen to prevent plugging. This pressure controller is adjusted with varying production rates so as to maintain the minimum 1.0 ft/sec. superficial gas velocity in the reactor.

A second automatic vent valve is also controlled by this pressure controller. The second vent valve will start to open if the vent flow becomes too great for the normal vent valve to handle. The second vent valve discharges the vent gases to the atmospheric scrubber. Vents that normally go to the incinerator are automatically diverted to the atmospheric scrubber during incinerator shutdown.

I. <u>Reaction/Control</u>

The reaction of HCl, ethylene, and oxygen in the presence of catalyst produces EDC, water and heat. The major portion of the reactor vent is recycled to recover the ethylene. Oxygen is reacted with HCl to liberate chlorine that can be further reacted with the ethylene to form EDC. This reaction is known as the "Deacon" reaction.

Several variables enter into the performance characteristics of an OHC reaction. The basic reactions are:

1) The Deacon reaction:

$$2\ HCl + 1/2\ O_2 \xrightarrow{\text{Catalyst}} Cl_2 + H_2O$$

2) The subsequent chlorination reaction:

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2(EDC)$$

Reaction "1" must be going before chlorine is available to give reaction "2". Other undesirable reactions also occur:

3) "Burning" - complete:

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

"Burning" - Partial:

$$C_2H_4 + 2\ O_2 \longrightarrow 2\ CO + 2\ H_2O$$

Burning of EDC may also occur:

$$C_2H_4Cl_2\ \ 5/2\ O_2 \longrightarrow 2\ CO_2 + H_2O + 2\ HCl$$

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4) EDC Chlorination:

$$C_2H_4Cl_2 + Cl_2 \longrightarrow 1,1,2\ C_2H_3Cl_3\ (TCE) + HCl$$

5) Formation of carbon tetrachloride is another undesirable side reaction.

The Deacon reaction follows the basic law of chemistry which states that any excess of reacting components (those on the left hand side of the equation) will tend to drive the reaction of the remaining reacting components to completion. Thus, if an excess of oxygen is fed to the reactor with respect to the HCl, the HCl will tend to be more completely reacted. If very large excesses of O_2 are fed, essentially all of the HCl will be used up; however, the formation of CCl_4 then becomes excessive. Thus, a balance must be made between HCl loss due to incomplete reaction and C_2H_4 loss due to CCl_4 formation. Our plant design calls for 11.5% (on a mole or volume basis) excess oxygen (above theoretical for Deacon reaction) in the feeds when recycling gas to the reactor.

Carbon tetrachloride is formed by too large an excess of oxygen in the presence of the organic within the reactor. Carbon tetrachloride is removed from the EDC in the lights still. (See the EDC Purification System section of this manual.)

The amount of TCE formed by reaction "4" is controlled by the reactor temperature, the amount of EDC in the recycle, and the percent ethylene conversion per pass.

The OHC reactor will operate within an average temperature range that will minimize TCE formation at the desired production rates. The Dowtherm cooling capacity will determine the optimum operating condition. Increasing the temperature will result in higher TCE formation. Lowering the temperature will decrease TCE formation. When operating at maximum cooling capacity, a cut in reactor rates will be necessary to lower the temperature. To protect against loss of reaction, the reactor temperature should never be allowed to go below 490°F; a shutdown system provides protection against this occurring.

The amount of EDC in the recycle stream is a function of the exit temperature of the refrigerated reactor condenser. The refrigerated reactor condenser is designed to lower the reactor vent temperature sufficiently to insure that the recycle EDC content is low.

The make-up ethylene feed is adjusted to obtain an ethylene content in the recycle of approximately 45%. By controlling the percent ethylene in the recycle at this value, a lower recycle gas flow will result for a specified percent conversion of ethylene to EDC per pass through the reactor. The smaller volume of recycle gas results in improved condenser efficiency, so that the amount of EDC in the recycle is decreased, thus lowering the rate of TCE formation.

Other than TCE, Chloral (CCl_3CCHO) and carbon tetrachloride will be the largest organic impurities. The chloral leaving the reactor is destroyed by treatment with caustic. (See the Chloral Treatment and Aqueous System sections of this manual.)

m. Operation/Control

The operation of the reactor-condenser-recycle system should be considered all together because of the close interrelation of variables involved. Any changes in the reactor feed rates will cause changes in the recycle gas composition. The condensing system must be properly operated in order to help maintain reactor EDC purity. A routine sample of the condensed crude and aqueous-out of the reactor degassers will be analyzed to help maintain reactor EDC purity.

n. HCl Feed/Control

The operating rate of the OHC plant will be fixed by the HCl available from the producing plants. The HCl flow to the OHC plant will be maintained constant with the exception of major rate changes.

o. Oxygen Feed/Control

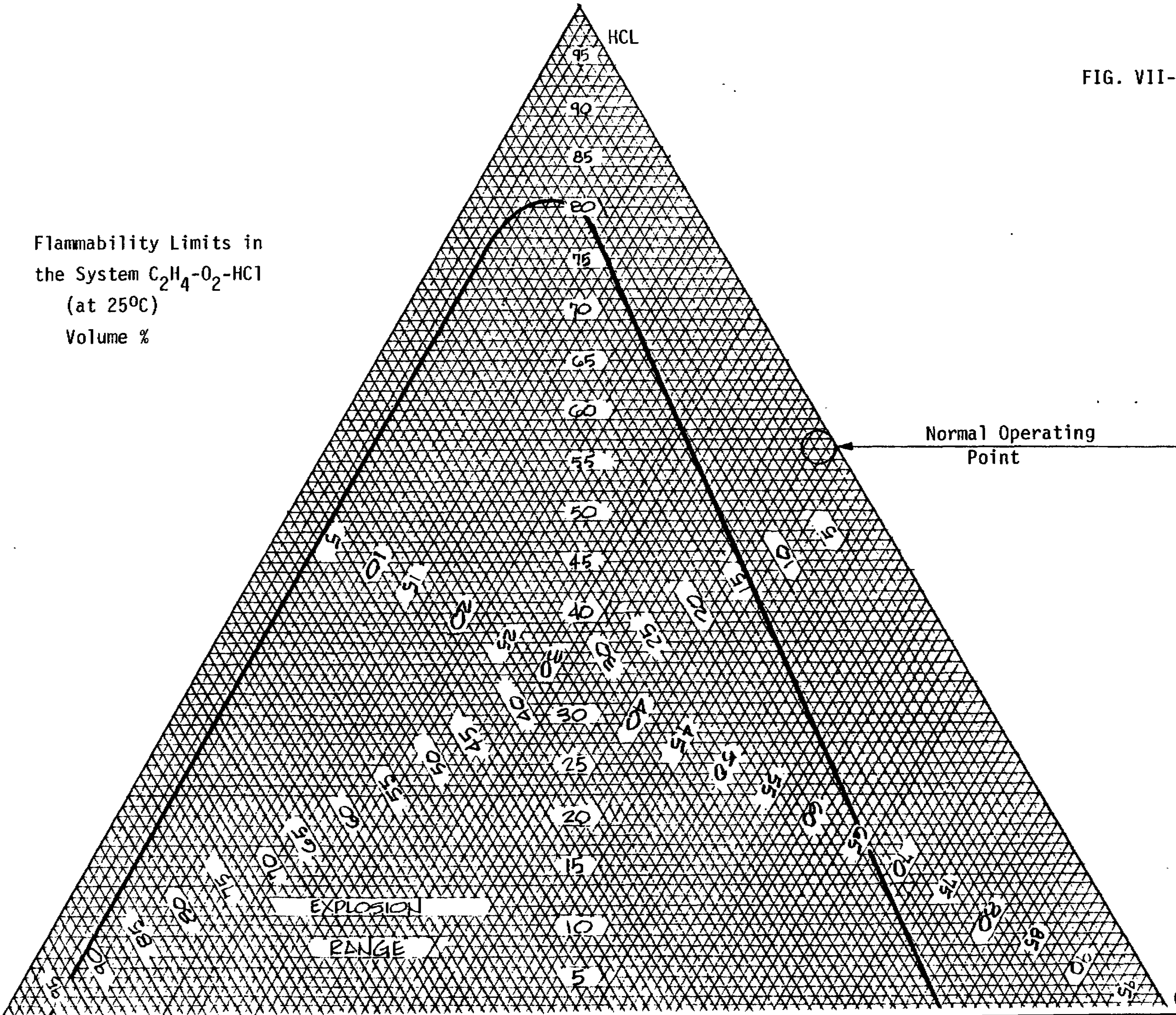
It is imperative that there never be too much O_2 in relation to HCl in the reactor feeds. This is true because unreacted O_2 in too great an excess would drive the system into the explosive range in the reactor vapor space or condensing system. For this reason, each reactor O_2 and HCl feed is ratio-controlled. If HCl flow should drop (which would increase O_2 concentrations in the system), the O_2 controller would sense the temporary flow ratio change and automatically decrease the O_2 flow. It is extremely critical that care is taken in order to keep the system out of the explosive range.

Normal control of oxygen feed while operating outside the explosive range can be done by considering the HCl utilizations and the analysis of the crude product. High oxygen in the recycle, combined with very high HCl utilizations and excessive carbon tetrachloride in the product all are indications of too much oxygen feed. Low HCl utilizations combined with exceptionally low oxygen in the recycle are indications of too little oxygen feed.

The OHC reactor system is designed to operate at an HCl utilization of at least 98.5%. Lower HCl utilizations can be compensated for by increasing the O_2: HCl ratio (assuming O_2 content in the system is within the above-described limits). HCl yields also suffer at higher ethylene conversions. The HCl utilization is determined by analyzing the acidity in the condensed aqueous phase of the condensed crude sample. A high HCl utilization is very important to the economics of this process, because an overall low chloride cost is thus obtained.

FIG. VII-8

Flammability Limits in the System C_2H_4-O_2-HCl (at 25°C) Volume %



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p. Recycle/Control

The recycle gas stream is perhaps the most hazardous stream in the OHC plant. Most of the condensible components have been removed in the condensing system; thus, the oxygen and combustible components are concentrated in the vent streams. The most important operating point to remember in the OHC plant is to keep this stream out of the explosive range. An explosive curve can be found in this manual and the "Standard Operating Procedures Manual". The guide to be used as to explosibility of this stream is the oxygen content. The maximum oxygen content will be as indicated by the explosive curve. This safety margin will give the operator time to correct the cause of high oxygen before reaching the danger point.

The oxygen concentration must be closely watched for safety as well as process control reasons. It is stressed that no feed adjustment should be made that will bring the oxygen content of the recycle into the explosive range. Oxygen content can be quickly reduced by increasing either ethylene or nitrogen, or by decreasing oxygen. The oxygen content of the recycle gas is continuously analyzed by 3 oxygen analyzers. The samples are taken off the entrainment separator vent just downstream of the recycle header take-off. The shutdown system provides protection against high oxygen in the vent. A more complete analysis of the recycle gas is determined by a continuous gas chromatograph. The chromatograph analyzes for ethane, carbon dioxide, ethylene, oxygen, nitrogen and carbon monoxide. The primary function of the chromatograph is in control of reactor feeds. It can also be a check on the oxygen analyzers.

As a further check on the content of the recycle gas stream, the operator is required to run samples on a gas chromatograph periodically. When an oxygen analyzer or on-stream chromatograph is out-of-order, this alternate test will be run at a designated frequency as outlined in the "Standard Operating Procedures Manual".

The composition of the recycle stream must be kept in the non-explosive range. In addition, it is an important indication of the reactor operation; the recycle stream composition is therefore closely followed. The recycle analyses, vent purge rate, crude product composition and HCl utilizations normally give enough information to specify any feed adjustments to the reactor. Operation at design recycle composition, purge rate, and HCl utilizations is a strong indication that the feeds are properly balanced.

The amount of chlorinated organics in the recycle will be dependent upon the exit temperature of the refrigerated reactor condenser.

q. Ethylene Feed/Control

The ethylene feed rate will be mainly dependent upon HCl feed rate, utilization, ethylene in the recycle stream, and vent purge rate. At fixed HCl feed rate and utilization, the burning should be relatively constant. Thus, the CO_2 and CO inert load should be fixed. These inerts are purged from the system and vented to the incinerator at a rate sufficient to keep the reactor system pressure constant. Since this vent stream is simply a side stream off the recycle gas system, it must carry ethylene and the other recycle gas components with it. Therefore, the ethylene feed rate is controlled at a rate which maintains a satisfactory recycle composition. High inerts in the feed (ethane, nitrogen, etc.) require a high vent rate and subsequent high ethylene loss.

Nitrogen purges on equipment, such as pressure transmitter impulse lines and catalyst addition valves, should be maintained at minimum, since any additional increase in inert loading results in more ethylene loss.

A further consideration in C_2H_4 feed rate lies in the actual composition of the recycle stream. The critical importance of maintaining a non-explosive gas mixture will override any economic consideration. In other words, if the O_2 content of the recycle gas increases to a dangerous range, do not hesitate to add ethylene to move away from this range (in addition to a decrease in oxygen). The response of the percent oxygen in the recycle is much greater due to an ethylene increase than an oxygen decrease.

The ethylene feed will be adjusted to allow the ethylene content in the recycle stream to line out at 45%. If the ethylene drops below this value, enough excess ethylene will not be present in the reactor to allow good HCl utilizations and high purity product. Too little ethylene feed will cause the ethylene to be consumed from the recycle stream. A decrease in ethylene in the recycle combined with a decreased purge means that too little ethylene is being fed. A slight increase in ethylene feed will correct this situation. An increasing ethylene content in the recycle with an above-design purge means that the ethylene feed is too high, and too much ethylene is being lost.

It is possible that the ethylene concentration will change because of other reasons. A sudden increase in the inert loading will cause the ethylene composition to decrease. This will be associated with an increased purge. Thus, a decreasing ethylene concentration with an increasing purge means that some other non-reactive gas is entering th system.

r. Reactor Shutdown System

Each reactor is equipped with a shutdown system that is actuated automatically or by board-mounted pushbuttons.

A general description of the OHC reactor shutdown system is as follows: The OHC Reactor Shutdown System is provided to stop ethylene, recycle and oxygen flows, and keep the reactor fluidized with HCl and nitrogen in the event that undesirable conditions develop during operation. The conditions to be protected against are:

1) Operating the reactor with an imbalance of feeds.
2) Operating the reactor at temperatures lower than that required to sustain a reaction.
3) Operating the reactor with too high of an oxygen excess in the reactor condensing system.
4) Defluidization of the reactor catalyst bed as a result of low feed flows which would cause plugging of oxygen and mixed feed orifices.

By providing protection against the above-listed circumstances, protection is then afforded against pressure releases, fires within the reactor vapor space and equipment failures.

When the shutdown system trips, the following happens:

1) The oxygen and ethylene feeds are stopped by closing the flow-control valve and the automatic block valve.

2) Nitrogen fluidization to the oxygen header is started by closing the automatic bleed valve, opening the automatic flow-control valve to a preset rate, and opening the automatic block valve.

3) The recycle feed is stopped by closing the flow-control valve on the het and the automatic block valve.

4) The HCl flow is not stopped, since it is an acceptable fluidizer and an inert gas, which helps to maintain the system out of the explosive range.

5) The Sabine water flow to the atmospheric scrubber is increased to a preset amount to prepare the scrubber to receive the higher vent flow.

Detailed descriptions of the shutdown system are covered in the "Standard Operating Procedures Manual".

s. <u>HCl Source</u>

Although the primary HCl feed will be from the VCM section of the VCM II plant, the OHC reactors are also capable of receiving HCl from the HCl distribution header in Plant B. The OHC section in VCM II could start up without the VCM section HCl. The rates at which it could operate would depend on the amount of HCl available and EDC storage capacity; this is generally true with normal operation conditions also.

When the OHC section of VCM II is started up or shut down with the HCl system floating on the Plant B system, good communication between the operating units must be maintained. This is essential to prevent operating upsets and avoid continuous venting of HCl to the scrubbers or incinerator.

t. Start-up

The actual start-up of the OHC reactor with feed introduction must be based upon the basic criteria for the operation of the plant; that is, the system, at all points, must be operated with non-explosive mixtures. Further, this type of operation requires very thorough checks and rechecks during all phases of operation. As described previously, the criteria for determining whether the mixtures are safe is the oxygen content - the concentration of oxygen must be maintained below the maximum as indicated by the explosion curve.

The OHC reactor is started up by first fluidizing the reactor catalyst with nitrogen. The catalyst is heated by circulating Dowtherm through a Dowtherm heating furnace.

During the early stages of the reactor start-up, the main vent stream will be through the MLS vent valve immediately downstream of the primary condenser. A small flow may go forward through the condensers and is vented to the start-up scrubber by the large reactor system pressure control valve system. The reactor pressure control valves should be open on manual. The downstream block valve on the small pressure control valve should be closed.

The nitrogen fluidization is phased out as the reactor feeds are put into the reactor. The HCl feed is put in first, ethylene second, and then oxygen. The recycle is put in after the vent stream has been analyzed.

u. Shutdown

Shutdown of the OHC plant will be necessary for major maintenance jobs and emergency situations. During any shutdowns, the major operating points to maintain are non-explosive atmosphere in the vessels and lines, and adequate gas velocities in the reactor for good fluidization.

Reactor pressure changes and feed changes should be slowly and evenly made to prevent excess catalyst carryover. The reactor or Teflon-lined pipe is not designed for full vacuum; use N_2 to avoid this condition.

The general scheme of reactor shutdown will be the replacement of all feeds with nitrogen to purge oxygen, HCl, and organics from the system.

The reactor feeds are taken out of the reactor and replaced with nitrogen; recycle first, then oxygen, ethylene and then HCl, in that order.

Detailed descriptions of OHC reactor operation, start-up and shutdown can be found in the "Standard Operating Procedures Manual".

4. Condensed Crude Processing System:

The purpose of the condensed crude processing system is to remove dissolved gases and aqueous (water) formed in the two OHC reactor systems.

The dissolved gas is removed by lowering the pressure on the condensed crude, allowing the gas to flash more readily. The gases that are flashed off are vented to the OHC Process Vent System.

The aqueous is removed by retaining the condensed crude in a vessel long enough to allow the aqueous to phase out of solution. The aqueous that phases off gravity flows to the aqueous system.

The condensed crude processing system is a relatively easy method of removing most of the dissolved gas and aqueous from the condensed crude. This allows the chloral treatment and drying systems to utilize fewer pieces of equipment with less operating cost.

The condensed crude processing system begins at the discharge side of the reactor degasser level-control valve. The system includes the

OHC CRUDE PROCESSING AND CHLORAL TREATMENT SYSTEMS

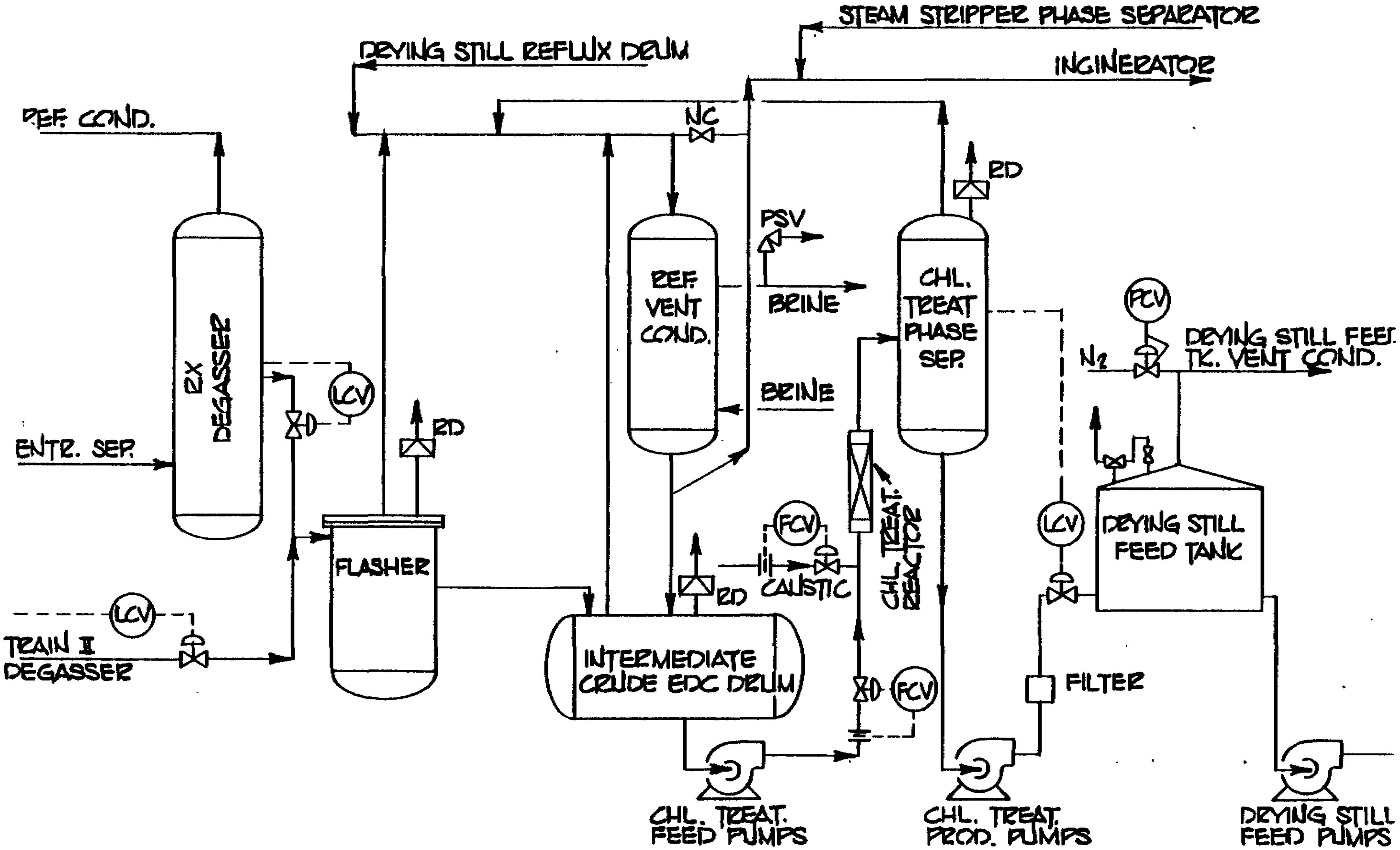

FIG. VII-9

flasher, the intermediate crude EDC drum, and the chloral treatment feed pumps.

The system is protected against over-pressurization by a rupture disc on the flasher, designed to relieve at 50 PSIG, and a rupture disc on the intermediate crude EDC drum designed to relieve at 30 PSIG.

The condensed crude from the reactor degassers in each OHC reactor system collects in a common header. The crude flows into the teflon-lined flasher.

The system pressure at this point is reduced to a few pounds. When the crude enters the flasher, the gases flash off and are vented from the top of flasher through a header, then to the process vent system.

The liquid from the flasher flows through a header to the glass-lined intermediate crude EDC drum. The intermediate crude EDC drum also receives condensate from the process vent system, recovered heavy organic from the covered separator, and organic recovered from the aqueous system effluent.

The crude organics and aqueous are allowed retention time to separate in the intermediate crude EDC drum. The crude organics, being heavier, sink to the bottom and the lighter aqueous phases off and forms a layer on top.

The level at which the two layers separate is called the interface level. Sight glasses are provided for monitoring this level. A level transmitter will monitor the organic level only.

The crude organics are pumped from the bottom of the intermediate crude EDC drum to the chloral treatment system through teflon-lined piping. The rate which the crude is pumped out is flow-controlled. This flow will be set to maintain the organic or interface level at 50% of the total sight glass span.

The crude EDC is pumped to the chloral treatment system by special corrosion-resistant Duriron pumps. These pumps are constructed of Durcon 6, an epoxy resin which is resistant to acid and abrasive fluids.

The aqueous will accumulate on top and overflow through a furan header to the aqueous system

The vent from the intermediate crude EDC drum flows through a furan header to the process vent system.

Drawings of the condensed crude processing system can be found on process flow sheet 56A-10005 and P & I drawings 56A-10031, 56A-10032.

5. Chloral Treatment System

The purpose of the chloral treatment system is to remove chloral, formed in the OHC reactor system, from the crude EDC.

Chloral (CCl_3CHO) is an oxygen-bearing compound that inhibits the cracking of EDC to vinyl chloride. The chloral is formed in the reactor in small quantities. It would be very difficult to remove from EDC by distillation, but it is readily reacted with caustic soda to form water soluble sodium formate (NaOCOH) and chloroform $CHCl_3$. The sodium formate is removed from the EDC in the aqueous phase. Chloroform is then relatively easy to remove by distillation.

The chloral is distributed between the organics (EDC) and aqueous phase in the intermediate crude EDC drum. Some is removed with aqueous draw-off. The chloral that remains in the EDC is reacted with caustic soda to form sodium formate and chloroform by the following chemical reaction.

$$\underset{\text{Chloral}}{CCl_3\,CHO} + \underset{\text{Caustic Soda}}{Na\,OH} \longrightarrow \underset{\text{Sodium Formate}}{NaHCO_2} + \underset{\text{Chloroform}}{CHCl_3}$$

The chloral system begins at the discharge of the crude EDC feed flow control valve. The system ends at the discharge of the drying still feed tank. The system includes the chloral treatment reactor, chloral treatment phase separator, chloral treatment product pumps, drying still feed filters, and the drying still feed tank. A caustic feed system consisting of a storage tank and caustic feed pumps are also included.

The system is protected against over-pressurization by a rupture disc on the phase separator designed to relieve at 30 PSIG. A pressure safety valve on the drying still feed tank is designed to relieve pressure at 1.7 PSIG and 3 oz. vacuum.

The crude EDC, bearing chloral, is pumped through a chloral treatment reactor. Diluted caustic soda enters the EDC steam just before the crude EDC enters the reactor.

The reactor is a teflon-lined 3" carbon steel spool 4' long. It has teflon baffles inside for mixing. The crude EDC enters through teflon-lined pipe. The caustic soda enters through carbon steel pipe. The discharge header on the reactor is carbon steel.

The caustic soda, cell liquor, enters the system from Plant B-1 and is fed into a caustic storage tank. (See the cell liquor system section of this manual.)

Caustic soda is pumped to chloral treatment from a caustic storage tank. Cell liquor is diluted with condensate in the caustic tank before being pumped to chloral treatment. Regular cell liquor (10-12% NaOH) is strong enough to give two potential problems if mixed with EDC; first, emulsion formation with EDC; and, second, it is so close in specific gravity with EDC that it might invert with EDC in phase separation. For these reasons, the cell liquor is diluted by one-half by holding equal settings on the water and cell liquor rotameters. These flows must be manually set so as to maintain the tank level at about two-thirds full. The caustic is checked for strength periodically, and any adjustments necessary to hold 5-6% NaOH made. If inversion does take place, then further dilution of the caustic may be necessary.

The reacted caustic and chloral-free EDC solution flow into the chloral treatment phase separator. The aqueous layer overflows to the aqueous system. The crude EDC is pumped off the bottom at a rate automatically regulated to control the interface level in the phase separator.

The phase separator is vented to the process vent system.

The level-control valve must maintain the interface level in the phase separator, such that only the EDC is pumped to the drying still feed tank. There are two filters, one being a spare, that the EDC flows through before the level-control valve. These are to filter out catalyst and sludge that could drop out in the chloral treatment phase separator and would accumulate in the drying still feed tank and eventually in the drying still.

The crude EDC is sampled on a routine basis and analyzed for chloral. The sample is taken at the sampling connections provided on the discharge piping of the chloral treatment product pumps. If the chloral level is found to be too high, the crude EDC can be reworked to the intermediate crude drum for reprocessing.

The drying still feed tank is padded with nitrogen through a pressure-control valve. The tank is vented, through another pressure-control valve to the drying still feed tank vent condenser. The uncondensed gases from the vent condenser are routed via the EDC storage vent compressors to the incinerator. The condensate from the DH feed tank vent condenser along with the condensate from the EDC storage vent condenser and the vent compressor suction drum are returned to the DH feed tank.

Since the EDC is still wet at this point, a layer of water will accumulate on top of the EDC. This must be checked routinely and phase water drawn off and pumped to the aqueous surge drum. The EDC is pumped from the drying still feed tank to the drying still through a flow-control valve.

Since the piping to the phase separator, drying still feed tank, and drying still are all constructed of carbon steel, it is important to maintain the proper EDC to caustic feed ratio, not only for chloral control, but for pH control also. This ratio must be maintained so there will always be an excess of caustic.

Drawings of the chloral treatment system can be found on P & I Drawings 56A-10033 and Process Flow Sheet 56A-10005.

6. <u>Drying Still System</u>

The purpose of this system is to remove water from the crude EDC to less than 20 parts per million. Crude EDC is fed to the liquid phase EDC reactor. Wet crude EDC will cause loss of reaction in the LP-EDC reactor and corrosion problems. The water is removed by heating the wet crude EDC in the drying still, removing the water out the top of the still.

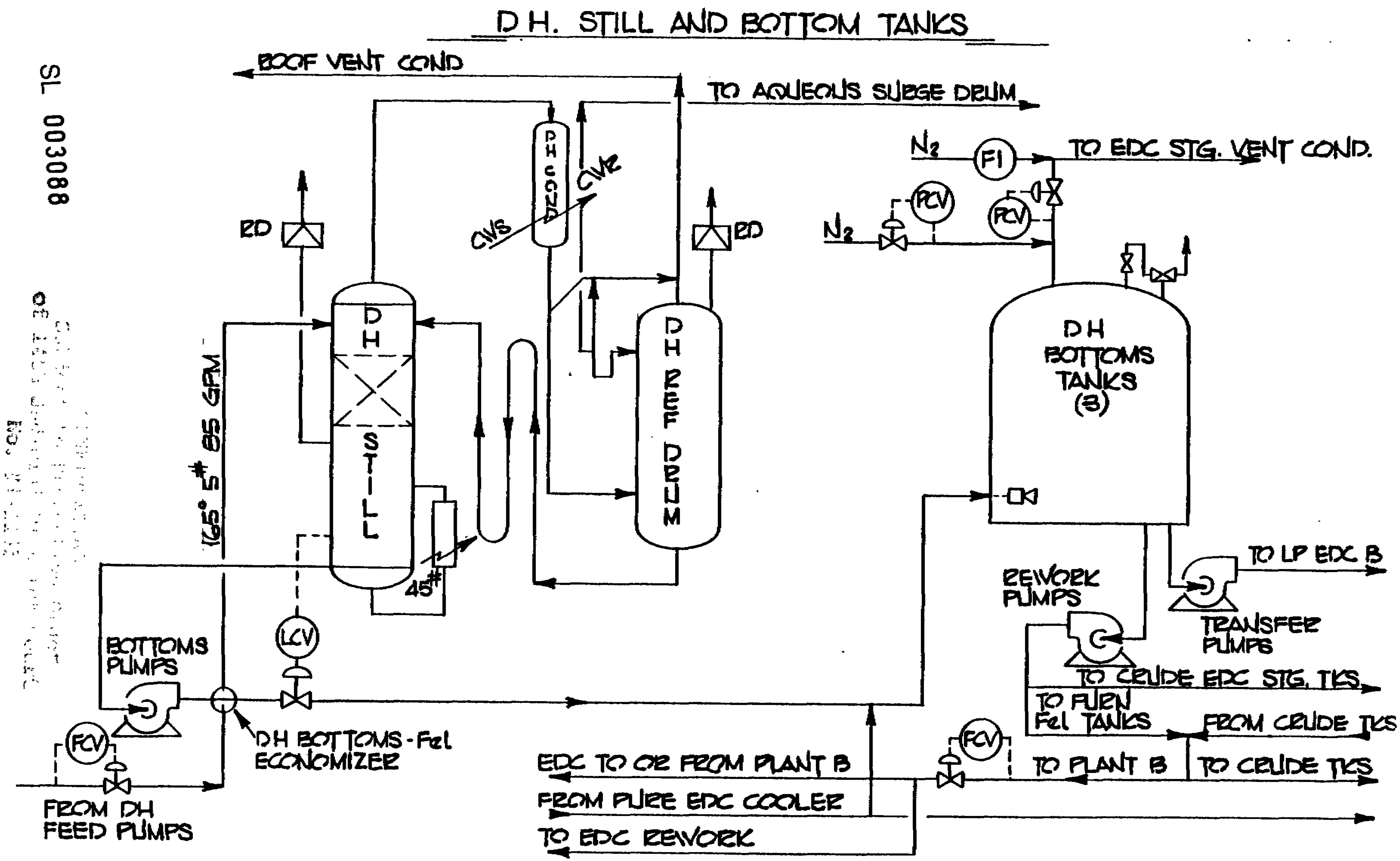

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FIG. VII-10

The drying still system begins at the discharge of the drying still feed tank and ends at the inlet to the drying still bottoms tank. The system consists of the drying still feed pumps, feed bottoms economizer, drying still, reboiler, condenser, reflux drum, and the drying still bottoms pumps.

The crude EDC feed is preheated before entering the drying still by an economizer. The economizer is a heat exchanger that uses the hot drying still bottoms flow to heat the crude EDC feed.

The feed enters the top of the drying still and is distributed over a packed section by a weir-trough distributor plate. The EDC flows down through the packing to the bottom of the column, where it is heated to its boiling point by a steam-heated reboiler.

The reboiler uses 45 PSIG steam that is flow-controlled at a rate sufficient to maintain the desired rate of EDC boilup. The EDC vapors flow back up the column, stripping water from the down-flowing material. The water and EDC vapors flow out the top of the column and through the drying still condenser. The drying still condenser is a vertical downflow Karbate heat exchanger that uses cooling tower water for cooling.

The condensed EDC and water flow to the drying still reflux drum, where the water phases out and overflows to the aqueous surge drum. The EDC flows out the bottom of the reflux drum and back to the column by gravity as reflux. There is an upward loop in the reflux return line designed to hold a sufficient level in the reflux drum to allow retention time for the water to phase off.

Vents from the reflux drum, the reflux return line, the water overflow line, and the condenser condensate line are equalized and vented to the incinerator via the vent header.

The drying still bottoms flow through the economizer and a level-control valve at a rate sufficient to maintain an operating level in the column. The flow goes to one of three drying still bottoms tanks.

Because the drying still, reboiler, and packing are carbon steel, precautions must be taken to protect the equipment from corrosion. The drying still overhead, at times, can become highly acidic, and should never be allowed to settle and accumulate in the column when it is shutdown.

There is an inline moisture analyzer that will constantly monitor the drying still bottoms stream for water; high moistures will be alarmed in the control room. The drying still bottoms flow is sampled at the sampling connections provided on the bottoms pumps discharge piping. The sample will be analyzed for moisture and results compared to the on-stream analyzer.

The bottoms flow may be recycled back to the drying still feed tank when needed, such as for start-up or reworking high moisture crude EDC.

The drying still has a steam shutdown system provided to stop steam flow to the reboiler if the bottom pressure on the column becomes too high. The shutdown system causes the steam flow-control valve to fail closed by de-energizing a dump solenoid in the air supply line to the valve.

The shutdown system is provided to prevent the still from being operated at excessive pressures that could result in releases of organics to the atmosphere, damage to equipment, and off-spec product. The drying still is also protected against over-pressurization by a rupture disc set to relieve at 30 psig.

When a drying still steam shutdown occurs, the crude EDC feed is not affected. However, depending on the cause of the shutdown, the crude EDC feed will have to be shut off or cut back and the bottoms recycled back to the feed tank.

The drying still feed tank has enough storage capacity for the OHC reactor systems to contunue to run several hours without the drying still operating. Thus, the OHC reactor systems can be started up before the drying still system. Normally, the drying still system will be on recycle before the reactor systems are started up.

Drawings of the drying still system can be found on process flow sheet 56A-10005 and P & I drawing 56A-10034.

AQUEOUS TREATMENT SYSTEM

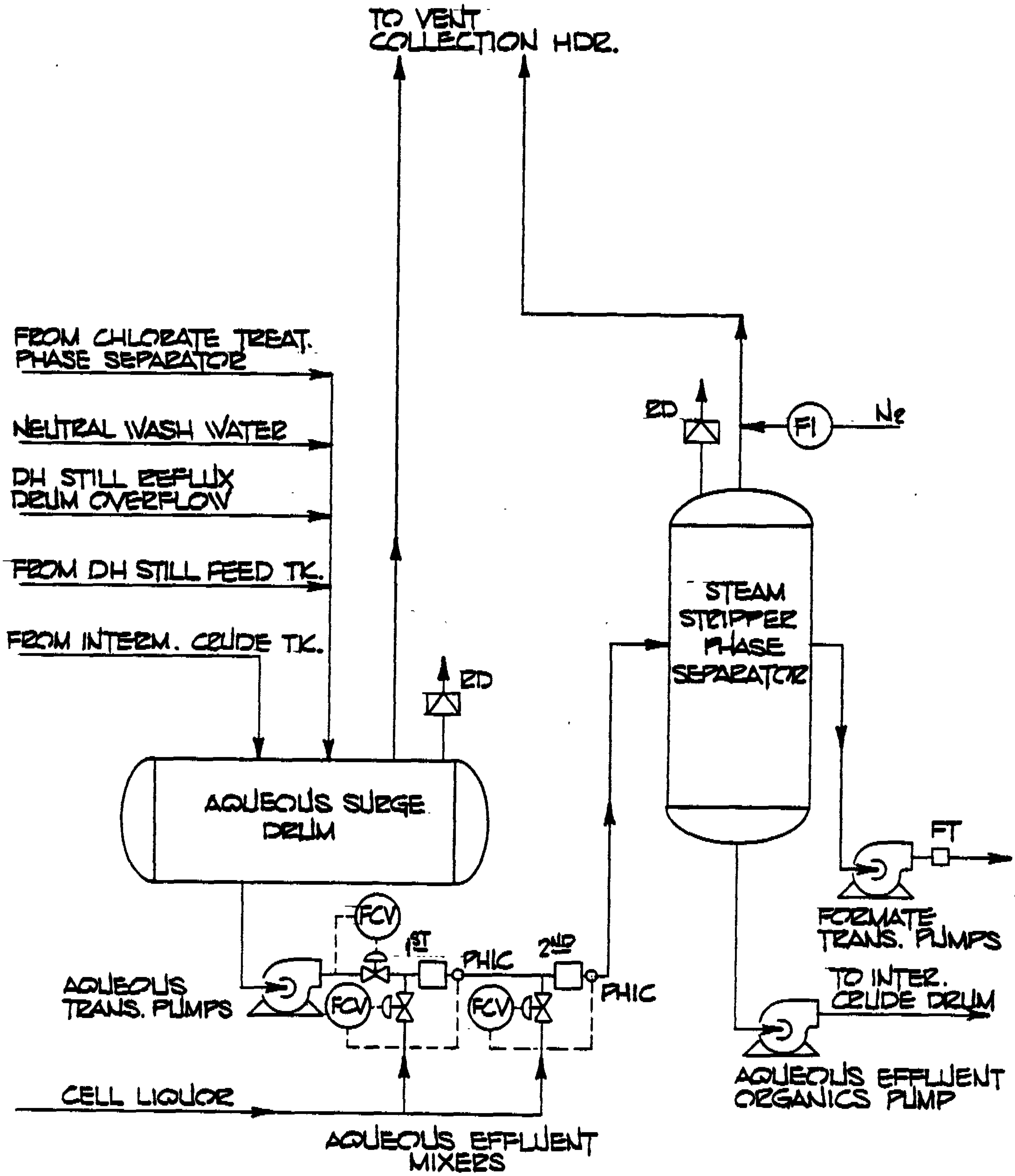

FIG. VII-11

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7. Aqueous System

The purpose of the aqueous system is to collect the various aqueous streams, treat with caustic for chloral removal and neutralization, and reclaim entrained organics. The system consists of the aqueous surge drum, first and second stage effluent mixers, and a phase separator.

The various aqueous streams are first collected in the aqueous surge drum. These streams are the chloral treatment phase separator overflow, the drying still reflux drum overflow, the intermediate crude EDC drum aqueous drain-off, the drying still feed tank drain-off, and the VCM neutralizer wash water. Most of these streams are acidic and very corrosive. For this reason the aqueous surge drum is made of furan and the associated piping is furan or lined pipe. Some neutralizing will take place in the aqueous surge drum, since the chloral treatment phase separator overflow has already been neutralized and the VCM neutralizer wash water will contain caustic. The aqueous surge drum is vented to the incinerator. The aqueous surge drum is protected from over-pressurization by a rupture disc designed to relieve at 14 PSIG.

The aqueous is pumped off the bottom of the aqueous surge drum through two effluent mixers. Before entering each mixer, cell liquor is added to the stream. The cell liquor is pumped into the stream by cell liquor booster pumps. The aqueous mixers are static mixers made from teflon-lined pipe with Kynar elements.

The aqueous rate to the effluent mixers is flow-controlled at a rate sufficient to maintain an operating level in the aqueous surge drum. The cell liquor feed before the first stage effluent mixer is flow-controlled. This flow is ratio-controlled by the aqueous flow. This ratio will be set to maintain a desired pH on the first stage mixer outlet. An inline pH meter monitors this stream. The pH sample is taken by throttling the outlet valve on the mixer to force a portion of the flow through the pH meter. The cell liquor feed before the second stage effluent mixer is pH-controlled by another inline pH meter on the second stage outlet. The piping and equipment downstream of the mixers is steel, so complete neutralization must take place in the effluent mixers.

The neutralized aqueous is fed to the stream stripper phase separator. The entrained organics settle out in the phase separator and are pumped to the intermediate crude EDC drum. The aqueous overflow of the phase separator is pumped to Plant B. Any organics that might be carried out with the aqueous are reclaimed in the Plant B steam stripper system.

The phase separator has a sight glass and level transmitter located in both the top and bottom sections. The transmitters provide level indications and alarms of both sections to the control room.

The aqueous flow to Plant B is controlled by adjusting a manual block valve on the formate transfer pump discharge. The formate transfer flow indication is transmitted to the control room. The flow rate is adjusted to maintain the aqueous level in the top section of the phase separator.

The bottom level, or interface level, is maintained within the bottom section of the phase separator. This is accomplished by pumping the organics out batchwise. When the organics level in the bottom section alarms high, the pump is started, and the organics are pumped out until a low level alarm is reached. The organics are allowed to accumulate until the operation is repeated. The steam stripper phase separator is vented to the incinerator.

Drawings of the aqueous treatment system can be found on process flow sheet 56A-10006 and P & I drawing 56A-10035.

8. OHC Refrigeration System

The purpose of this system is to provide sufficient cooling to insure complete condensing of crude EDC in the OHC reactor condensing and venting systems. This is done by refrigerating a 25% by wt. calcium chloride brine solution, and circulating it through the reactor refrigerated condensers and the refrigerated vent condenser. Failure to maintain the refrigeration system operating within guidelines will result in costly venting of reclaimable organics to the incinerator.

The brine is cooled by a 130 ton York Refrigeration Unit. The refrigerant used in the refrigeration unit is Freon 22. The system is designed to cool 610 GPM of brine from 40°F to 34°F.

VCM II
OHC REFRIGERATION UNIT

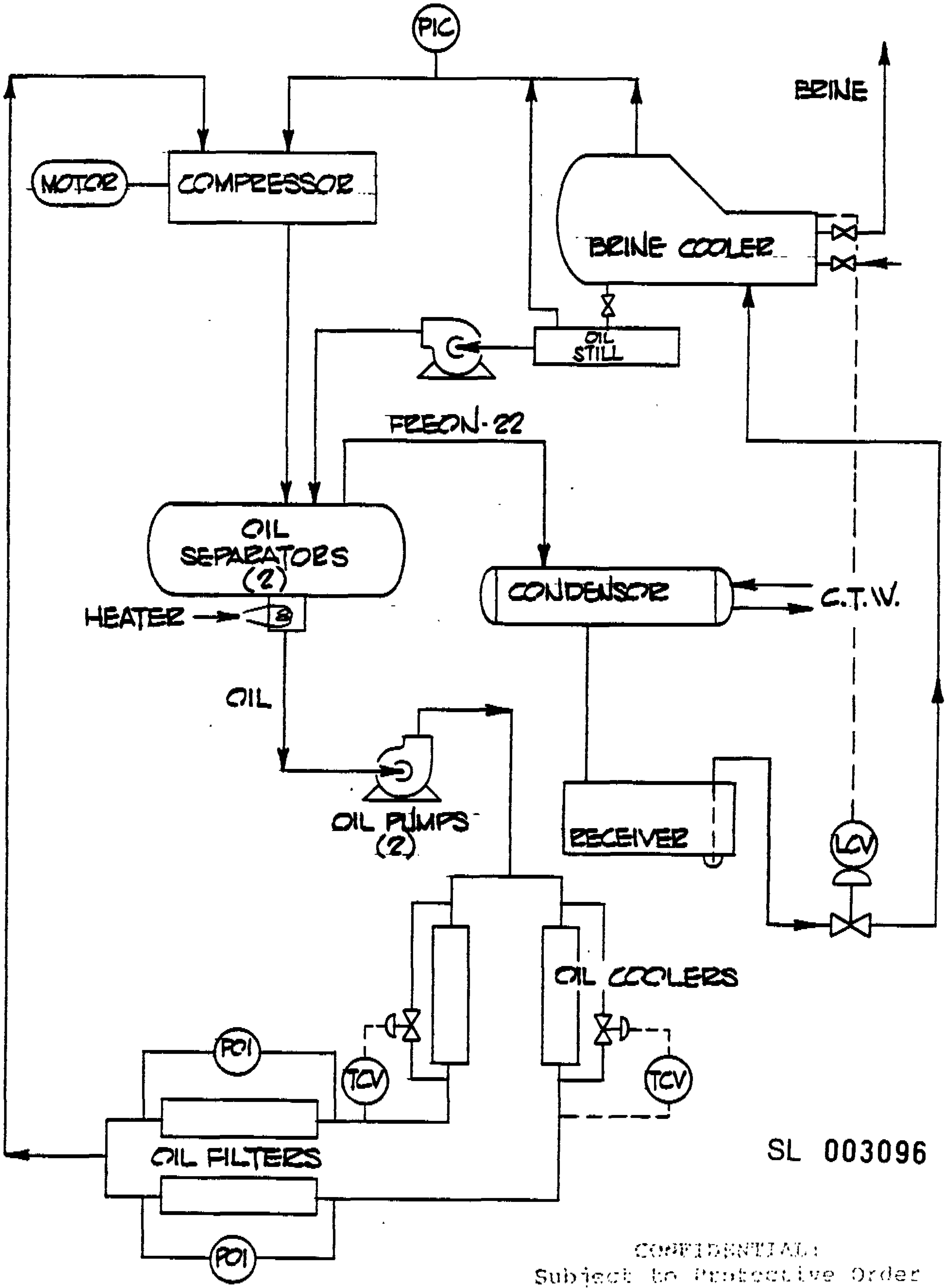

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FIG. VII-12

a. Brine System

The brine system consists of a storage tank, a head tank, circulation pumps, and a brine addition pump. Brine is made up by adding calcium chloride to water. The procedure for making up the brine solution is detailed in the S.O.P. manual. Chemicals are added for corrosion protection. The brine is sampled and analyzed regularly for chromate level, pH, and strength to determine the freezing point. If the calcium chloride strength is allowed to get too low, the brine could possibly freeze in the brine cooler and damage the tubes.

Once all the piping and head tank are filled, the storage tank is isolated from the system. A good operating level is to be maintained in the brine head tank at all times to assure that air is not pulled into the pump suction. To maintain the level in the head tank, brine can be added as needed, by an air driven brine addition pump, from the brine storage tank.

The brine refrigeration system consists of a brine cooler, a compressor, two oil separators, a freon condenser and a receiver. The oil system consists of 3 oil pumps, 2 oil coolers, 2 filters and an oil still.

The refrigeration system is equipped with safety relief valves to protect equipment from damage due to upsets which could cause overpressurization.

In the refrigeration process, the warm brine passes through the tubes of the brine cooler. The liquid freon, on the shell side of the cooler, removes the heat from the brine. In doing so, some of the liquid freon is boiled off or vaporized. The liquid level of freon in the shell side of the cooler is controlled by a level control valve on the freon inlet to the cooler. The proper control of this liquid level is very important. Although screw compressors can handle more liquid than other types of refrigeration compressors, it has its limits. "Slop-over" from the evaporator caused by operating at too high a level can cause significant amounts of liquid to enter the compressor. The refrigerant level should be set so that the freon just wets the top tubes.

The evaporated freon is drawn from the brine cooler by a Howden rotary-screw compressor. The gas passes through a y-type strainer and a check valve prior to entering the compressor. The purpose of the strainer is to keep trash from entering the compressor. The check valve is necessary to prevent the compressor from turning backwards when it is shut down with high gas pressure at the outlet.

The rotary-screw compressor consists of two intermeshing rotors. The freon gas is drawn in to fill the interlobe space between the adjacent lobes (rotors) at the inlet port. As the rotors rotate, the interlobe space moves past the inlet port and seals the interlobe spce. Continued rotation progressively reduces the space occupied by the gas, causing compression. During this phase of the cycle, the outlet port is sealed by the rotors. When the interlobe space becomes exposed to the outlet port, the gas is discharged at discharge pressure.

The compressed freon and oil discharge to the primary and secondary oil separators. The entrained oil is removed from the freon in the separators. The primary separator extracts the bulk of the oil from the refrigerant stream before it passes to the secondary separator. The lower portion of the primary separator serves as an oil reservoir from which the oil pump draws its suction. There is an electrical heater in the reservoir to aid in removing freon from the oil.

The oil removed in the primary separator is pumped through an oil cooler and filter, and then back to the oil manifold. From the manifold it is fed into the bearings, balance pistons, shaft seal, compression chamber and hydraulic actuator. The oil system serves several purposes:

1) Provides pressurized lubrication for all vital compressor parts.
2) Cools discharge gas to allow operation at high compression ratios.
3) Seals the space between the compressor rotors to assure high volumetric efficiency.
4) Provides hydraulic pressure to operate the capacity control slide valve.

The oil manifold pressure is maintained approximately 15 to 30 PSI above the compressor discharge pressure by a differential pressure relief valve. The excess oil is returned to the primary oil separator. The secondary oil separator removes the remaining oil from the refrigerant gas stream down to approximately 15 ppm. The oil removed in the secondary oil separator flows through oil float valves and is returned to the compressor suction.

In the main oil system, there are two oil pumps. Normally, one will be running with the other as a spare. The two cooler/filter systems are in parallel and can be used with either oil pump. The oil is cooled by cooling tower water. The oil temperature is maintained at design by a pneumatic oil temperature regulating valve at the filter outlet, which controls the amount of oil bypassing the cooler.

There is a check valve at the outlet of the secondary oil separator to prevent backward rotation of the compressor upon shutdown.

The high pressure freon gas at this point is hot due to heat of compression. It flows through a cooling tower water-cooled condenser, where it is returned to a liquid state. The freon flows through the shell side of the condenser and the cooling tower water flows through the tube side.

The liquid freon is collected in a receiver at compressor discharge pressure. The receiver serves as a storage space for the fluctuation of refrigerant quantity required in the evaporator and maintains a liquid seal before the control valve. The high pressure liquid freon enters the top of the receiver.

The freon discharges out the receiver through a standleg extending to the bottom of the receiver. The liquid freon passes through a filter/

drier and a moisture indicator. The pressure drop from discharge to suction pressure is taken as the liquid freon flows across the brine cooler level control valve. The cooling of the brine takes place as the freon absorbs heat and boils at suction pressure. The temperature of the brine out of the cooler is controlled by maintaining compressor suction pressure within specified guidelines. This control is accomplished by a pressure-indicating controller which senses the suction pressure and sends a pneumatic signal to the pneumatic electrical switch which controls the capacity control slide valve. The pneumatic signal is converted to an electrical signal which operates relays to position the capacity control valve. The slide valve in the compressor casing moves to change the point in the rotor length at which compression begins. This effectively changes compressor displacement as necessary to suit the required load and maintain the set suction pressure. The capacity control system can also be operated on manual to load, unload or hold the compressor at a desired loading.

Some oil will be carried over into the brine cooler with the freon liquid. Most of this oil will remain behind in the cooler as the freon vaporizes. There are three drawoffs on the side of the brine cooler. By using one of these drawoffs, the oil/freon mixture is drained into the oil still. The oil still is a horizontal vessel equipped with an electrical heater to boil freon out of the oil. The oil flow to the oil still is controlled by a solenoid valve in the line to the oil still. The electrical heater is thermostatically controlled. The freon that is boiled out of the oil in the oil still is returned to the compressor suction. The oil is returned to the primary oil separator by the oil transfer/charging pump as needed.

Oil can be added into the system as needed by using the oil transfer/ charging pump. When the system is started up initially, or after an outage during which the oil was removed, the refrigerant circuit will have an oil-free refrigerant charge. Upon operation, the freon will absorb oil until it reaches an equilibrium condition. This will require the addition of oil to the lube circuit. Once the system reaches equilibrium, it will not be necessary to add oil unless oil leaks develop. Oil additions after initial start-up or after outages can be minimized by adding oil to the evaporator before the system is started.

Freon can be added to the system, if required, as either a liquid or a gas. The liquid charging valve is located on the line out of the receiver. The vapor charging valve is located on the compressor suction line.

b. Shutdown Features and Alarms

Shutdown features are provided to protect the refrigeration system against damage to equipment during abnormal operating conditions. Automatic shutdown features are high discharge pressure, low suction pressure, low oil pressure differential, high discharge temperature, high oil temperature, and high freon temperature in brine cooler. High compressor vibration will initiate an alarm in the control room. Loss of the brine recirculation pumps will also shut down the unit. Prior to automatic shutdown, alarms are provided at the refrigeration unit control panel. A general trouble alarm will sound in the control room when an alarm occurs at the refrigeration unit control panel. Details of the shutdown system are included in the shutdown system manual.

If the shutdown system is activated by an abnormal condition, and the refrigeration system is shutdown, the cause of the abnormal condition must be determined and corrected prior to attempting a restart of the compressor.

The refrigeration unit must be operable before the OHC section can start up.

The OHC refrigeration system is shown on P & I drawing 56A-10043. Detailed operating and start-up/shutdown procedures are given in the S.O.P. Manuals.

9. Reactor Air Fluidization System

The purpose of the reactor air fluidization system is to provide a way to keep the OHC reactor catalyst bed fluidized during start-up and prolonged reactor shutdowns.

The system consists of the blower, an intake silencer, a discharge silencer, and a discharge vent silencer. Each OHC reactor has a fluidization blower with interconnecting piping so the blowers can be used with either reactor.

The fluidization blower pulls in ambient air and discharges it into the mixed feed header. The air enters the mixed feed header after the tie-in for HCl, ethylene and recycle. The air flow indication can be monitored at the transmitter and inside the control room. Failure to maintain sufficient air fluidization to a charged OHC reactor will result in plugging of the feed nozzles with catalyst. The catalyst would then have to be dumped, the head removed and cleaned. This would be very costly and time-consuming.

The fluidization air blower is capable of delivering more air than is needed for reactor fluidization. The excess air is vented through a manual throttle valve to the vent silencer. This block valve will be used to vent all the air to the silencer on start-up and then throttled to discharge air into the mixed feed header. Each blower is protected by a relief valve set at 20 psig. There is a check valve in the discharge line from each blower to prevent backflow.

A high discharge temperature shutdown feature is provided to protect the blower. High discharge temperature can be caused by equipment failure or by operating at above rated discharge pressure or below rated suction pressure (restricted intake).

The fluidization air system is not to be put into service after a reactor shutdown until the reactor has been purged with nitrogen to remove all flammables. This is to prevent the oxygen in the air from forming an explosive mixture with EDC or ethylene. For the same reason, the fluidization should be switched back to nitrogen prior to a reactor start-up to purge out all of the air before the feeds are introduced.

Operating guidelines can be found in the "Standard Operating Procedures" manual. Drawings of the reactor air fluidization system can be found on P & I drawings 56A-10029 and 56A-10040.

10. <u>OHC Process Vent System</u>

The purpose of this system is to recover EDC in the vents from the flasher, chloral treatment phase separator, intermediate crude EDC drum, drying still condenser, and drying still reflux drum. The system consists of the refrigerated vent condenser, piping connecting the condenser to the above named equipment, and the vent line to the incinerator.

The refrigerated vent condenser is a vertical shell and tube exchanger with graphite tubes in a steel shell. The vent gases enter the top of the condenser and flow downward through the tubes. Refrigerated brine on the shell side cools the vent gases. The condensate, which is mostly EDC, ethyl chloride, and water, gravity flows out the bottom and back to the intermediate crude EDC drum. The vent condenser exit gases discharge to the incinerator header. These vent streams contain a lot of moisture. If the temperature of the brine cooling the vent condenser is allowed to get too low, freezing could take place in the vent condenser and restrict the flow or possibly damage the tubes. A manual valve is provided to bypass the vent condenser and route the vent gases directly to the incinerator header if freezing does occur. This condition must be corrected quickly to avoid the loss of reclaimable organics and to prevent overpressurizing the vent system. Operation with insufficient brine flow ro a higher than design brine inlet temperature will result in a loss of EDC to the incinerator. There is an annubar located in the brine inlet line to the condenser. The brine flow should be checked routinely to insure that the flow is not too high, which could set up vibrations which could damage the tubes.

and condensers, gas separator, gas separator condenser, associated piping and instrumentation.

Because of the corrosive nature of the material within the LP reactor, and overhead vapors, the reactor, reactor internals, and associated piping are constructed of nickel-clad steel, nickel and 304 stainless steel.

Chlorine gas from the chlorine feed system is routed to a circular manifold at the bottom of the reactor. The manifold distributes the flow to four spargers inside the reactor. The spargers are designed to feed the chlorine as evenly as possible across the bottom of the reactor.

a. Ethylene Feed

The ethylene feed system is designed to reduce and control the pressure of the ethylene and to meter the flow to the liquid phase reactor for safe and efficient operation. This is accomplished with a pressure control valve, safety relief valve, flow meters and a flow control valve.

The ethylene arrives at the liquid phase unit of VCM-II at pressures of 450 psig to 550 psig. This greatly exceeds the pressure required in the reactor. The pressure control valve reduces the pressure and maintains a constant downstream pressure. The ethylene is metered by two different types of meters in series. The first is a vortex meter. The second is an orifice meter. The orifice meter consists of two parallel runs. Only one run is in service at a time. The intent is to use one for low rates and the other for high rates as each is sized for accuracy at its respective flow rate. The flow control valve controls the flow based on the input from the transmitter on the orifice run and set point fixed by the operator.

The ethylene is piped through a circular header around the reactor to four inlet spargers above the chlorine spargers. This arrangement distributes the ethylene evenly into the reactor.

A safety relief valve set at 150 psig is installed downstream of the ethylene pressure control valve. Its purpose is to protect the piping in the system from the high pressure of the incoming ethylene. The pressure of the system is alarmed. Response to the alarm must be quick to prevent a large quantity of ethylene from being vented by the SRV. A high pressure would result if the pressure control valve failed to open. The field mounted pressure gauge is installed for comparison with the pressure transmitter to catch slow failures before they cause problems. Sudden changes in the flow from large rate cuts or shutoff by the shutdown system will place a demand on the pressure control valve to close. It is possible the control valve may not function quickly enough and blow the SRV. Also, the pressure control valve may leak through. Therefore, the control valve should be blocked manually upon a shutdown. The potential leak through must be watched during a startup. Do not put the pressure control valve in service until immediately prior to startup.

When the feed is shut off to the reactor, the block valves are to be closed to prevent the reactor contents from backing up into the feed piping.

The failure of either of the two control valves to a closed position causes a loss of ethylene feed and a shutdown of the reactor. The failure to the open position of the flow control valve leads to a shutdown of the reactor due to the ethylene to chlorine feed ratio.

b. OHC Crude Feed

The OHC crude contains trichloroethylene which is removed best by using chlorination and then distillation. The chlorination to heavier compounds is accomplished in the LP reactor. The crude is pumped from the drying still bottoms tanks through a meter and flow control valve.

Other impurities in the OHC crude such as catalyst can cause fouling in thermosiphon reboilers. The LP reactor is used to separate the impurities out by the boiling overhead of EDC leaving the metal salts (catalyst) behind for removal in the dopp kettle system.

The OHC crude is normally fed into the bottom of the LP reactor. The OHC crude can also be fed to the gas separator or directly into the lights still feed line. Whenever the routing of the OHC crude material is changed, the following points should be remembered:

1) Feeding OHC crude into reactor gas separator - lights still feed metered flow is actual flow.

2) Feeding OHC crude into lights still feed line - lights still feed flow is the total of metered flow plus OHC crude flow (OHC crude is introduced downstream of lights still feed meter).

3) Changing routing OHC crude into (out of) LP reactor - reactor level control system should compensate for introduction of (removal of) crude to reactor by decreasing (increasing) reactor reflux.

c. Reactor System

The LP-EDC reactor contains the spargers distribution system, a boiling bed and a demister. The reactor is filled to a desired operating level with EDC. A caralyst, ferric chloride, is added to provide control of the side reactions that take place in the reactor. The addition of chlorine to ethylene would continue past the EDC step to TCE and heavier compounds without the catalyst. The liquid in the reactor helps control the rate of reaction by removing the heat.

Located above the spargers is a boilding bed. The boiling bed is constructed of two layers of grating forming a basket which contains 3" lengths. The boiling bed breaks up large bubbles of chlorine and ethylene for better distribution. Its main purpose is to smooth out the boiling to prevent formation of large bubbles or turbulent flow causing a burp-over which would carry catalyst overhead.

A baffle and demister at the top of the reactor help reduce the amount of liquid entrainment.

The chlorination of ethylene is an exothermic reaction, that is, heat is given off. This heat of reaction is removed in two ways - by allowing some of the liquid to boil overhead and by circulating the liquid through a cooler to remove heat.

When one mole of ethylene and chlorine react to form one mole of EDC, enough heat is generated to boil six moles of liquid EDC. Some reactors are designed to allow the six moles of EDC to boil overhead. This reactor is designed so that at full rates, only part of the liquid will be boiled overhead. This was done to reduce the size of the equipment. The one mole of product plus some additional liquid boils out of the reactor. This does an effective job of separating the product EDC from the catalyst. The additional liquid is condensed with the product but is returned to the reactor to maintain the liquid level.

d. Reactor Temperature Control

In order to limit the amount of liquid boiled overhead the remaining heat must be removed. This is done by taking a stream off the side of the reactor and pumping it through an air cooled exchanger and back to the reactor. The stream is flow controlled.

The operator can regulate the amount of boilup by changing the amount of circulation. At maximum rates the heat removed is designed to be done half by boiling and half by circulation. Below maximum rates the combination may vary based on the operating conditions. For example, the reactor may be run at 50% rates without the sidearm cooler. The reactor cannot be run without the overhead condensing system. This is the only way the product is separated from the ferric chloride and heavies formed in the reactor.

e. Reactor Gas Condensing

The overhead vapor from the reactor goes to the reactor condenser. This condenser is an air cooled exchanger. One fan has an adjustable pitch which is controlled by the temperature of the condensate from the exchanger. The operator sets the desired temperature setting for the controller.

Vapors that are not condensed in the reactor condenser go forward to the reactor gas separator condenser which is also an air cooled exchanger. Condensate from the reactor condenser and the reactor gas separator condenser gravity flow to the reactor gas separator.

Vapors not condensed in the reactor gas separator condenser are routed to the LP-EDC vent condenser which is discussed in the Process Vent System writeup.

The material in the reactor gas separator is pumped by the reactor reflux pump both forward as feed to the purification section and as reflux back to the reactor for level control. The feed to the lights still is controlled by a flow control valve which is set by the operator to maintain a steady level in the gas separator. The gas separator level must be monitored to ensure that the tank is not allowed to go empty, which would result in loss of reflux to the reactor and a possible emergency shutdown of the reactor and purification section. The reactor product can also be routed from the gas separator to the crude EDC storage tanks after passing through the crude EDC cooler. This would be done when the purification section is down, upon startup of the reactor, and if the reactor became contaminated with materials not easily removed in the purification section, such as H_2O.

f. Reactor Level Control

The reflux flow back to the reactor is controlled by a level control valve using a level transmitter on the reactor. The level in the reactor is very important. A low level may allow chlorine and ethylene to break through the liquid into the vapor space. The reaction in the vapor space without the cooling medium will take place rapidly and a violent explosion could occur. A low level can lead to no boiling. If the level gets below the sidearm cooler drawoff, there will be the loss of that cooling capacity. This will require a reduction in rates. If rates are not cut quickly enough, the system could be over-pressurized.

High level can cause excessive carryover containing catalyst. Since the level is so critical the methods of measuring have been duplicated and are redundant. There are two sight glasses and two level transmitters. The level can also be checked by using the pressures on the top and bottom of the reactor as described in the S.O.P. Manual.

g. Tars and Catalyst Removal

Heavies that are not boiled overhead in the reactor will accumulate in the reactor. These heavies, or tars, and spent catalyst must be removed periodically. This is accomplished with the use of a dopp kettle. The reactor is normally reworked at a frequency sufficient to keep tars at a level of less than 3 - 6% as determined by analysis.

The reactor liquor is gravity fed to the dopp kettle. The reactor liquor is heated in the dopp kettle by 175 psig steam. The EDC in the liquor is vaporized and returns to the vapor space of the reactor. The tars, other heavies and spent catalyst are concentrated in the dopp kettle. The kettle is then dumped to the tar buggy. The tar buggy is hauled off and contents are incinerated.

The kettle level should be controlled near the top of the kettle steam jacket. This will require periodically dumping some liquid to the tar buggy. The steam jacket chest pressure is controlled by the field mounted steam pressure controller at the dopp kettle. The steam flow is metered.

An agitator with scraper blades is provided to keep tars and catalyst from coating the walls and reducing heat transfer.

Since some catalyst is removed while reworking the reactor liquor through the kettle, new catalyst must be added to the system. This is done by taking a side stream of the recycle to the reactor through a catalyst charging chamber. The catalyst is charged to the chamber and the recycle sidestream flushes it into the reactor. The catalyst charging procedure is described in the S.O.P. Manual.

The Dopp Kettle System is shown on P & ID 56A-10057.

h. Reaction Control

The reactor is to be operated with an excess of ethylene at all times. When the production rate is to be increased, the ethylene feed is increased first, and then the chlorine. The chlorine flow is reduced first when the production rate is decreased, and then the ethylene is cut. The consequence of going into a chlorine excess and then back to an ethylene excess could be a violent reaction or an explosion in the reactor or vent system.

Despite the presence of the catalyst, there will be some side reactions. TCE, heavies and some lights will be formed. The HCl from the formation of TCE will be in the vent.

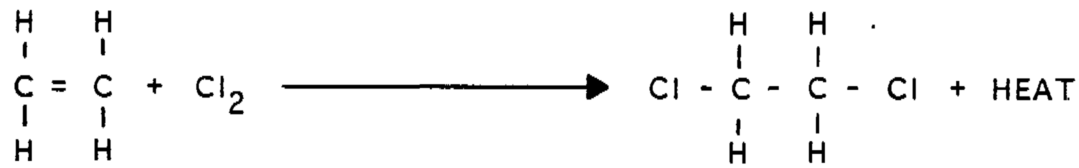
The basic reactions that take place in the liquid phase reactor are:

LP-EDC REACTIONS

MAIN OR DESIRABLE REACTION:

$$\underset{\text{ETHYLENE}}{C_2H_4} + \underset{\text{CHLORINE}}{Cl_2} \xrightarrow{Fe\ Cl_3} \underset{\substack{\text{ETHYLENE DICHLORIDE} \\ \text{(1,2-EDC)}}}{C_2H_4\ Cl_2} + \text{HEAT}$$

OR



1 MOLE 1 MOLE → 1 MOLE 1,2 DICHLORO-ETHANE

<u>SIDE REACTIONS</u>

$C_2H_4 + Cl_2 \longrightarrow C_2H_2Cl_2 + H_2$
1,2-DICHLOROETHYLENE
(CIS AND TRANS)

$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$
1,1-DICHLOROETHANE
(1,1-EDC)

$C_2H_4Cl_2 + Cl_2 \longrightarrow C_2H_3Cl_3$
(1,1-EDC) → 1,1,2-TRICHLOROETHANE
(1,1,2-TCE)

$C_2H_4 + HCl \longrightarrow C_2H_2Cl_4 + HCl$
(1,1,2-TCE) → TETRACHLOROETHANE
(SYM AND UNSYM)

$C_2H_4 + HCl \longrightarrow C_2H_5Cl$
ETHYL CHLORIDE (EC)

$C_2H_2Cl_4 + Cl_2 \longrightarrow C_2HCl_3 + HCl$
(SYM AND UNSYM) → TRICHLOROETHYLENE (TRI)

$C_2H_2Cl_4 + Cl_2 \longrightarrow$ TARS
(SYM AND UNSYM)

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Any lights or heavies carried forward with the reactor product are removed in the purification section.

The excess ethylene, HCl and the lights that are not condensed are removed in the Process Vent System. The vent stream is analyzed by a chromatograph and ethylene and chlorine analyzers which take their samples downstream of the vent knock out drum. These are used to verify the ethylene excess. Another method is the use of ortho-tolidine solution. A red color indicates a chlorinated reactor, yellow = good ethylene, clear = too much ethylene.

i. Reactor Shutdown System

The LP-EDC reactor is equipped with a shutdown system that is actuated automatically or by a board-mounted push-button.

A general description of the shutdown system is as follows. The LP-EDC Reactor SDS is provided to stop feeds to the reactor operation. The conditions to be protected against are:

1) Liquid chlorine break-through into the reactor.
2) Excess reactant resulting in chlorine break-through into the reactor vapor space, condensing, and venting systems.
3) Flow ratio of ethylene to chlorine outside acceptable bounds.

4) High pressure on the reactor system.

5) Low ethylene concentration in the vent.

6) Backup of liquid organics into the chlorine feed system.

7) Chlorine flow indications in an imbalance condition.

8) Ethylene flow indications in an imbalance condition.

9) Low level in the reactor.

To insure that the feeds are stopped when the shutdown system operates, the control valves are provided with dump solenoids in the air supply to each of them. Upon activation, power is removed from the solenoids to move the valves to their fail position:

1) Chlorine is stopped by closing the pressure control, flow control and anti-backup valves.

2) Ethylene is stopped by closing the pressure control and flow control valves.

3) OHC crude EDC is stopped by closing the flow control valve.

4) Chlorine to EDC recycle is also stopped by closing the flow control and anti-backup valves.

A relay in the EDC vent compressor motor start circuit is also de-energized causing the compressor to be shut down.

In addition to the vent analyses and the determination of the tar level in the reactor liquor, the reactor liquor is also analyzed routinely for iron, water and composition (by GC analysis).

The iron level in the reactor liquor should normally run around 3000 - 5000 ppm. Catalyst should be added when the reactor is being re-worked through the Dopp Kettle to replace the iron that is removed.

The analysis for water in the reactor liquor is interfered with by iron and HCl. For this reason, the analysis is unable to accurately detect levels of H_2O below around 200 ppm. The analysis is useful to detect abnormally high levels of H_2O. The effect of water in the system, in addition to causing corrosion of downstream steel equipment, is to poison the ferric chloride catalyst.

The GC analysis is useful to determine if the catalyst is performing effectively and is available in sufficient quantity. The TCE level should normally run less than 1 - 2% in the reactor liquor.

j. Startup

The LP reactor system can be started up and operated independently of the VCM, OHC and purification sections, as long as there is storage room available in the crude EDC tanks for reactor product. The normal procedure is to start up the reactor system after the purification section is operational.

The reactor liquor level must be established and proper catalyst concentration verified prior to starting up. The condensing and vent system must be ready to accept the reactor gases. The reactor should be purged with nitrogen for 30 minutes, entering on the ethylene feed line, to clear the system of any residual chlorine or air. The startup bypass timer is then activated. When the startup bypass button is pressed, it provides 60 minutes of startup time. The ethylene system should be put into service and the reactor purged with ethylene for about 30 minutes to saturate the reactor liquor and the vent system. This helps guard against possible chlorination.

The ethylene flow should be increased and the chlorine introduced slowly. Always keep more ethylene than chlorine in the reactor. Allow the reactor to heat up slowly to avoid burping over.

After the reactor has lined out, the OHC crude may be fed into the bottom. The S.O.P. Manual contains a detailed startup checklist.

At the end of the startup time, the startup bypass feature is taken out of service automatically by the shutdown system so that it cannot be used to bypass the system during operation.

k. Shutdown

There will be times that the LP-EDC reactor will be shut down with VCM and OHC left on line. The EDC storage area does provide some surge time to allow the liquid phase unit to take a short outage without affecting the other units. The OHC crude EDC and the

EDC recycle can be fed directly to the lights still during a LP-EDC reactor outage. However, any trichlor in the OHC crude will end up in the VCM furnace feed.

After a reactor shutdown has occurred, either manual or automatic, the startup bypass pushbutton will only become functional again 10 minutes after a shutdown has occurred. This time delay after shutdown is to prevent a startup from being initiated immediately after a trip. The feed spargers and reactor must be nitrogen purged. The startup sequence can then be started. If all of the shutdown parameters are not at acceptable limits at the end of the startup time, then a trip will be activated. The S.O.P. Manual provides exact procedures to be followed in the event that a trip occurs.

Drawings of the LP-EDC reactor system can be found on Process Flow Sheet 56A-10010 and P & ID's beginning on 56A-10046.

3. Liquid Phase EDC Process Vent System

The purpose of the Liquid Phase Process Vent System is to remove any condensible organics from the gases leaving the LP-EDC reactor system, vent the noncondensibles and control the LP Reactor System pressure. The system also provides a method of recovering the ethylene in the LP Vent System by compressing the vent and routing it into the HCl feed to OHC. The system begins with the discharge of the reactor gas separator condenser and ends downstream of the vent compressor discharge pressure control valve. Included in this system are the gas separator condenser disengaging tee, the vent condenser, knockout drum, vent compressor and compressor recirculation cooler.

The reactor gases that are not condensed in the reactor condenser and the reactor gas separator condenser flow through the refrigerated vent condenser after passing through a disengaging tee where any condensate is removed. The vent condenser is cooled by Freon 22 which is supplied by the process and intermediate storage refrigeration unit.

The cooled vent flows through a knockout drum where any condensed organics are returned by gravity flow to the reactor gas separator. The vapors from the knockout drum consist of the excess ethylene, other lights, and inerts from the reactor system.

The freon temperature in the vent condenser is controlled by the suction pressure of the refrigeration unit. The freon level is level controlled. An oil recovery system consisting of an oil still and pump is provided to return oil to the refrigeration unit.

The refrigeration system is discussed in Section VII, E-4 of this manual.

The vent stream can exit the LP-EDC unit as feed into the OHC reactor HCl feed system, to the scrubber or to the low pressure vent header. The normal route will be as feed to the OHC Reactor System. If for some reason the vent cannot be compressed, the desired routing of the vent is to the vent header and the incinerator so the fuel value of the ethylene will not be lost and so ethylene will not be vented to the atmosphere. While the vent compressor is in operation, the valves should be lined up to route the vent to the scrubber so in case the compressor trips off or the reactor shuts down and trips the compressor, the incinerator will not be tripped off.

The vent must be compressed in order to route it into the OHC HCl feed system. The pressure at the suction of the compressor is normally approximately 5 psig, which corresponds to a reactor pressure of about 15 psig. The compressor is a two-stage reciprocating compressor which discharges the vent at approximately 110 psig. The knockout drum prior to the compressor is designed to prevent liquid from entering the compressor. The knockout drum is equipped with a demister. Liquid in a positive displacement compressor can foul the valves and cause severe damage to equipment, possibly even resulting in a cracked head or cylinder. There is a level switch on the knockout drum which will trip the compressor if a high liquid level is detected. There is a bypass around the knockout drum. The compressor is not to be operated if the knockout drum is bypassed.

The vent compressor is equipped with a control, alarm and shutdown system. The shutdown system is described fully in the Safety Control System Manual. Basically, the compressor will be shut down by high second-stage discharge temperature, high level in the knockout drum, low suction pressure, and trip of the LP-EDC reactor shutdown system. Any alarm conditions which develop within the compressor system activate a general trouble alarm in the control room.

The compressor head, and first and second-stage cylinders are coolec with cooling tower water which flows through the jackets. The intercooler between the stages is also cooled with cooling tower water.

To prevent shaft packing leaks from getting to the atmosphere, the compressor distance pieces are purged with nitrogen to the vent header (or the scrubber).

The vent system maintains and controls the pressure in the LP reactor system. When the vent compressor is operating, system pressure is controlled as follows: The desired system pressure (measured at the top of the LP reactor) is determined by the operator and set by PIC 1450, which controls the amount of vent recirculated from the compressor discharge back into the suction. This in essence controls compressor suction pressure at a pressure equal to reactor pressure minus the pressure drop through the reactor condenser and separator condenser or normally about 5 psig. The compressor discharge pressure is controlled by a pressure controller and control valve on the line to OHC. This pressure control valve should be set to maintain a discharge pressure high enough for the vent to be fed into the HCl feed line to OHC. A third control valve (PV 1490) protects the system from overpressure in the case of excess flow above the capacity of the compressor or in the event of a compressor malfunction. This valve opens to a header which can be routed to either the vent header or the scrubber.

When reactor vent flow is very low, the compressor will essentially be on total recirculation with only a small flow to OHC. A recirculation cooler, cooled by cooling tower water, is provided to prevent the compressor from overheating or shutting down because of high discharge temperatures. As the vent flow increases, the recirculation flow will cut back and the flow increases, the recirculation flow will cut back and the flow to OHC will increase until the system reaches a steady state at the desired system pressure. The set point of the pressure control valve to the vent header (or scrubber) should normally be set slightly higher than compressor suction pressure. This pressure control valve will then act as a safety vent valve which will open if compressor capacity is exceeded, or if the compressor trips off. A portion of the vent can be scrubbed (or incinerated) through the pressure control valve while also feeding OHC.

If the vent system is to be operated without the compressor, the system pressure is controlled by PV 1490 which takes its impulse downstream of the knockout drum.

When the LP reactor system is started up, the vent system will be lined up to the scrubber with the compressor down. After the reactor has lined out at the desired rates, the compressor will be started up on total recirculation. By raising the set point on the vent system pressure control valve, the flow to the scrubber will be reduced and the flow to OHC will begin.

To stop the flow to OHC, the set point on the vent system pressure control valve is lowered until the valve begins to open. The compressor can then be taken out of service.

The vent stream composition is monitored by a gas chromatograph (discussed in the LP-EDC reactor system write-up) which takes its sample downstream of the knockout drum.

The knockout drum is protected from overpressure by a safety relief valve set at 50 psig. The compressor is protected against a blocked discharge condition by a safety relief valve set at 150 psig, which relieves back into the compressor suction.

Drawings of the LP-EDC Process Vent System can be found on process flowsheet 56A-10010 and P&I Drawings 56A-10047, 56A-10048, and 56A-10049.

4. EDC Recycle Reaction System

The purpose of the EDC Recycle Reaction System is to chlorinate the recycle EDC to remove chloroprene, which is formed in the VCM section. The chloroprene is chlorinated to heavier compounds which are removed in the heavies still system. If the chloroprene is not removed, it will be carried forward into the lights still. The chloroprene can be removed by the lights still; however, it can build up in the column and polymerized resulting in plugging of the trays. This can result in extensive downtime. If the chloroprene is allowed to pass through the EDC purification section and get into the furnace feed, it can cause VCM product purity to be off-specification, since chloroprene is cracked to MVA in the furnaces.

The system begins with the chlorine feed from the chlorine surge drum and EDC feed as it enters the LP-EDC unit downstream of the recycle flow control valve. Included in this system are an inline mixer, a reaction drum, associated piping, and instrumentation.

The chlorine feed is flow-controlled from the chlorine surge drum. The chlorine feed rate is adjusted based on the chromatograph and free chlorine analyses of the stream out of the reaction drum. If the LP-EDC system and the chlorine vaporizer system are down, the chlorine can be fed into the EDC recycle header upstream of an inline mixer. The static mixer provides an even and thorough mixing of chlorine into the EDC. The reaction tank provides some reaction time before the EDC is fed into the LP reactor gas separator. The recycle stream can also be fed directly into the bottom of the lights still if the LP reactor system is down.

The temperature of the EDC recycle stream must be maintained at approximately 165°F for the chlorination of chloroprene to be effective. This is accomplished in the VCM process section by a temperature controller which allows a portion of the EDC fed to the primary lean oil cooler to bypass the cooler to maintain this temperature.

The recycle stream after chlorination is sampled and analyzed regularly for chloroprene levels (G.C. analysis) and free chlorine. The free chlorine should be maintained at the minimum required level to accomplish removal of the chloroprene. Excessively high chlorine excess can result in high corrosion rates in downstream equipment. High chloroprene levels detected by the G.C. analysis are an indication that either the chlorine flow is insufficient or the temperature of the recycle stream is not being properly controlled.

The chlorine feed to the EDC recycle system is stopped anytime the EDC reactor shutdown system stops feeds to the EDC reactor. This is necessary since the chlorine vaporizer is isolated when the shutdown system is activated, and therefore, there is no chlorine available for the EDC recycle system. Refer to the Safety Control System manual for complete details on this system. A bypass of the chlorine to EDC recycle feature of the LP-EDC reactor is down for extended periods and a chlorine cylinder is used to provide chlorine to EDC recycle instead of the vaporizer.

In addition to being tied into the LP-EDC reactor shutdown system, the chlorine feed to EDC recycle is provided with a PLC managed anti-backup system. This anti-backup system is as follows:

The anti-backup trip of the chlorine feed to the EDC recycle stream is provided to protect against getting EDC recycle back into the chlorine feed system and/or chlorine surge drum. Undesirable reactions might occur if EDC recycle is allowed into the chlorine surge drum or the EDC reactor feed system. In order to protect against this occurrence, the anti-backup system will stop chlorine feed to the EDC recycle stream based on a low differential pressure across the chlorine to EDC recycle feed flow control valve. To assure that the chlorine feed is stopped, two valve closures are provided when the anti-backup valve is tripped. The chlorine flow control valve and an on/off anti-backup valve are both closed when the anti-backup feature is activated. These same valves are also closed by the LP-EDC reactor shutdown system.

The recycle reaction drum is protected from overpressure by a safety relief valve set at 150 psig.

The recycle chlorination system must be in service anytime the EDC cracking furnaces are in operation and recycle EDC is being fed forward to the gas separator (or lights still). It is normally not necessary to operate the chlorination system if the furnaces are down and the VCM section is on recycle.

Start-up is accomplished by first closing the chlorine feed flow control valve to EDC recycle. The chlorine feed supply pressure must then be established either by chlorine coming from the chlorine surge drum, or by chlorine cylinders. When the pressure is sufficiently high, the reset button is the pressed. Chlorine feed may then be started, using the flow controller, at the desired flow rate.

Drawings of the EDC recycle reaction system can be found on process flowsheet 56A-10013 and P&I drawing 56A-10059.

D. EDC PURIFICATION SYSTEM

1. Lights Still System

The primary function of the lights still is to separate light (low boiling) components, primarily chloroform, ethyl chloride, and carbon tetrachloride, from the crude EDC (OHC-EDC and LP-EDC). The separation of these lights from the crude EDC is achieved by utilizing the 90 tray lights distillation column and its associated equipment. Lights removal is the first step in the EDC purification process.

If the lights are allowed to enter the heavies still, they would go overhead with EDC product as an impurity. These impurities, when fed to the VCM plant in the furnace feed, contribute to the coke build-up that occurs in the VCM cracking furnace tubes. The impurities, especially ethyl chloride, can also contaminate the VCM product. The lights still system includes the lights still, two lights still reboilers, two lights still reflux pumps, reflux drum, calcium chloride dryer, filter, and three air-cooled condensers. The system is shown on process flowsheet 56A-10011 and P & ID's beginning on 56A-10051.

Crude EDC, contaminated with chloroform, carbon tetrachloride, ethyl chloride and trace amounts of other lights along with heavies, is pumped to the lights still by the LP-EDC reactor reflux pump from the LP-EDC reactor gas separator. This is the normal feed source. The VCM EDC recycle stream after chlorination, which is normally routed to the reactor gas separator, can also be routed directly into the bottom of the lights still during LP-EDC reactor gas separator outages. The EDC recycle after chlorination is fed to the lights still to remove free chlorine, lights, and chloroprene (if the chlorination hasn't removed it all). The lights still is also capable of receiving OHC crude, which is normally fed to the LP-EDC reactor, directly from the drying still bottoms tanks. This is also done during LP-EDC reactor system outages. The OHC crude is fed to the lights still to remove lights that are formed in the OHC reactor system. EDC from the crude EDC storage tanks, pumped by the crude EDC rework pumps, can be routed directly into the lights still feed line from the rework header.

The feed is flow-controlled to provide a steady feed rate to the column. The feed rate should be adjusted to maintain a constant level in the LP-EDC reactor gas separator. There are four feed point locations provided on the lights still. These feed points are at trays 55, 62, 69, and 77. Normally the feed will enter the column at tray 62; however, the alternate feed points are to be used when the source of the feed, or feed composition is changed.

The lights are boiled overhead and condensed in three parallel air-cooled exchangers. Each exchanger has two fans that pull air across the tubes for cooling. These fans are in series. The first fan has fixed pitch blades. The second fan in each exchanger has auto-variable pitch blades and is used in the control of the temperature of the condensate out of the exchanger. The stream out of the lights still condenser is temperature-controlled to provide a condensing rate sufficient to maintain reflux to the column at a constant temperature. This is essential for steady efficient operation of the column and to minimize the effects of ambient temperature changes.

The condensate and uncondensed vapors travel to a disengaging tee. The liquid drains from the tee by gravity into the reflux drum. The vapors are vented into the vent header and then to the incinerator (or the atmospheric scrubber). The total "lights" removed from the feed are actually the sum of this vented uncondensed material and the condensed material. The pressure on the lights still system is maintained by a pressure control valve to the vent header. The impulse for the pressure controller is taken upstream of the reflux condenser. This pressure control is provided to maintain a constant pressure on the system. Pressure changes on the system change the condensing and boiling temperatures of the process. The impulse is taken upstream of the condenser so that restrictions such as plugged tubes in the condenser can be detected and so that pressure drop across the exchangers, which varies with flowrate, will not affect column pressure. The temperature across each section of the condenser is measured to aid in determining which section is plugged or is fouling.

The reflux drum level, the distillate flow rate, and the reflux rate are all indirectly controlled by a temperature control point on the column. The control point is a point on the column at which a controlled variable, in this case temperature, is maintained within set limitations to assure proper control of the separation taking place in the column. As the composition of the process material at the control tray changes, the temperature will change. The control system will react to the change in temperature to try to keep it constant and thereby maintain the desired composition. As heavier or higher boiling components increase in composition at this point, the temperature will increase. As lighter or lower boiling components increase, the temperature will decrease.

The distillate or light ends flow is controlled directly by the temperature control point. The control temperature is set to obtain the desired EDC composition in the light ends. The control point manipulates the distillate stream by causing the temperature control valve to close when the temperature increases and open when the temperature decreases. The manipulation of distillate also adjusts the reflux flow rate by affecting the level in the reflux drum. The reflux drum is level-controlled by adjusting the reflux flow. When the temperature control valve closes back due to an increase in temperature, the level in the reflux drum starts to increase. This is sensed by a level transmitter and causes the level control valve to open up and increase reflux to keep the level constant. This increase in reflux will cause the temperature at the control point to decrease toward the setpoint. Thus, the control point temperature is kept essentially constant. If the temperature at the control point decreases below its control setpoint temperature, the distillate flow will increase and the reflux drum level will decrease causing the reflux flow to be decreased. This in turn will cause the temperature at the control point to increase to the setpoint. The temperature control point is one out of several points throughout the length of the column that will be monitored for operator control.

The lights can be pumped to the waste storage drum, from which they are fed to the incinerator. This stream is normally routed to Plant B so the chloride value can be recovered.

A calcium chloride dryer is provided to dry the lights still reflux. Any moisture that enters the lights still system will concentrate in the overhead. This concentration of moisture would become corrosive to the equipment and in upset conditions it could contaminate the heavies still feed and eventually, the furnace feed. A filter located downstream of the dryer is provided to filter out any calcium chloride that could carry over from the dryer. A bypass around the dryer/filter system is provided for routine maintenance, or in the event that the dryer or filter plugs and restricts flow.

The boilup within the column is accomplished by two thermosyphon reboilers. Heat is supplied to the reboilers from the 45 psig steam system. The steam is flow-controlled by a single flow-control valve. The condensed steam is returned to the condensate collection system through the low pressure condensate header. There is a steam trap on each reboiler to remove condensate. The steam flow rate must be adjusted in proportion to changes in the crude EDC feed flow to maintain boilup and achieve desired bottoms purity. A constant level in the reboiler pot is maintained by an internal overflow to a drum located in the skirt of the column. The drum is in effect a lights still bottoms or heavies still feed drum. Sight glasses are provided on each section. The bottoms drum also has a level transmitter that indicates its level. Reliable control of the reboiler pot level is essential to prevent rapid fouling of the reboiler tubes. Fouling can be accelerated by flooding (high level - above the reboiler return ell) or by loss of recirculation (low level - below the reboiler top tube sheet). Vapors in the bottoms drum are equalized back to the vapor space of the reboiler pot by way of a vent nozzle extending up through the reboiler pot liquid level. A chimney-type tray, on which both the overflow and vent nozzles are attached, separates the reboiler pot from the bottoms drum.

One problem that may be incurred in the operation of the lights still is the loss of one or more condenser fans. Whenever a fan shuts down, the remaining fans must be able to pick up the additional load until the fan can be restarted. If the problem is such that maintenance will have to be performed on the fan, the feed rate may have to be adjusted so as not to overload the condenser. A sudden loss of all fans will cause the still to pressurize almost immediately. To protect against damage to the lights still caused by over-pressure, the still is equipped with two SRV's set to relieve a 50 psig. During cold-weather operation, it may be necessary to shut down a condenser fan to maintain column pressure.

Lights-free EDC is pumped from the bottom of the lights still to the heavies still feed flow-control valve. This bottoms stream will be checked routinely by chromatographic analysis. The key components that will be watched for in the bottoms stream are carbon tetrachloride or chloroform, depending on feed source and composition. If lights breakthrough out the bottom of the column is detected, adjustments to steam flow to the column and/or increasing the temperature control setpoint must be accomplished. The light ends stream (lights still reflux) is analyzed routinely to determine composition and water content. The wt. % EDC in the overheads should be within guidelines to prevent significant losses of EDC to the incinerator. The lights stream is analyzed for water content as any water which enters the system, either in the feed or from a reboiler tube leak, accumulates in the column overhead. The reflux stream is also analyzed for water after the dryer to monitor effectiveness of the dryer.

The VCM II unit can be operated for approximately 48 hours at half rates with the lights still out of service by optimum use of storage inventory. This is to allow for reboiler changeout or other maintenance work on the lights still system.

LIGHTS STILL

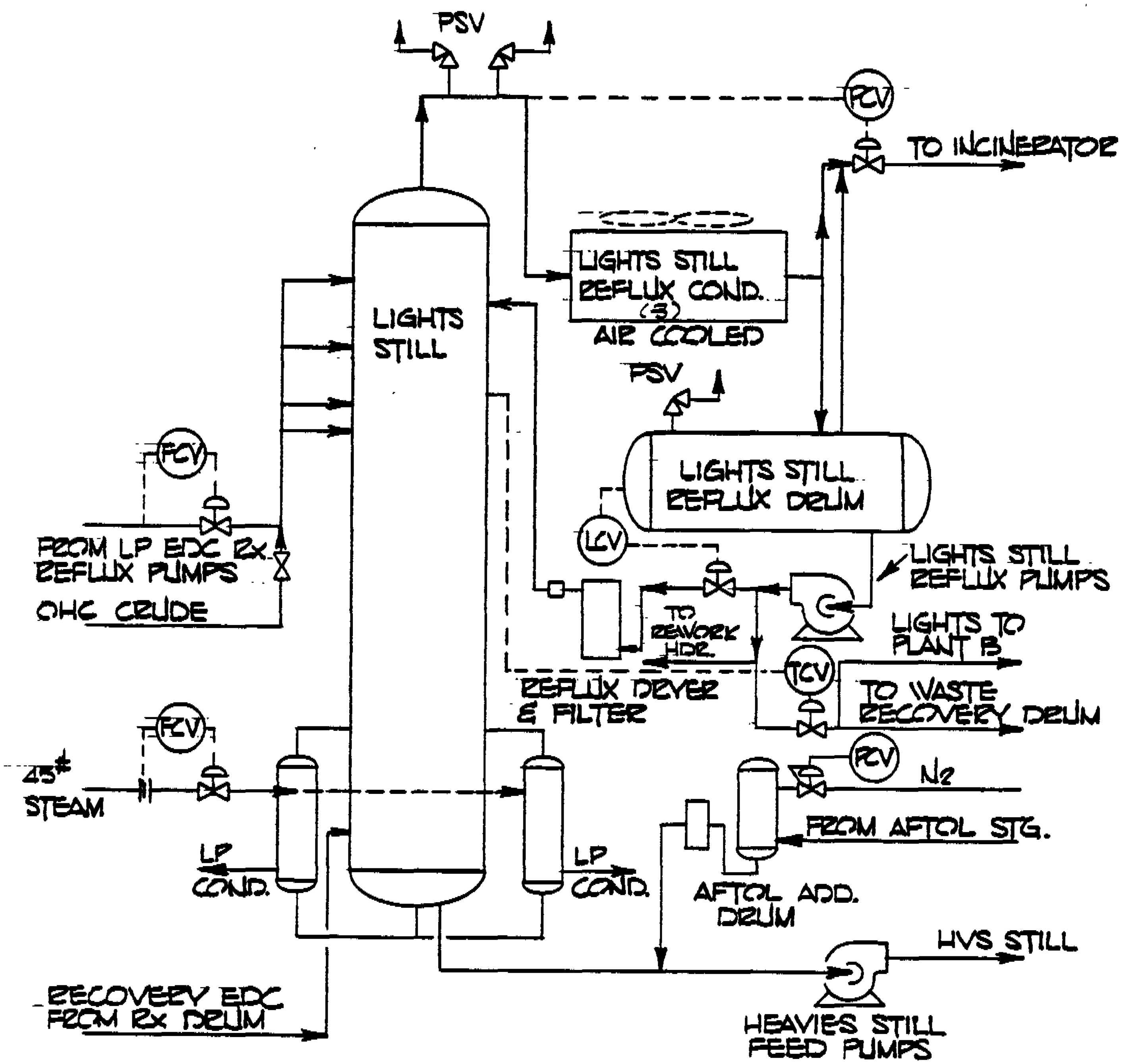

FIG. VII-14

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Start-up of the lights still system is one of the first steps in putting the VCM II plant into operation, assuming all of the necessary support equipment is already in operation. Normally the lights still is started up in conjunction with the heavies still system such that the EDC purification section is operated in a recycle loop. Once the distillation train is in operation, the LP-EDC reactor or an OHC reactor can be started up. The VCM purification section and the EDC purification system must be tied together on recycle and lined out prior to starting up the cracking furnaces. The EDC purification system can also be operated while other sections of the VCM II plant are down to process or rework crude EDC from storage.

2. Heavies Still System

Crude EDC, essentially free of lights after being processed through the lights still, contains approximately .25 - .75 weight percent of heavier chlorinated compounds that must be removed before the EDC can be used as feed to the EDC cracking furnaces. The separation of heavies from EDC is achieved by the utilization of the 54 tray heavies distillation column and its associated equipment. Removal of heavier compounds is a very important and necessary step in the EDC purification process, since the presence of heavies in the furnace feed inhibits the cracking reaction and/or causes unnecessary coking of the furnace tubes.

Equipment included in the heavies still system are the heavies still, heavies still feed pumps, heavies still condenser, heavies still reflux drum and pumps, heavies still bottoms pumps, the pure EDC cooler, and the anti-foulant addition system. The heavies still system is illustrated on process drawing 56A-10011 and P & I drawings 56A-10054, 56A-10055 and 56A-10056.

EDC contaminated with heavies, principally TCE and Tetra, is pumped from the lights still bottom drum into the heavies still where the heavies removal process transpires. The feed rate to the still is flow-controlled to help provide a steady load on the column. Periodically, the feed rate has to be adjusted to maintain the lights still bottoms drum within operating limits.

Two thermosyphon reboilers, consuming 175 psig steam, provide the necessary heat to boil the EDC overhead. Steam flow to the reboilers is regulated to maintain a specific heavies concentration in the bottom of the still. Condensate from the reboilers is collected in either the low or high pressure condensate headers. Whenever possible, the reboiler condensate should be lined up to the high pressure header where it can be used to flash off 45 psig steam. During start-up of the heavies still or when it is operating at low rates, the condensate will probably be tied into the low pressure header. The reboiler steam chest pressure at the time will determine which header the condensate is lined up to.

Essentially pure EDC vapors are boiled overhead in the heavies still and condensed in two parallel air-cooled exchangers. The condensate draining to the reflux tank is temperature controlled, primarily to maintain steady column operation by providing a constant reflux temperature. This also helps to minimize the column steam consumption by preventing excessive subcooling of the reflux. Temperature control of the condensate is accomplished by regulating the amount of cooling air pulled through the condenser. Two variable pitch fans (one per exchanger) are simultaneously adjusted to regulate the cooling air flow. During periods of low operating rates or cool weather, it may be necessary to shut down one or both of the fixed pitch fans (one per exchanger) in order to keep the temperature controller within controlling range. Pumped from the reflux drum, EDC is returned to the heavies still as reflux and the remaining excess transferred to the furnace feed storage tanks.

The reflux rate is flow controlled to maintain the required reflux ratio (reflux flow ÷ distillate flow). Insufficient reflux (low ratio) will result in heavies contamination of the overhead product, whereas excessive reflux (high ratio) unnecessarily increases reboiler steam consumption, decrease column capacity, and, if severe enough, causes flooding. The EDC flow to the furnace feed tanks is regulated by the reflux drum level controller to maintain the proper drum level. Prior to entering the feed tanks, either part or all of the EDC is cooled in a single air-cooled exchanger to prevent excessive venting of vapors from the low pressure storage tanks. The bypass flow around the cooler is manually regulated to maintain the EDC temperature at approximately 130°F, and, therefore will have to be adjusted as weather conditions change. The availability of three furnace feed tanks provides sufficient surge time for qualifying the contents of a tank before it is needed for feed to the furnace.

As the separation process takes place in the heavies still, heavies accumulating in the reboiler pot overflow into the bottoms drum causing the bottoms drum level to rise. To maintain the bottoms drum level within operating limits, batchwise pumping of heavies from the bottoms drum to the Plant B bottoms plant is utilized. The bottoms plant processes heavies streams collected from different operating units throughout the organics area to recover the remaining EDC. From the bottoms plant, the reclaimed EDC is used for feedstock to the Per-Tri plant, and the remaining heavy ends are incinerated. If for some reason the bottoms plant cannot accept heavies, a 3-inch line is provided to pump heavies to the crude EDC tanks via the crude EDC cooler.

The liquid level in the bottom of the heavies still is controlled by an internal overflow nozzle that allows liquid in the reboiler pot to gravity drain to the bottoms drum. The physical location of the overflow nozzle is such that the resultant liquid head in the reboiler pot is sufficient to provide the necessary liquid recirculation through the reboiler tubes. Reliable control of the reboiler pot level is essential to prevent rapid fouling of the reboiler tubes caused by flooding (high level - above the reboiler return ell) and loss of recirculation (low level - below the reboiler top tubesheet). As in the lights still, the heavies still bottoms drum is located in the column skirt just below the reboiler pot. Vapors in the bottoms drum are equalized back to the vapor space of the reboiler pot by way of a vent nozzle extending up through the reboiler pot liquid level. A chimney-type tray, on which both the overflow and vent nozzles are mounted, separates the reboiler pot from the bottoms drum.

The heavies still level control scheme provides a positive control operation as long as the bottoms drum is not flooded. Since the magnitude of the heavies still bottoms stream is small in comparison to the feed and reflux streams, and because it is also sensitive to changes in column operation, control of the reboiler pot level could become difficult during rate changes and upset conditions. To help alleviate this problem, the bottoms pumps are used to recirculate a continuous stream of heavies from the bottoms drum back to the reboiler pot. This should increase the heavies still underflow rate enough to help stabilize the bottoms level.

Control of the heavies still temperature is essential to produce the desired overhead purity and still maintain an acceptable EDC recovery. In the heavies still, the control temperature is a function of two factors; one, the composition of the bottoms stream, and two, the operating pressure of the column. In most cases, the control temperature is set to yield a specific heavies concentration in the bottoms stream.

The higher the control temperature, the greater the heavies are concentrated, and the higher the EDC recovery. Normal heavies concentration will be approximately 40-50 weight percent total heavies (50-60 percent EDC). The reboiler design will allow even higher EDC recovery concentrating the heavies in the bottoms up to 75 percent total heavies. It should be noted here that as the bottoms temperature increases, reboiler fouling also increases; therefore, the EDC recovery must be regulated in accordance with an acceptable reboiler fouling rate.

As noted above, the heavies still control temperature is also a function of pressure, specifically, the column's bottom pressure. As the bottom pressure of the heavies still changes, the boiling point temperature of the bottoms stream for a given heavies concentration changes. Since the top pressure of the column is controlled at a steady value, the bottom pressure varies only as the pressure drop through the column varies. Changes to column pressure drop are caused mainly by rate adjustments to the feed and reflux streams. Therefore, as large rate changes are made to the heavies still, the control temperature will have to be adjusted accordingly to maintain the desired heavies concentration.

To help provide steady column operation, the top pressure of the heavies still is controlled by two independent control valves in conjunction with a single split-range controller.

The control point for the controller is taken off the column overhead line just upstream of the condenser. As the process pressure rises above the controller setpoint, the vent valve opens purging vapors from the reflux drum to the low pressure vent header. Likewise, as the process pressure falls below the setpoint, the nitrogen makeup valve opens, bleeding low pressure nitrogen into the reflux tank. The vent valve and the makeup valve should never be open simultaneously. Ideally, the process pressure should be operated as low as possible to minimize energy consumption, yet it must be high enough to insure a positive vent flow from the reflux tank to the vent header.

One problem that may be incurred in the operation of the heavies still is the loss of one or more condenser fans. Whenever a fan shuts down, the remaining fans must be able to pick up the additional load until the fan can be restarted. If the problem is such that maintenance will have to be performed on the fan, production rates may have to be adjusted so as not to overload the condenser. A sudden loss of all fans will cause the heavies still to pressurize almost immediately. To protect against damage to the heavies still caused by over-pressure, the still is equipped with three SRV's set to relieve at 50 psig.

An important consideration to keep in mind when operating the heavies still is that of reboiler fouling. Although fouling is inherent in the process of heating up chlorinated hydrocarbons to high temperatures, it can be retarded by adhering to acceptable operating practices, and by enlisting the aid of an anti-foulant agent wherever practical. In the heavies still system, the anti-foulant is added to the process by nitrogen padding the liquid agent from an addition drum through a small filter and flow regulator into the suction line of the heavies still feed pumps. The anti-foulant is heavy enough (high boiling point), such that it travels to the bottom of the column where it is circulated through the reboiler tubes. As heavies are purged from the system to the bottoms plant, the anti-foulant is depleted. Therefore, the anti-foulant is added on a continuous basis and at such a rate as to maintain a specific concentration in the bottoms stream. Periodically, the addition drum has to be refilled from a separate storage tank.

Two special factors were taken into account in the design of the heavies still. First was the necessity of having to rework out-of-spec EDC during normal plant operation. Second was the capacity of processing higher than normal EDC rates due to process changes in the VCM and EDC production units. Surplus EDC can be created in the following situations: 1) when the furnaces are operated at lower than design conversion rates increasing the recycle EDC stream; 2) when the liquid phase reactor is operated at rates necessary to make up lost EDC production; and 3) when the OHC reactors are consuming additional HCl from other units in Plant B. To satisfy these considerations, the heavies still is designed to process an additional 10 percent above the necessary EDC rate needed to produce the design VCM II plant production (750 TPD).

Start-up of the heavies still system is one of the first steps in putting the VCM II plant into operation, assuming all of the necessary support equipment is already in operation. Normally, the heavies still is started up in conjunction with the lights still such that the EDC distillation train is operated in a recycle loop. Once the EDC distillation train is in operation, the LP-EDC reactor can be started. (An OHC reactor can also be started if it is to consume additional HCl from other units in Plant B). Whenever both the EDC and VCM purification sections are operating on recycle, they can be tied together in a single recycle loop using the EDC rework system. The intent of the start-up procedure is to get all the necessary equipment in service and lined out prior to starting the cracking furnaces.

As previously stated, the purpose of the heavies still is to remove heavier organic compounds from a crude EDC stream. To monitor the separation process, frequent GC analyses are completed on the overhead and bottoms streams. Although distillation processes are not 100 percent efficient, they are designed to produce essentially pure product with minimum levels of impurities. GC analysis of the heavies still product may at times indicate the presence of lights and/or heavies, but their concentrations should be below maximum acceptable levels. If analysis of the heavies still overhead product indicates high levels of TCE and other heavy compounds, the heavies still control temperature is too high, or there is insufficient reflux. The analysis of the bottoms stream is necessary to verify that the desired heavies concentration is being achieved.

It is of extreme importance that the heavies still system be relatively free of water. The presence of high moisture levels in the heavies still overhead normally means the presence of a leak in the process. Possible locations for such a leak would be the heavies still reboiler; product still reboiler, or the lights still reboiler (if its chest pressure is operating higher than the bottom pressure of the column). If high moisture levels are allowed in the system, corrosion of steel equipment and out-of-spec product will be unavoidable. To warn of high moisture levels in the heavies still overhead product, a continuous moisture analyzer has been installed one discharge header of the heavies still reflux pumps. If for any reason the moisture concentration rises above the accepted limit, the product stream can be quickly diverted to the crude EDC tanks to prevent contamination of a partially full furnace feed tank. In this case, the furnace feed tanks will provide some surge time for the moisture problems to be corrected.

One of the more significant factors contributing to reboiler fouling is iron concentration in the bottoms. Normal iron concentration in the heavies still bottoms is expected to vary around 100 ppm. During periods of higher iron concentrations, it is best to increase the heavies blowdown rate in order to keep the iron concentration below an accepted maximum level. The blowdown rate is increased by increasing the frequency at which heavies have to be transferred to the bottoms plant. This is accomplished by lowering the heavies still control temperature which decreases the heavies concentration, and thus results in a faster buildup of level in the bottoms drum. Other unexpected impurities that could possibly be present in the heavies still bottoms stream and that would contribute to reboiler fouling include metal salts from the OHC-EDC crude and $FeCl_3$ from the liquid phase EDC crude.

E. EDC STORAGE SYSTEM

1. <u>Drying Still Bottoms Storage System</u>

The purpose of the DH still bottoms storage system is to provide sufficient process surge time such that batchwise qualification of the OHC-EDC crude can be completed prior to it being sent forward for EDC purification. The proper operation of this system is necessary to insure that off-spec OHC-EDC crude is not transferred to the EDC purification section where it could cause undesirable conditions to develop.

Of primary importance is that the OHC-EDC crude be essentially dry and free of chloral. The downstream process equipment through which the OHC-EDC crude is processed is not designed for or capable of accomodating high concentrations of water. Not only is the wet crude very corrosive to steel piping and equipment when combined with HCl, but the presence of water in this stream will contaminate other crude EDC streams, eventually resulting in a plant shutdown and a loss of VCM production. Any chloral entering the EDC purification section ends up contaminating the furnace feed stream where it is thought to inhibit the cracking reaction and contribute to coking when fed to the furnaces.

Included in the DH still storage system are the DH still bottoms tanks, the crude OHC-EDC transfer pumps, a nitrogen pad and vent system, piping for filling, emptying, recirculating and sampling the storage tanks, and associated instrumentation for monitoring tank levels and pressure. The DH still storage system is also tied into the EDC storage vent recovery system and the EDC rework system. It is illustrated on process drawing 56A-10022 and P&I drawing 56A-10093.

All three DH still bottoms tanks are identical, each sized to hold 12 hours of OHC-EDC production at design rates and having a nominal capacity of approximately 58,000 gallons. During normal operations these tanks will serve as shift tanks, meaning that as one tank is filling for an 8 hour shift, a second tank is isolated (and recirculating if resampling is necessary), and a third tank is being transferred forward to the EDC purification section.

Crude EDC from the bottom of the DH still is pumped through the DH still economizer prior to entering one of the three DH still bottoms tanks. As the bottoms stream enters the tank, a small side stream is diverted to the tank's sampling system. The sampling system is a closed loop system that incorporates the use of an eductor to pull a sample stream from that tank, circulate it through the sample rig, and then back into the tank. The eductor uses either the normal bottoms stream, or the recirculation discharge stream as the motive fluid in drawing the sample from the tank and into the sample rigs. By circulating a portion of the tank's contents through the sample container for a reasonable time period, a fairly composite sample can be obtained.

When the tanks are switched, the sample obtained from the full tank is analyzed for water and chloral content by the VCM II lab. If the tank proves to be in-spec, it remains isolated until the following shift switches tanks, at which time its contents are transferred by the crude OHC-EDC transfer pumps to one of three locations: the LP-EDC reactor, the LP-EDC gas separator, or the lights still. During normal operations, the OHC-EDC crude will be lined up to the LP-EDC reactor. The purpose of processing OHC crude through the LP-EDC reactor prior to being fed to the lights still is to react out trichloroethylene (TRI), which is one of the major impurities in the OHC-EDC crude. Removal of metal salts (catalyst) from the OHC crude is also accomplished in the LP-EDC reactor. Out-of-spec crude is transferred by one of the rework pumps to the crude EDC storage tanks for reworking at the earliest possible convenience.

Tank levels in the DH still bottom storage system are monitored by field-mounted level gauges (varecs) and level transmitters mounted on each tank. The level gauge serves as a backup to the transmitter and is used each day to calculate inventory. Both the gauge and transmitter span the same range and are calibrated in the same units, so comparison between the two indications can be made quite easily.

To protect from overfilling a DH still bottoms tank, a high level switch is mounted on each tank. The level switch sounds an alarm in the control room. Whenever the high level switch is activated, action must be taken immediately to prevent a potentially disastrous situation from occurring. In addition to the level switch, the level transmitter is also used to generate high and low level alarms.

Because storage systems in general do not require as much operator attention as production units, their operation is sometimes over-looked. However, the DH still bottoms tanks, being low pressure vessels (design: 3oz. vacuum to 1.7 psig at 200°F), can easily be over-pressurized or sucked in on a vacuum if operated in a careless manner. Vacuum and over-pressure protection is provided by two separate means: First, by an automatic nitrogen pad and vent system that is common to all three tanks; and second, by a safety relief valve (SRV) mounted on each tank. The SRV's are set at the design limitations of the tank. The nitrogen pad and vent systems consist of two independent pressure regulators, the vent pressure regulator, and the nitrogen pad regulator. Individual vent lines from the tanks are connected to a common header, equalizing the tank pressure to each other. The resultant vent stream from the DH still bottoms tanks flows through the vent pressure regulator to the EDC storage vent recovery system. The vent pressure regulator is set to maintain 1.0 psig positive pressure on the bottoms tanks.

Just upstream of the vent regulator, the nitrogen pad regulator ties in. The purpose of this regulator is to purge nitrogen into the vent system to prevent the tanks from going under a vacuum. It is set to maintain a minimum tank pressure of 10 inches water (.36 psig). Located on the DH still bottoms storage vent header is a pressure transmitter used to indicate vent header pressure and to activate high and low alarms in the control room.

One problem associated with the operation of the DH still bottoms storage system is dealing with out-of-spec material. Normally, the EDC rework pump and recirculation lines are used to transfer off-spec material can be reworked directly from the DH still bottoms tank. Whenever material needs to be reworked, the EDC rework system is used to transfer material to the appropriate vessel. The point of rework depends upon the impurity causing the material to be out-of-spec. Refer to the EDC rework system write-up for all the rework tie-ins and the points of rework for off-spec material.

To help guard against misalignment of lines in the DH still bottoms storage system when transferring, recirculating, or reworking material, flow switches have been installed on the DH still bottoms storage recirculation lines. Each time the recirculation lines are used, their respective flow switches activate alarms in the control room. Improperly lining up the recirculation lines could result in overfilling a tank or contaminating a good tank with off-spec material.

Qualification of the OHC-EDC crude is necessary to insure that its water and chloral content are within acceptable limits. Since the production of water is inherent in the OHC process, the OHC-EDC crude represents the most probable source of water entering the LP-EDC reactor and EDC purification section. The consequences of high water levels in these two systems can be quite severe. If the water content is high enough in the LP-EDC reactor, the effectiveness of the ferric chloride catalyst will be reduced, and more heavies will be formed. Any moisture entering the EDC purification section, whether it originates from the OHC-EDC crude, LP-EDC crude, or the VCM recycle EDC, will eventually concentrate in the lights still overhead. Because the lights still overhead also contains a fair amount of HCl, corrosion of steel equipment (column, overhead condenser, reflux tank) will be unavoidable.

Although the OHC chloral treatment system is closely monitored, it is possible for some of the chloral to pass through the treatment system unreacted, and thereby contaminate the OHC-EDC crude entering the bottoms tank. If processed forward through the EDC purification section, the chloral will end up contaminating the furnace feed stream. Chloral in the furnace feed stream is undesirable, since it is thought to inhibit the cracking reaction and contribute to coke formation. By analyzing the DH still bottoms material for chloral, any chloral-contaminated crude can be reworked back to the treatment system prior to being processed through the EDC purification section.

The DH still bottoms tanks are surrounded by a concrete dike designed to contain orgnics spilled from the storage tanks. Located in one corner of the dike area is a small sample basin. From the sample basin, material collected within the dike area is periodically drained to either the plant's storm sewer, or the process sewer by opening the proper dike valve. Both dike valves always remain closed, except when the dike area is being drained. Prior to draining the dike area, liquid in the sample basin must be analyzed for organic content, oil and other possible pollutants. Contaminated water is drained to the process sewer whereas rainwater is drained to the storm sewer.

2. Crude EDC Storage System

The crude EDC storage system is designed to serve a number of functions. Its primary purpose is to provide sufficient process surge time to enable the EDC purification section to be shut down to replace reboilers (spare reboilers, interchangeable on both lights and heavies stills) and perform other maintenance work while the VCM, LP-EDC, and OHC sections remain in operation at reduced rates. The crude EDC storage system is sized to hold 48 hours of crude EDC production (lights still feed) when the crude production is one-half of its design rate. Another purpose of the crude EDC storage system is to provide storage capacity for out-of-spec EDC from the furnace feed tanks and DH still bottoms tanks. This allows batchwise qualification of the feed and bottoms tanks to be resumed as soon as the off-spec material is transferred into the crude tanks. The crude tanks can also provide storage capacity for the heavies still bottoms stream if the Plant B bottoms plant cannot accept bottoms because of inventory problems.

Included in the crude EDC storage system are the crude EDC tanks, piping for filling, emptying, recirculating, and sampling these tanks, a nitrogen pad and vent system, and associated instrumentation for monitoring tank levels and pressure. The crude EDC storage system is also tied into the EDC storage vent recovery system and the EDC rework system. The storage system is illustrated on process drawing 56A-10022 and P & I drawing 56A-10094.

All three crude EDC storage tanks are identical, each sized to hold 8 hours of crude EDC production at design rates and having a nominal capacity of 160,000 gallons. The crude tanks will remain empty whenever possible, available for off-spec material transfers and crude EDC storage when needed. From the curde tanks, off-spec material can be reworked at a rate consistent with plant design and current operation.

During an EDC purification section outage, crude EDC normally processed through the lights and heavies still (includes LP-EDC crude, OHC-EDC crude, and VCM recycle EDC) is diverted to the crude EDC storage tanks via a 4-inch line off the lights still feed header. The flow to the crude tanks is regulated by the LP-EDC gas separator level controller to maintain a steady level in the gas separator. Prior to entering the crude tanks, the crude stream flows through a water-cooled exchanger and the gas separator LCV. The crude EDC cooler is provided to cool the normally hot stream feeding the lights still to minimize venting in the storage tanks. Tying into the crude line just upstream of the cooler is a 3-inch line from the heavies still bottoms pumps, used for transferring bottoms into the crude EDC tanks.

As the crude EDC enters one of the storage tanks, a small side stream is diverted to the tank's sampling system. The sampling system is a closed loop system that incorporates the use of an eductor to pull a sample stream from the tank, circulate it through the sample rig, and then back into the tank. The eductor uses either the crude inlet stream or the recirculation discharge stream as the motive fluid in drawing the sample from the tank and into the sample rig. By circulating a portion of the tank's contents through the sample container for a reasonable time period, a fairly composite sample can be obtained.

There are three liquid lines piped to each of the crude EDC tanks; the crude EDC inlet header, and the recirculation suction and discharge lines. The recirculation lines are used in conjunction with the EDC rework pumps for transferring material to the VCM II plant EDC rework system and for resampling a crude tank.

Tank levels in the crude EDC storage system are monitored by field-mounted level gauges (varecs) and level transmitters mounted on each tank. The level gauge serves as a backup to the transmitter and is used each day to calculate inventory. Both the gauge and transmitter span the same range and are calibrated in the same units, so comparison between the two indications can be made quite easily.

To protect from overfilling a crude tank, a high level switch is mounted on each tank. The level switch sounds an alarm in the control room. Whenever this switch is activated, action must be taken immediately to prevent a potentially disastrous situation from occurring. In addition to the level switch, the level transmitter is also used to generate high and low level alarms.

Because storage systems in general do not require as much operator attention as production units, their operation is sometimes over-looked. However, the crude EDC tanks, being low-pressure vessels (design: 3 oz. vacuum to 1.7 psig at 200°F), can easily be over-pressurized or sucked in on a vacuum if operated in a careless manner. Vacuum and over-pressure protection is provided by two separate means; first, by an automatic nitrogen pad and vent system that is common to all three tanks; and, second, by a safety relief valve (SRV) mounted on each tank. The SRV's are set at the design limitations of the tank. The nitrogen pad and vent systems consist of two independent pressure regulators, the vent pressure regulator and the nitrogen pad regulator. Individual vent lines from the tanks are connected to a common header, equalizing the tank pressure to each other. The resultant vent stream from the crude tanks flows through the vent pressure regulator to the EDC storage vent recovery system. The vent pressure regulator is set to maintain 1.0 psig positive pressure on the tanks. Just upstream of the vent regulator, the nitrogen pad regulator ties in. The purpose of this regulator is to purge nitrogen into the vent system to prevent the tanks from going under a vacuum. It is set to maintain a minimum tank pressure of 10 inches water (.36 psig). Located on the crude EDC storage vent header is a pressure transmitter used to indicate vent header pressure and to activate high and low alarms in the control room.

As previously stated, one of the main functions of the crude EDC storage system is to store off-spec material needing to be reworked. The EDC rework system is then used to transfer material from the crude tanks to the appropriate vessel. The point of rework depends upon the impurity causing the material to be out-of-spec. Refer to the EDC rework system write-up for all the rework tie-ins and the points of rework for off-spec material.

To help guard against misalignment of lines in the crude EDC storage system when transferring, recirculating, or reworking material, flow switches have been installed on the crude EDC storage recirculation lines. Each time the recirculation lines are used, their respective flow switches activate alarms in the control room. Improperly lining up the recirculation lines could result in overfilling a tank or contaminating a good tank with off-spec material.

The crude EDC tanks are surrounded by a concrete dike designed to contain organics spilled from the storage tanks. Located in one corner of the dike area is a small sample basin. From the sample basin, material collected within the dike area is periodically drained to either the plant's storm sewer or the process sewer by opening the proper dike valve. Both dike valves always remain closed, except when the dike area is being drained. Prior to draining the dike area, liquid in the sample basin must be analyzed for organic content, oil and other possible pollutants. Contaminated water is drained to the process sewer, whereas rainwater is drained to the storm sewer.

3. Furnace Feed Storage System

The primary purpose of the furnace feed system if to provide sufficient process surge time, such that batchwise qualification of the pure EDC can be completed prior to it being used for feed to the cracking furnaces. Qualification of the pure EDC is a very essential and necessary step in the VCM production process because of the many possible detrimental effects impurities can have upon the operation of the furnaces and VCM purification section. The adverse consequences of high impurity levels can include such things as additional coke laydown in the furnace tubes, inhibition of the cracking reaction, corrosion of process equipment and piping, and loss of VCM production.

The furnace feed storage system is also designed to provide enough storage capacity such that the VCM furnaces and purification section can remain in operation during short-term maintenance outages in the EDC purification section. These outages are necessary to replace the lights still and heavies still reboilers when they become fouled. The storage system can provide approximately 48 hours of surge time if the furnaces are operated at one-half of their design rate.

The proper operation of the furnace feed storage system is necessary to insure that the quality of the EDC material being fed to the furnaces is within acceptable limits and to maintain stable operation of the furnace feed system. Upsets in the storage system could possibly cause unexpected furnace shutdowns due to a temporary loss of feed or unacceptable EDC feed quality.

Included in the furnace feed storage system are the three furnace feed tanks, piping for filling, emptying, recirculating, and sampling these tanks, a nitrogen pad and vent system, and associated instrumentation for monitoring tank levels and pressure. The furnace feed storage system is also tied into the EDC storage vent recovery system and the EDC rework system. The storage system is illustrated on process drawing 56A-10022 and P & I drawing 56A-10095.

All three furnace feed tanks are identical, each sized to hold 12 hours of pure EDC production at design rates and having a capacity of approximately 232,000 gallons. During normal operations, the three tanks will serve as shift tanks, meaning that as one tank is filling for an 8 hour shift, a second tank is isolated (and recirculating if it needs to be resampled), and the third tank is being transferred forward to the cracking furnaces.

Pure EDC from the heavies still system is pumped through the pure EDC cooler prior to entering one of the three furnace feed storage tanks. As the EDC product stream enters the tank, a small side stream is diverted to the tank's sampling system. The sampling system is a closed loop system that incorporates the use of an eductor to pull a sample stream from the tank, circulate it through the sample rig, and then back into the tank. The eductor uses either the product inlet stream or the recirculation discharge stream as the motive fluid in drawing the sample from the tank and into the sample rig. By circulating a portion of the tank's contents through the sample container for a reasonable time period, a fairly composite sample can be obtained.

When the tanks are switched, the sample obtained from the full tank is analyzed for water, iron, HCl, and organic purity by the VCM II lab. If the tank proves to be in-spec, it remains isolated until the following shift switches tanks, at which time its contents are transferred by the furnace feed pumps to the cracking furnaces. An off-spec tank is transferred by one of the EDC rework pumps to the crude EDC storage system.

Tank levels in the furnace feed system are monitored by field-mounted level gauges (varecs) and level transmitters mounted on each tank. The level gauge serves as a backup to the transmitter and is used each day to calculate inventory. Both the gauge and transmitter span the same range and are calibrated in the same units; so comparison between the two indications can be made quite easily.

To protect from overfilling a furnace feed tank or losing furnace feed flow due to a low level, high and low level switches are mounted on each tank. Both switches sound alarms in the control room. Whenever one of these switches is activated, action must be taken immediately to prevent a potentially disastrous situation from occurring. In addition to the level switches, the level transmitter is also used to generate high and low level alarms.

Because storage systems in general do not require as much operator attention as production units, their operation is sometimes over-looked. However, the furnace feed tanks, being low pressure vessels (design: 3 oz. vacuum to 1.7 psig at 200°F), can easily be over-pressurized or sucked in on a vacuum if operated in a careless manner. Vacuum and over-pressure protection is provided by two separate means; first, by an automatic nitrogen pad and vent system that is common to all three tanks; and, second, by a safety relief valve (SRV) mounted on each tank. The SRV's are set at the design limitations of the tank. The nitrogen pad and vent systems consist of two independent pressure regulators, the vent pressure regulator and the nitrogen pad regulator. Individual vent lines from the tanks are connected to a common header, equalizing the tank pressure to each other. The resultant vent stream from the furnace feed tanks flows through the vent pressure regulator to the EDC storage vent recovery system. The vent pressure regulator is set to maintain 1.0 psig positive pressure on the feed tanks. Just upstream of the vent regulator, the nitrogen pad regulator ties in. The purpose of this regulator is to purge nitrogen into the vent system to prevent the tanks from going under a vacuum. It is set to maintain a minimum tank pressure of 10 inches water (.36 psig). Located on the furnace feed storage vent header is a pressure transmitter used to indicate vent header pressure and to activate high and low alarms in the control room.

One problem associated with the operation of the furnace feed storage system is dealing with out-of-spec material. Normally the EDC rework pump and recirculation lines are used to transfer off-spec material to the crude EDC storage tanks. If the crude tanks are full, off-spec material can be reworked directly from the furnace feed tank. Whenever material needs to be reworked, the EDC rework system is used to transfer material to the appropriate vessel. The point of rework depends upon the impurity causing the material to be out-of-spec. Refer to the EDC rework system write-up for all the rework tie-ins and the points of rework for off-spec material.

To help guard against misalignment of lines in the furnace feed storage system when transferring, recirculating, or reworking material, flow switches have been installed on the furnace feed storage recirculation lines. Each time the recirculation lines are used, their respective flow switches activate alarms in the control room. Improperly lining up the recirculation lines could result in overfilling a tank or contaminating a good tank with off-spec material.

As previously stated, qualification of furnace feed EDC is very important to the proper operation of the VCM furnaces and purification systems. Furnace feed storage samples are routinely analyzed for water and iron content, and organic purity. Water analyses are run to insure that the water concentration in the furnace feed is within acceptable limits. Since the EDC cracking reaction results in the formation of HCl, any water entering the furnaces will eventually react with the HCl, forming an acid, and contributing to corrosion of steel equipment. Any iron present in the furnace feed will be deposited along the furnace tube walls as the EDC is vaporized, hurting heat transfer efficiency in the vaporization section. It also becomes a catalyst for the coking reaction. Iron in the furnace feed stream is the result of corrosion occurring in the overhead of the heavies still and the furnace feed storage tanks and piping. Organic impurities that can be identified in the furnace feed include such compounds as ethyl chloride, vinylidene chloride, cis and trans-dichloroethylene, chloroform, carbon tetrachloride (CCl_4), chloroprene, trichloroethylene, benzene, and 1,1,2-Trichloroethane (TCE). The effects of these impurities upon the EDC cracking process are quite varied, ranging from either inhibiting or promoting the cracking reaction to contributing to coke laydown. For a more detailed discussion on the effects of impurities in the cracking process, refer to the furnace system write-up.

The furnace feed tanks are surrounded by a concrete dike designed to contain organics spilled from the storage tanks. Located in one corner of the dike area is a small sample basin. From the sample basin, material collected within the dike area is periodically drained to either the plant's storm sewer, or the process sewer by opening the proper dike valve. Both dike valves always remain closed except when the dike area is being drained. Prior to draining the dike area, liquid in the sample basin must be analyzed for organic content, oil, and other possible pollutants. Contaminated water is drained to the process sewer, whereas rainwater is drained to the storm sewer.

4. Process and Intermediate Storage Refrigeration System

The purpose of the process and intermediate storage (P&S) refrigeration system is to supply low temperature refrigeration to five process heat exchangers located within the VCM II plant. These exchangers are: (1) EDC storage vent condenser, (2) VCM storage vent condenser, (3) DH still feed tank vent condenser, (4) LP-EDC vent condenser, and (5) VCM absorber vent condenser. All of the above condensers are used to recover organics from various vent streams prior to the vent stream being either incinerated or transferred to the HCl distribution system. It is emphasized that improper operation of this refrigeration system can result in significant losses of usable organic material from the VCM II plant and/or plugging of the OHC reactor's mixed feed nozzles, depending upon the vent streams.

The P & S refrigeration system consists of two Penjerdel refrigeration units operating in parallel as a single system to provide approximately 100 tons of refrigeration. Each unit is rated to deliver 50 tons of refrigeration using Freon-22 as the refrigerant.

Equipment common to both of the refrigeration units includes the high pressure liquid receiver, freon liquid subcooler, freon liquid supply and vapor return headers, a hot gas system, and the refrigerated vent condensers and their associated oil stills and oil transfer pumps. Besides the screw compressor, each refrigeration unit has its own oil separator, freon condenser, lube oil system, and compressor capacity control system. The P & S refrigeration system is shown on P & I drawing 56A-10099.

Basically, the P & S refrigeration system is designed to provide a minimum refrigeration level of around 0°F. Due to the physical location of two of the vent condensers and a temperature limitation on a third condenser, two higher levels of refrigeration, approximately 10°F and 35°F, are also incorporated into this system. All five vent condensers are sized such that their process streams are cooled to within 10 degrees of the freon temperature.

Both the LP - EDC vent condenser and the absorber vent condenser are located at far distances away from the refrigeration units in comparison to the other three vent condensers. Because of this, these two vent condensers face additional line pressure drop between themselves and the suction of the compressors. The extra pressure drop raises the freon pressure at the vent condensers, and, consequently, increases the freon evaporation temperature resulting in the slightly higher refrigeration level.

Unlike the absorber and LP-EDC vent condensers where the higher condenser freon pressure is inherent within the system, the DH still feed tank vent condenser freon pressure is artificially increased in order to raise the refrigeration level. The necessity for the higher refrigeration level is because the DH still feed tank vent contains water vapor that will begin to freeze inside the condenser tubes at temperatures approaching 32°F. The freon pressure in the DH still feed tank vent condenser is controlled by a field-mounted pressure controller to maintain the freon evaporation temperature at a minimum of 35°F.

To avoid any confusion in the ensuing discussion concerning the operation of the P & S refrigeration system, this write-up is broken down into the following sections:

a. Refrigerant Flow

b. Oil System

c. Liquid Subcooling System

d. Compresor Capacity Control System

e. Hot Gas Bypass System

f. Pumpdown System

g. Safety Shutdown Features

h. Abnormal Operation

Since both refrigeration units are identical, the following discussion refers to one compressor, unless otherwise noted.

a. <u>Refrigerant Flow</u>

The refrigerant flow of the P & S refrigeration system is basically the same as the other refrigeration systems employed in the VCM II Plant. Both refrigeration units employ oil-injected, positive displacement, screw compressors.

Low pressure freon gas from the five vent condensers (from here on referred to as freon evaporators) is drawn into the suction of each compressor through a Y-type strainer and check valve. The purpose of the strainer is to keep trash from entering the compressor. The check valve is necessary to prevent the compressor from turning backwards when it is shut down with a high gas pressure at the compressor discharge.

The screw compressor uses two helical intermeshing rotors to provide compression. Freon gas drawn into the compressor flows through the inlet port and fills the interlobe space between the adjacent rotors (lobes). As the rotors rotate, the interlobe space moves past the inlet port sealing the interlobe space. Continued rotation progressively reduces the interlobe space occupied by the gases, causing the gases to compress. During the compression cycle, the outlet port is also sealed by the rotors. When the interlobe space becomes exposed to the outlet port, the gas is discharged at a much higher pressure.

The high pressure freon gas is first discharged into an oil separator where most of the oil entrained in the refrigerant during compression is removed. Leaving the oil separator, the freon gas flows through a check valve to a water cooled exchanger where the freon gas is condensed. The high pressure freon condensate then gravity drains to a freon liquid receiver common to both refrigeration units. The check valve is installed on the oil separator outlet to prevent refrigerant backflow when only one refrigeration unit is shut down.

The freon receiver provides the necessary surge room needed due to fluctuations in the refrigerant quantity required by the individual evaporators. It also serves to maintain a liquid seal upstream of each evaporator level control valve. The high pressure liquid freon is pressurized out of the receiver through a standleg extending up from the bottom of the receiver. Leaving the receiver, it flows through a filter-drier element and a liquid subcooler prior to being distributed among the various vent condensers. The filter-drier aids in removing all moisture and foreign particles present in the system at this point. Subcooling the liquid freon is necessary to prevent it from flashing in the long pipelines leading to the various vent condensers. Just upstream of the subcooler, small sidestreams of the high pressure liquid are withdrawn to aid in the operation of the liquid subcooling system and the hot gas system. A more detailed explanation of these two systems follows later on in this discussion.

After undergoing subcooling, the high pressure freon liquid is distributed to the various evaporators (vent condensers) via the liquid supply header. Prior to entering each evaporator, the individual liquid streams flow through a level control valve where their flows are regulated by a field-mounted controller maintaining the proper level in the evaporator. It is recommended that the level in the evaporators be maintained at the minimum level at which the evaporators can meet their design requirements. The reason for maintaining a minimum level is to prevent liquid carryover in the freon vapor leaving the evaporator. Although screw compressors can handle more liquid than other types of compressors, they have their limits, at which time severe damage can be inflicted upon the compressor. Usually, the freon level is controlled such that the liquid freon just wets the top tubes of the evaporator.

The evaporator level-control valves are the dividing point between the high and low pressure sides of the refrigeration cycle. As the high pressure freon liquid flows through the control valve, its pressure is reduced to that of the evaporator pressure, causing a portion of the liquid stream to vaporize. This pressure reduction and subsequent partial vaporization step cools the remaining freon liquid and vapor down to the saturation temperature consistent with the freon pressure in the evaporator. As previously noted, the P & S refrigeration system involves three levels of refrigeration: 0° (24 psig), 10°F (32 psig), and 35°F (62 psig).

The resultant cold freon liquid and vapor stream flows into the shell side of the evaporator where the freon liquid absorbs heat from the process stream flowing through the tube side. As the freon liquid absorbs enough heat to reach its boiling point, it vaporizes and flows out of the evaporator into the vapor return header. Vapors from all of the evaporators combine in the vapor return header and flow to the suction of the compressors. Upon reaching the compressor suction, the refrigerant flow cycle is repeated.

b. Oil System

Each P & S refrigeration unit has its own oil system that is essential for the safe and proper operation of its compressor. The oil system serves several purposes.

1) Provides lubrication for all vital compressor parts.
2) Cools the discharge gas to allow operation at high compression ratios.
3) Seals the mating zone of the two rotors to assure high compressor efficiency.
4) Provides hydraulic pressure to operate the compressor capacity control system.

A system of external and internal oil circuits distributes the oil to the compressor parts. All of the oil injected into the compressor is eventually discharged from the compressor along with the high pressure freon gas.

Separation of the oil from the freon gas is completed through the use of a horizontal oil separator. The separator is divided into two chambers by an internal baffle plate. The refrigerant gas and oil mixture discharged from the compressor enters the inlet chamber of the oil separator where most of the oil drops out of the gas stream. Entering the outlet chamber, the freon gas flows past the baffle plate and through a filter assembly that removes more of the entrained oil. The bottom portion of the inlet chamber serves as an oil reservoir from which the compressor oil pump draws its suction. Oil accumulating in the outlet chamber is discharged back to the compressor suction valve by way of a high pressure oil trap. Bullseyes are mounted on the two chambers to check for high oil levels.

During the time in which the compressors are down, oil stored in the separator will become saturated with freon as the oil cools off. To prevent this from occurring, the oil separator is equipped with heaters activated by a low temperature switch monitoring the oil temperature in the separator. Whenever the compressor is down, the temperature switch energizes the heaters as necessary to maintain the desired oil temperature.

Oil accumulating in the inlet chamber of the oil reservoir is pumped back to the compressor for re-use by one of two oil pumps. A recirculation line from the discharge of the oil pumps back to the separator is equipped with a pressure regulator to control the compressor oil supply pressure. Prior to entering the compressor, the oil is circulated through a cooling tower water-cooled heat exchanger to cool the oil and then through one of two filters to remove any trash that may be present in the oil system.

The freon gas leaving the oil separator still contains a small amount of oil. The remaining oil is eventually carried forward in the liquid freon to the various evaporators, where it accumulates as the liquid freon is vaporized. Using one of three oil drawoff valves the accumulated oil gravity drains from the evaporator into its oil still.

Each evaporator has its own oil still to which the accumulated oil is intermittently drained. The oil still is equipped with a heater to vaporize any freon falling into the oil still back to the evaporator vapor line. A thermostat controls the oil temperature in the oil still by energizing and de-energizing the heater as necessary. The thermostat also activates a control valve on the evaporator oil drain line. As the oil temperature drops below the control point, the thermostat simultaneously energizes the heater and closes the control valve, stopping the oil from draining into the oil still. Above the control temperature, the heater is de-energized and the control valve is opened re-establishing the draining process. A manual block valve on the drain line is throttled such that the drain valve is opened 50 percent of the time.

When the level in the oil still reaches a high level, as indicated by the sightglass, the oil transfer pump is used to return the oil to the primary oil separator. The DH feed tank vent condenser and the EDC storage vent condenser share a common oil pump; the other evaporators have their own oil transfer pumps.

Oil can be added into the system as needed by using the DH feed tank vent condenser/EDC storage vent condenser oil transfer pump. When the system is started up initially, or after an outage during which the oil was removed, the refrigerant circuit will have an oil-free refrigerant charge. Upon operation, the freon will absorb oil until it reached an equilibrium condition. This will require the addition of oil to the lube circuit. Once the system reaches equilibrium, it will not be necessary to add oil unless oil leaks develop. Oil additions after initial start-up or after outages can be minimized by adding oil to the evaporator before the system is started.

c. Liquid Subcooling System

Due to the remote location of the vent condensers away from the P & S refrigeration units, the liquid freon supply has to be subcooled to prevent it from flashing in the pipelines leading to the vent condensers. Subcooling is accomplished by using a shell and tube liquid subcooler having two independent circuits, one circuit connected to a side port of each compressor. The subcooler operates under the same principle as that of the evaporators, only in this case an intermediate freon refrigerant level is used to cool the remaining high pressure freon liquid. Having two independent circuits permits subcooling with only one compressor in operation.

Saturated high pressure freon liquid from the freon receiver is pressurized through the shell side of the liquid subcooler where its temperature is lowered a minimum of 15°F below its saturation point. The subcooling process is effected by vaporizing an intermediate low temperature liquid freon stream flowing through the tube side of the subcooler. This intermediate refrigeration stream originates by diverting a small sidestream from the high pressure freon liquid prior to it entering the subcooler and subsequently reducing its pressure to produce the lower refrigerant temperature. As the pressure of the liquid drawoff stream is reduced, part of the liquid stream vaporizes, cooling the remaining liquid down to a temperature consistent with the pressure at the side port of the compressor (design: approximately 47°F). The low temperature freon liquid eventually vaporizes as it absorbs heat from and thereby cools the high pressure freon liquid flowing through the subcooler. Leaving the subcooler, the freon vapors are recycled back to a side port on the compressors.

As previously mentioned, the tube-side of the subcooler is comprised of two independent subcooling circuits, one per compressor. Each subcooling circuit is equipped with its own thermostatic expansion valve that represents the dividing point between the high and low pressure sides of the intermediate refrigerant stream. The thermostatic expansion valve performs only one very simple function; it keeps the subcooling circuit supplied with enough intermediate refrigerant to satisfy the load requirement. Being both sensitive to pressure and temperature of the intermediate freon vapors leaving the subcooling circuit, the expansion valve regulates the temperature of the existing vapors to maintain a specific amount of superheat by adjusting the high pressure liquid drawoff rate.

The subcooling capacity provided by each compressor is limited by the operating capacity of the compressor. As compressor capacity is reduced, the side port to which the subcooler outlet vapors are returned begins to close (by the slide valve) reducing the subcooling capacity. When the compressor reaches approximately 60 percent of capacity, the side port is fully closed, rendering the subcooling circuit inoperative. Reed switches mounted on the compressor slide valve indicator monitor the compressor loading and activate accordingly a solenoid valve on the high pressure liquid freon drawoff stream feeding the subcooling circuit. Once the side port is closed, as indicated by the position of the slide valve, the liquid drawoff valve is closed by one of the reed switches. As the side port begins to open, the second reed switch opens the liquid drawoff valve reinstating the operation of the subcooling circuit.

To maintain the required subcooling effect at reduced refrigeration loads, the compressor capacity controls must be adjusted such that one compressor operates at close to 100% capacity while the remaining compressor operates at some reduced capacity to meet the total load requirement. At slightly less than 50% of total load, the lag compressor can be shut down and the capacity of the lead compressor can be adjusted to meet the remaining load requirement. This scheme will provide liquid subcooling down to 60% of one compressor or 30% of system capacity.

It is anticipated that at system capacity less than 30%, liquid subcooling will not be required. However, should it be determined that subcooling is needed at this low capacity, the hot gas bypass system can be used to keep the lead compressor operating at slightly above 60% capacity.

In addition to providing liquid subcooling, the subcooler increases the compressor capacity and also considerably increases its efficiency. Therefore, from an economical standpoint, it is desirable to operate the compressors at capacities in the subcooling range.

d. Capacity Control System

Because the P & S refrigeration compressors are positive displacement compressors, it is not necessary to balance the load between the two compressors. They can be operated together at unequal capacities, as one can lead the other. Since the maximum compressor efficiency is at full load, the most economical mode of operation is achieved by operating one compressor at full load while the second compressor varies its capacity to handle load fluctuations. To operate the refrigeration system in this manner, the fully loaded compressor is operated in the manual mode, while the floating compressor is operated in the automatic mode.

The operating capacities of the two compressors are controlled by their own capacity control systems. As noted, the control system can be operated in either the automatic or manual mode by adjusting the capacity control switch. In the automatic mode, the control system is activated by high and low pressure switches mounted on the compressor suction line. The high pressure switch is set such that once the suction pressure goes high, the compressor begins to load up (slide valve closes). It continues to load up until the suction pressure falls to its normal value, at which time loading is discontinued. Whenever the suction pressure begins to fall, the compressor will begin unloading (slide valve opens) until the pressure rises back to its normal value. In the manual mode, the compressor capacity is varied by operating a "load-unload" switch. The compressor will continue to load or unload until the switch is released or the slide valve has reached the fully closed or open position. When the switch is released, it will return to the center position and the control system will maintain the resulting load.

The capacity control system has a built-in current limiting control system that automatically unloads the compressor should it exceed the compressor motor design full load amp rating. This safety control feature is in effect whether the compressor is operating in the automatic mode or manual mode.

Basically, the capacity control system varies the compressor loading by adjusting an internal gas recycle stream. Internal gas recycle is accomplished through the use of a slide valve located on the bottom side of the compressor rotor housing. During times in which the compressor is operating at full load, the slide valve remains closed. As the compressor is unloaded, the slide valve opens allowing gas to recycle from the opening created in the bottom of the rotor housing back to the inlet port area prior to the gas being compressed. Continued opening of the slide valve increases the recycle flow rate and decreases the amount of gas to be compressed. In principle, enlarging the opening in the bottom of the rotor housing effectively reduces compressor displacement.

Initiated by the capacity control system, axial movement of the slide valve is accomplished using a hydraulic control system. This system consists of a hydraulic cylinder mounted on the compressor with its piston connected to the slide valve and two hydraulic control solenoid valves. The length of time the control solenoids are energized determines the degree of loading or unloading, as the slide valve can be stopped anywhere between 100% compressor capacity and 10% capacity. This gives the compressor the ability to have infinite steps of capacity control with corresponding savings in power requirements.

e. Hot Gas Bypass System

Hot gas is used to artificially load the operating compressor (or compressors) to permit operation at low refrigeration loads without lowering the compressor suction pressure too low. The hot gas bypass system is simply a scheme for externally recycling compressor discharge gas back to the suction side. Since the discharge gas is much too hot to be recycled directly back to the compressor suction, high pressure freon liquid is injected into the hot gas to lower its temperature compatible with the normal suction temperature. A field-mounted pressure controller on the compressor's suction header controls the compressor suction pressure at the desired pressure by regulating the amount of hot gas allowed to bypass the freon condenser. High pressure liquid freon is controlled through a thermostatic expansion valve to cool the bypass hot gas to within 10°F or 15°F of the compressor saturated suction temperature.

The hot gas bypass system is activated by either one of the compressors when operating at low capacities. Both the hot gas bypass solenoid valve and the liquid injection solenoid valve are controlled by reed switches mounted on the compressor's slide valve indicator rod. The solenoid valves are opened at about 10% of slide valve travel and are closed around 15% of slide valve travel of either compressor. Both the hot gas and liquid injection valves open and close simultaneously.

f. Pumpdown System

Prior to shutting down the P & S refrigeration system, it is desirable to move liquid freon out of the various vent condensers to prevent excessive carryover of refrigerant during the subsequent compressor start-up. To accomplish this, each compressor is equipped with a pumpdown feature. The pumpdown cycle is put into effect by turning the hot gas switch from the "auto" position to the "pumpdown" position. This bypasses the hot gas system and allows the compressor to continue to operate until it shuts down on low suction pressure. Before pumping down the refrigeration system, the high pressure freon liquid must be blocked to all of the associated evaporators. Then, as the compressor begins to pump down, the suction pressure will begin to fall causing the freon liquid in the evaporators to flash. The refrigerant eventually accumulates in the high pressure freon liquid receiver. The pumpdown cycle automatically shuts off as the low suction pressure trip is reached.

g. Safety Shutdown Features

Each refrigeration unit has its own safety control system that assures safe and proper operation of the unit. The main function of the safety control system is to warn of deteriorating operating conditions and to shut down the unit whenever any abnormal conditions exist that could possibly damage the compressor and other unit components. Some of the conditions protected against include over-pressure or over-heating of the equipment beyond design limitations and loss of lubrication due to insufficient oil flow or oil cooling.

To protect the refrigeration unit from severe mechanical damage when detrimental operating conditions exist, the control system will shut down the compressor based upon the following:

1) High discharge pressure
2) High discharge temperature
3) Low suction pressure
4) High oil temperature
5) Low oil temperature
6) Low oil differential pressure
7) Motor overload

Prior to a shutdown, a general trouble alarm will sound in the control room. For more information on the safety control system, refer to the VCM II Plant Safety Control Systems Manual.

It is emphasized that the cause of any compressor shutdown must be determined and corrected before attempting to restart the compressor.

Each unit is an expensive piece of equipment that can easily be severely damaged by momentary carelessness.

h. Abnormal Operation

The most serious problem incurred in the operation of the P & S refrigeration system is the unexpected shutdown of one or both refrigeration units. As noted, all of the vent condensers associated with the P & S refrigeration system are used to recover usable organics from various vent streams in the VCM II plant. Loss of refrigeration to the vent condensers will result in a loss of organics from the VCM II system, lowering plant yields and efficiencies.

Of immediate significance is the organic contamination of the HCl vent streams leaving the absorber vent condenser and the LP-EDC vent condenser during a loss of refrigeration. Since these vent streams are tied into the HCl distribution system, the organic impurities will end up plugging the OHC reactor mixed feed nozzles as the HCl stream is fed to the reactors. If only one refrigeration unit is lost, the absorber vent condenser should have first priority on the remaining refrigeration capacity. Next in line would be the LP-EDC vent condenser. Refrigeration to the remaining vent condensers can be re-established as capacity becomes available.

Following the loss of one refrigeration unit and prior to the time in which corrective actions are taken to stabilize the refrigeration system, the remaining refrigeration unit can be overloaded. If the capacity control system of the operating unit is in the automatic mode, the compressor will load up to the point at which the current limiting control system will prohibit the compressor from loading any further. In the manual mode, the compressor will only load up as the freon gas density increases (due to a rise in compressor suction pressure), again up to the point at which time the current limiting control system takes over.

Immediately after the compressor trips, the remaining unit may not be able to provide the refrigeration load being called upon by the evaporators. Although the evaporators will be provided with sufficient liquid refrigerant for a short time (by surge volume in the receiver), the compressor cannot compress all of the freon vapors being generated by the evaporators. As a result, the compressor suction pressure increases, raising the refrigeration level in the system. The process streams circulating through the evaporators are then not cooled properly. It is important to make sure that the high process temperatures are a result of high suction pressure, and not insufficient level in the evaporator. As the suction pressure increases, so does the compressor discharge temperature. However, the freon condensers operating in parallel and equalized to each other will condense the discharge gas down to its normal temperature. The lone refrigeration unit should continue to operate with a high suction pressure until the refrigeration requirement is reduced. As this is done, the suction pressure will begin dropping to its normal value.

In a compressor overload situation, the compressor will probably first shut down on overload (high amps) if its current limiting control system fails to work properly. The second most likely trip feature will be that of a high compressor discharge temperature.

The loss of both refrigeration units will necessitate a shutdown of the OHC reactors if they are operating totally on the HCl being produced in the VCM II plant. VCM production rates will have to be reduced and the by-product HCl stream scrubbed until refrigeration is again restored to the absorber vent condenser. A loss of refrigeration to the other vent condensers is not nearly as critical, since they are very small streams in comparison to the HCl stream and can be incinerated.

5. Storage Vent Collection System

The EDC storage vent recover system is designed to perform two important functions. First, it recovers any usable organic material vented from the low pressure EDC storage systems by condensing the organics in refrigerated vent condensers. Second, it displaces the remaining non-condensable vapors to the vent header so that they may be incinerated by compressing the low-pressure vent stream to a sufficient pressure to enter the vent header.

The recovery of organics from the various vent streams is necessary to be in compliance with EPA guidelines set forth on the VCM II plant and to maintain plant yields and efficiencies as high as possible. The amount of recovered organics from these vent streams represents what would otherwise be a loss to the plant by way of incineration or atmospheric scrubbing.

Equipment comprising the EDC storage vent recovery system includes the EDC storage vent condenser, DH still feed tank vent condenser, EDC storage vent compressors (2) and suction drum, and associated piping and instrumentation. Both vent condensers are also part of the process and intermediate storage refrigeration system. The vent recovery sytem is illustrated on process drawing 56A-10022 and P & I drawings 56A-10096 and 56A-10097.

Vent streams from four separate low pressure EDC storage systems are processed through the vent recovery system. They are the DH still bottoms storage vent, furnace feed storage vent, crude EDC storage vent, and the DH still feed tank vent. All of the vent streams except the DH still feed tank vent combine in the EDC storage vent header prior to entering the tube side of the EDC storage vent condenser. Using 0°F refrigerant, the EDC storage vent condenser is designed to cool the vent stream down to approximately 10°F. The DH still feed tank vent condenser, using 35° refrigerant is provided to cool the feed tank's vent down to 45°F. The reason for using a separate condenser and higher level refrigeration for the DH still feed tank vent is because this vent contains a small amount of water vapor which would freeze in the condenser tubes at the lower refrigeration level. The process and storage (P & S) refrigeration system supplies the refrigerant to the two vent condensers.

Condensate and non-condensables from the vent condensers flow through vapor disengaging tees where the non-condensables are vented to the EDC storage vent compressor suction drum and the condensate gravity-drains to the DH still feed tank. Any liquid in the suction drum resulting from carry-over in the vapor stream or condensation also gravity drains to the DH still feed tank. A high-level switch mounted on the suction drum is used to warn of a high liquid level in the drum.

To protect the related low-pressure storage tanks from possible over-pressure should either or both of the vent condensers freeze up, blocking the normal flow path of the vents streams, pressure-controlling devices are installed on the two vent headers. The EDC storage vent header is equipped with a control valve and field-mounted controller that regulates the vent header pressure at 1.0 psig by venting any excess pressure directly to the compressor suction drum, bypassing the vent condenser. The DH still feed tank vent header is controlled in the same manner, the only difference being that a pressure regulator is used in place of a controller and control valve.

Vapors from the suction drum flow to the EDC storage vent compressors where they are compressed from approximately .5 psig pressure to 5.0 psig. The compressed vapors are discharged through a pressure-control valve to the incinerator header. Two compressors are provided, each capable of compressing 250 cfm at design conditions (10°F and .5 psig). To protect against reverse flow from the incinerator header back through the compressors to the storage tanks when the compressors are down, a differential pressure transmitter monitors pressure drop across the control valve located on the compressor discharge line. When the pressure drop falls to zero, indicating no flow or backflow, a pressure differential switch is activated closing the control valve. The pressure switch resets automatically once the reverse flow transmitter is satisfied.

The control instrumentation associated with the EDC vent compressors is designed to provide a steady flow to the suction of the compressor by maintaining a constant suction pressure when the compressors are operating. Controlling the suction pressure is basically accomplished by recirculating vapors from the discharge of the compressor through a cooler back to the suction drum at a rate sufficient to maintain the suction pressure. Suction and discharge pressure controllers act in unison to regulate the recirculation rate. For instance, as the suction pressure controller senses a change in the suction pressure, it will adjust the control valve located on the compressor discharge line, changing the discharge pressure. The discharge pressure controller, reacting to an upset in its pressure, will vary the control valve on the recirculation line, changing the recirculation rate accordingly to regain control of the discharge pressure.

Since the load on the compressors can change significantly as tank levels and weather conditions vary, the compressors are provided with a system which automatically starts up or shuts down one of the vent compressors. The designated "primary" compressor is selected by operating a local hand switch. Pressure switches located on the compressor suction drum vapor outlet line are used to activate the system. Upon reaching a high suction pressure, the high pressure switch is tripped, starting the primary compressor. When the suction pressure falls below a specific value, a low pressure switch shuts down the compressor. The "secondary" compressor has to be started manually in the field. A hand switch in the control room can be used to shut down both compressors.

The vent compressors have one safety shutdown feature associated with them. A "Hi-Hi" level switch mounted on the compressor suction drum automatically shuts down both compressors should an abnormally high liquid level develop in the suction drum.

The EDC vent recovery system has to be put into operation prior to putting any of the low pressure EDC storage vessels into service. As long as these vessels contain organic material, the vent recovery system should be operating.

F. VCM SYSTEM

1. Furnace Feed System

The furnace feed system is designed to deliver the necessary quantity of pure EDC feed to the EDC cracking furnaces at a sufficient temperature and pressure to insure steady and proper operation of the furnaces. Multiple feed pumps and a heat economizer are used to accomplish this task. If for any reason the furnace feed system is not operated properly, the expected operating life between furnace decokings can be significantly shortened, resulting in additional plant downtime and loss of VCM production.

Included within the furnace feed system are the furnace feed pumps, furnace feed economizer, and associated piping and instrumentation.

The furnace feed system is illustrated on process drawing 56A-10022 and 56A-10014 and P & I drawings 56A-10095, 56A-10059, 56A-10061, and 56A-10062.

Pure EDC stored in the furnace feed tanks is transferred by the furnace feed pumps through a heat economizer to the inlet of both EDC cracking furnaces. There are three feed pumps, two of which are required to provide the necessary quantity of EDC to meet the design VCM production rate. With only two pumps operating, the unexpected shutdown of one pump will necessitate a reduction in the furnace feed rate until two pumps are put back into operation. Because these pumps are extremely critical to the safe operation of the furnaces, each is provided with board-mounted start buttons for quick restart and check valves on their discharge lines to prevent backflow through a non-operating pump.

Prior to entering the furnaces, the EDC feed is preheated in the furnace feed economizer. The economizer consists of two shell and tube heat exchangers operated in series, with one exchanger mounted directly above the other. Each exchanger is constructed with a floating head allowing removal of the tube bundle for shell side cleaning. The product still bottoms stream flows through the tube side of the economizer supplying heat to the furnace feed stream on the shell side.

After undergoing preheating, the furnace feed stream enters the VCM furnace area where individual feed streams split off to each pass of both furnaces. Since they are two-pass furnaces, there are two separate feed streams per furnace, each feed stream being individually monitored and controlled to admit the proper quantity of EDC to the furnace pass. All feed streams to the furnaces are identical, first flowing through a control valve, and then through two flow meters (mounted in series) prior to entering the convection section of the furnace.

It is important to remember that the furnace feed flow meters are connected to a furnace shutdown system. The shutdown system automatically shuts down the furnace should a loss of feed occur to either one of its two passes. Therefore, extreme care must be exercised to insure that the furnace feed flows are not accidentally interrupted due to improper switching of the furnace feed tanks, improper operation of the economizer, or spurious feed pump shutdowns. The pump operation must be closely monitored so that maintenance can be performed at the first sign of problems.

Whenever a total furnace shutdown occurs eliminating the need for furnace feed, the furnace feed economizer is taken out of service by bypassing the product still bottoms stream around the economizer. Whether the furnace feed system is left operating on recycle or shut down completely, taking the bottoms stream out of the economizer is a must. If the furnace feed system is operating on recycle, heating the feed stream will eventually upset the heavies still operation due to the unavoidable increase in its reflux temperature. Allowing the bottoms stream to circulate through the economizer when the feed stream is discontinued will cause increased fouling on the shell side of the economizer. Pressurization of the shell side will occur if the feed stream is completely blocked into the economizer. The shell side of the economizer is protected from overpressure by an SRV set at 500 psig.

Although the furnace feed system may seem simple compared to other systems in the VCM II plant, problems can develop here that can have severe consequences upon the operation of the furnaces, and thus the entire VCM plant. The most obvious problem is the loss of feed to one or both furnaces caused by either feed pump malfunctions, a plugged furnace pass, or faulty instrumentation, requiring the shutdown of one or both furnaces. Besides loss of production due to a furnace shutdown, repeated furnace start-ups during the middle of a furnace run become more critical as the chances of plugging a pass during the shutdown or start-up become much greater. Furnace shutdowns or rate reductions also have an impact on OHC unit operation.

Another problem that could develop is insufficient preheating of the furnace feed stream, resulting from either a fouled economizer, lower than normal EDC recycle flow (caused by an excessively high furnace conversion rate), or a higher furnace feed rate than required. Furnace design calls for the feed stream to be preheated to approximately 250°F. As the feed temperature drops below this value, the furnace itself must make up the lost preheat by consuming additional fuel gas. If the feed temperature is significantly low, vaporization of the EDC feed in the furnace convection section may not be complete, resulting in small amounts of liquid EDC entering the radiant section where it must be vaporized. This causes an accelerated coke buildup in the front end of the furnace pass in the radiant section.

The furnace feed pumps are operated such that the discharge pressure is sufficient to push material into the furnaces without exceeding the design pressure of the economizer. If the pressure drop through the shell side of the economizer becomes high enough, it may be necessary to bypass a portion of the furnace feed stream around the economizer to prevent over-pressurizing the shell side when maintaining the required EDC feed rate. This action, however, will result in a lower feed temperature and a higher lean oil temperature, possibly necessitating a production rate cut.

Start-up or shutdown of the furnace feed system is always done in conjunction with a furnace start-up or shutdown. Prior to the actual furnace start-up, the furnace feed system is started up and operated on recycle a sufficient period of time to heat the furnace feed stream to its approximate normal operating temperature. Operating the furnace feed system on recycle to preheat the furnace feed requires the use of special start-up lines that are tied to the individual feed streams at their flow control stations. Opening the start-up lines allows the feed streams to be recycled back to the heavies still reflux drum while they remain blocked to the furnace passes. From the reflux drum, the recycled material is pumped back to the furnace feed tanks.

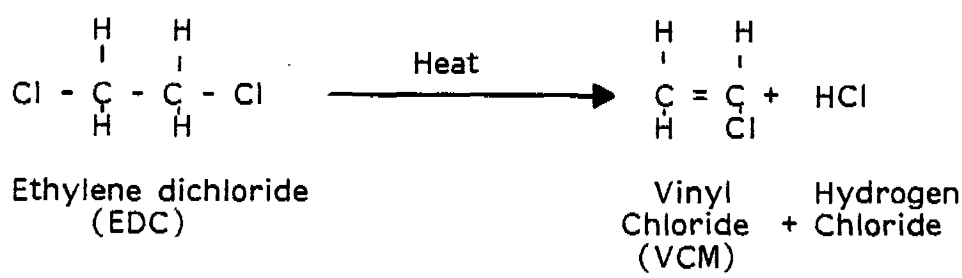
Laboratory analyses of the pure EDC feed to the cracking furnaces are completed during the time in which the feed material is stored in the furnace feed tanks. The EDC should always be approximately 100% EDC, essentially free of water, iron, and organic impurities. All furnace feed tanks are cleared by the VCM II lab prior to being used for feed material. If a feed tank proves to be out-of-spec, its contents are transferred to the crude EDC storage tanks to be reworked at the earliest possible convenience.

2. Furnace System

In order to produce VCM, EDC produced in other sections of the VCM II plant must undergo conversion to VCM via a chemical reaction commonly referred to as cracking.

The furnace section performs this conversion of EDC into VCM and co-product HCl.

The chemical reaction may be represented as follows:



$$1\ C_2H_4Cl_2 \xrightarrow{\text{Heat}} 1\ C_2H_3Cl \ + \ 1\ HCl$$

That is, one molecule of ethylene dichloride reacts to form one molecule of vinyl chloride and one molecule of hydrogen chloride.

The EDC vaporizing-cracking furnaces supply the heat necessary to vaporize the EDC, heat it up to temperature, and carry out the reaction.

The proper operation of the furnaces is essential for the smooth operation of the quench system, absorber-stripper system, and the OHC section. It can also impact on the operation of other plants in the Lake Charles Complex via the HCl distribution system. Improper operation of the furnaces may result in unacceptable levels of impurities in the VCM product and poor furnace on-stream time, preventing the plant from meeting production requirements.

The furnace system consists of two EDC vaporizing and cracking furnaces operated in parallel. Two furnaces are used instead of one, to allow the shutdown of one furnace for maintenance or decoking without necessitating a complete shutdown of the plant. A coke knock-out drum and a coke retention sump are also provided for decoking operations.

Due to the complexity of the furnace system, the figure is provided to aid in reading the following write-up. The write-up is divided into the following sections: a. Process Side -description and explanation; b. Furnace Side - description and explanations; c. Furnace Control; d. Coking - considerations and explanation; e. Abnormal Operation - explanation and corrective actions; f. Decoking; g. Start-up and Shutdown; h. Furnace Shutdown System

a. Process Side

Liquid EDC is supplied to the furnace system by the furnace feed system. The EDC divides into four streams in the furnace area. Two of these streams are flow-controlled into each furnace. These two streams pass through each furnace in parallel. The EDC charge enters the top of each furnace at the convection section. As it passes through the horizontal tubes in the convection section, it is heated, vaporized, and slightly superheated. There are eight rows of carbon steel and two rows of Incoloy 800H tubes in the convection section. The complete vaporization of the EDC in the convection section is important, since coke deposition is the greatest at the point in the tube where vaporization is completed. If this coke laydown occurs in the radiant section, where the heat going through the walls of the tubes (called heat flux) is much greater, then overheating will result. This can lead to more frequent outages for cleaning or decoking of the tubes.

After the vaporized EDC charge passes the crossover, it enters the vertical tubes of the radiant section at the top of the furnace firebox. These tubes are Incoloy 800H material. As the EDC passes through the radiant section, it is heated up to a final temperature of about 900°F. The cracking reaction or conversion of EDC to VCM and HCl begins to take place at about 700°F. As the temperature continues to increase, the rate of the conversion speeds up. The amount of EDC that is converted to VCM and HCl is dependent on the rate it is being converted and the amount of time it is held in the radiant section tubes. The time that the charge takes to pass through the radiant section tubes is called retention time. At the retention time and temperature (reaction rate) that the furnaces are designed to operate, 55% of the entering EDC is converted to VCM and HCl. The remaining 45% of the EDC and the VCM and HCl pass out of the furnace radiant section at the top of the firebox and enter the quench system.

Heat is required to vaporize the EDC and heat it up to the outlet temperature. In addition to the heat needed to increase the temperature, heat is needed to cause the reaction to proceed. At design rates, about 70% of the heat input by the furnace is used to heat up and vaporize the charge. The remaining 30% of the heat is used by the reaction in converting EDC to HCl and VCM. This heat is obtained by the burning of fuel in the firebox of the furnace.

The production rate of VCM and HCl is controlled by the heat input to the furnace. The fuel gas is flow-controlled to each furnace. The charge flowrate is held constant when the plant is operated at or near full production rates. Small adjustments in production rates are made by adjusting fuel gas. The charge flowrate is set so that conversion does not exceed 55%. Production rates are reduced by reducing fuel gas flowrate. This reduces the heat input, thereby reducing the heat available for the reaction and the heat available for heat-up. This also lowers conversion, thereby increasing the amount of unconverted EDC that flows to the VCM purification section and the EDC purification section. If the production rates are reduced greatly, then feed rates must also be reduced to limit the amount of EDC recycle.

The production rate from each furnace cannot be metered. It is, however, important that the amount of production coming from each furnace be equal. If it is not, that is, if one furnace is carrying more of the load, then it will result in that furnace having more coke laydown. This will cause the furnace to be shut down for decoking too frequently. In order to prevent this, the feed flowrates to each pass on each furnace must be the same and the fuel gas flow to each furnace must be the same. All rate adjustments should be made by identical fuel gas adjustments to both furnaces.

b. Furnace Side

Fuel gas is supplied to the furnace system by the plant natural gas system. Upon entering the furnace area, the pressure of the fuel gas is reduced from the natural gas system pressure of about 120 psig to 60 psig and flows into a gas supply header. From this supply header one pilot supply line and one main fuel gas supply line branch off to each furnace. The main fuel gas supply for each furnace passes through a metering station and a flow-control valve. Each flow-control station is equipped with a double block and bleed arrangement that is operated by its Flame Management System. After the flow-control station, the gas to each furnace divides into three supply lines. Each line is equipped with a flow meter and a manual adjustment valve. Each line supplies gas to the burners of one chamber in the radiant secton. Downstream of the manual adjustment valve, each line forms a header, off of which branch the lines to each burner. The line to each burner has an automatic fuel shutoff valve (Maxon) and a supervisory valve. These valves are a part of the Flame Management System. The supervisory valve is also used to adjust the gas flow to each burner, if necessary.

Combustion air enters the radiant section floor through plenum boxes below each chamber. The plenum provides for adjustment of air flow to a group of burners and lowers noise levels. Inside the plenum, the air flow distributes itself to each burner. There is an air door for adjustment of the air flow to each burner. The air enters the plenum by natural draft. This draft is created by the hot flue gases of the furnace flowing out of the stack.

The burners are mounted in the floor of the radiant section firebox. The burners are John Zink FFC combination direct gas burners. The direct means that there is no premixing of the fuel and air prior to the fuel gas being ignited.

The burners fire into the furnace radiant section firebox. The firebox is divided into three cells or chambers. The chambers are formed by two firebrick bridgewalls that extend up about 1/3 of the height of the firebox. The tubes are arranged in vertical rows in the radiant section. The first halves of each pass are both in the center chamber of the furnace forming two rows of vertical tubes. The second half of each pass is located in its own chamber formed by the intervening bridgewall and the furnace sidewall. Thus, the north and south chambers each have one row of vertical tubes. Each row of tubes is double fired, (that is, it has burners on both sides). In the north and south chamber, this is formed by two rows of four burners. In the center chamber three rows of four burners are required. The center row of burners, in the center chamber, is providing heat for two rows of tubes. For this reason, these burners are twice as large as the other burners. The first half of each pass is separated from the second half of each pass so that the heat input can be varied along the length of the pass, if desired. The second halves of each pass are completely separated from each other. Since the fuel flow to the chambers is metered, it is possible to adjust and balance the heat input to each pass.

The combustion products, or flue gases, flow up through the vertical radiant section firebox. The gases give up heat to the tubes by radiant heat transfer. The heat travels through the tube wall and into the charge. The flue gases in each chamber are fairly uniform in temperature. The temperature of the flue gases is measured at the top of the radiant section. This temperature is called the bridgewall temperature.

The flue gases in the firebox must operate at a pressure lower than atmospheric, resulting in air leakage into the furnace. If flue gases were allowed to leak out, it would cause overheating of the furnace structure. The pressure at the top of the radiant section is monitored at all times in the control room. This is the point where the furnace is most likely to go on a positive pressure. A field-mounted pressure indicator is also provided to check the draft pressure at the bottom of each chamber, at the top of the radiant section, at the outlet of the convection section, and above the damper in the bottom of the stack. The furnaces were designed to be fired at up to 1.3 times the fuel gas needed for 750 TPD VCM rates at 55% conversion and still have sufficient draft at the convection section inlet.

The flue gases flow out of the top of the radiant section and into an offset convection section. The offset convection section provides less exposure of the first row of tubes in the convection section to radiant heat transfer from the firebox. The offset convection section is also necessary to provide for removal of the radiant section coils.

In the convection section, the heat is transferred to the tubes, primarily by convective heat transfer. However, on the bottom two rows of tubes where the flue gases are still quite hot, there is a significant amount of radiant transfer. These are called the shock tubes, and they are bare tubes. In the remainder of the convection section the heat transfer is primarily by convection. Convective heat transfer from a gas (the flue gas) requires more area than radiant transfer. In order to provide sufficient heat transfer area in the convection section, these tubes have fins on the outside. These fins increase the heat flux. In order to keep the heat flux from being too great in the bottom three rows of finned tubes, where the final stages of vaporization are taking place, a fin density of 3 per inch was used. The top eight rows use a fin density of 4 per inch.

The flue gases leave the top of the convection section at about 400°F. They flow through a damper and up the stack. The damper is used to control the draft in the entire furnace.

c. Furnace Control

The combustion process of the fireside of the furnace must be controlled in an efficient and safe manner. The performance of the fireside is governed by the fuel gas firing rate and the draft pressure. The fuel gas firing is basically set by what is required to produce the desired amount of VCM at any given time. Thus, the operation of the fireside is adjusted by draft alone. In order to operate the fireside efficiently, only that amount of air needed for the complete combustion of the fuel gas can be admitted to the firebox. The draft, or vacuum in the furnace firebox, pulls this air into the furnace. In order to achieve complete combustion, a slight excess of combustion air is required. The furnaces are designed to get 86% efficiency at 20% excess air when burning methane fuel gas. If too much excess air is admitted, more fuel gas must be fired to heat up the extra air. This lowers the furnace efficiency, as the additional heat is not absorbed by the charge, but is carried out of the stack. If too little excess air is admitted, it will result in incomplete combustion and possibly afterburning.

In order to operate the furnace efficiently, it is necessary to analyze the flue gases to determine the amount of excess air. This is done with a flue gas oxygen analyzer. It measures the O_2 in the flue gases at the top of the radiant section. This point is preferred, since making this measurement in the stack may result in falsely high O_2 readings due to air leakage into the furnace in the convection section. Sampling points lower in the radiant section are provided so that the excess can be checked in each chamber of the radiant firebox. This check should be made any time adjustments of the individual plenum dampers are made.

The combustion air flow to the furnace and, thus, the amount of excess air (or oxygen) is adjusted by a damper in the furnace stack and six dampers in the plenums below the furnace cloor. The operation of these dampers governs draft. There is also an air door on each burner that adjusts the air to that burner.

Each time a furnace is started up, the stack and plenum dampers must be wide open. This is to insure there is enough air flow for complete combuston. The Flame Management System insures this criteria is met on each start-up. After the furnace is running at desired rates, the air flow must be reduced to give the proper excess air and draft. This is done by closing back on the six plenum dampers and the stack damper. This must be done in small steps and the excess O_2 in each chamber checked to prevent going too far and not having sufficient excess O_2. The draft at the bottom of each radiant chamber is used as a guide in closing the six plenum dampers. The flame patterns are also observed to insure proper operation. Due to the difficulty in adjusting plenum dampers, the stack damper alone is used to make small adjustments in excess air. The draft must be closely watched, since changing the stack damper alone will also vary the draft. If too great of an adjustment in excess air is needed, then the plenum dampers also must be adjusted. Whenever the plenum or stack dampers are adjusted, care must be taken not to fully close any, since it will result in a furnace shutdown.

The air doors on the individual burners should be adjusted after each start-up if any maintenance is performed on the burners, or any time the flame pattern on an individual burner indicates problems. Flame impingement on the tubes or the furnace walls is undesirable, and gas flow, or air, or both should be adjusted anytime this is observed.

The bridgewall and stack temperatures serve as good indicators of problems that can occur in the furnace. A high bridgewall or stack temperature can indicate afterburning at the top of the radiant or the outlet of the convection sections, respectively. A high bridgewall temperature can be an indication of high excess air or overfiring of the furnace. If afterburning occurs, gas firing should be cut immediately, and then the dampers opened to supply sufficient air.

d. Coking

It essential that the load carried by each pass of the furnace is the same. If one pass is converting more EDC than the other, even if the average is correct, it will lead to more coke laydown in that pass. This will cause the furnace to have to be shut down for decoking sooner than expected. In order to prevent a maldistribution of coke laydown, the furnace must be operated with equal feed flow and equal heat input to each pass. Two flowmeters are privided on each pass to assure the accuracy of the feed flowrate. The metering of fuel gas into each of the chambers serves as an indication that the heat input is balanced. The crossover temperature and the outlet temperature of each pass also serve as indicators of the balance. If the feed flowrates are the same, and the heat inputs are the same, then the temperatures at the crossover and the outlet will be the same.

Coke laydown in the tubes is a normal part of furnace operation. During the course of each furnace run, the tubes will go from clean to fouled or coked. The coking normally occurs in the last 30% of the radiant coil and in the last of the convection section. However, severe problems may result if coking is not properly controlled. The reactions that form coke in the radiant section are a result of the reaction that forms VCM & HCl. Therefore, the more VCM that is made, that is, the higher the conversion, the greater the tendency for secondary reactions to occur. These secondary reactions are also favored by high temperature; for this reason it is more desirable to run at as low an outlet temperature as possible at the desired conversion.

The secondary cracking the VCM to acetylene (C_2H_2) and HCl is a likely route to coke (C_2) formation.

$$C_2H_3Cl \xrightarrow{\text{HEAT}} C_2H_2 + HCl$$

$$C_2H_2 \longrightarrow C_2 + H_2$$

In addition to the above reactions, there are a number of other reactions that could cause coke formation starting with EDC.

The purity of the furnace feed is another important factor in coking. Certain impurities in the feed can result in coke formation. Compounds believed to result in increased coking are trichloroethane, carbon tetrachloride and tricholoroethylene. High iron concentrations in the feed may also result in coking. The purity of the furnace feed must be monitored and maintained at specification to limit coking.

There are two primary indicators that signify the amount of coke laydown in one pass versus the other. Pressure drop is the first indicator, and tube metal temp (TMT) is the other. If the flowrates are the same, and the amount of coke deposited is the same, then the pressure drops will be the same. At the start of a run, the clean P through the furnace will be about 45 psi. If there is a large variation in the ΔP between the two passes immediately following a decoking outage, then it is an indication that one pass was not decoked properly.

At the start of a run, the clean tube metal temperature at the outlet of the radiant section will be about 1100°F. During the course of the run, as coke laydown occurs, this temperature will increase. It can be allowed to go up to about 1425°F. This gives an average run temperature of about 1350°F. The tubes are designed to last about 100,000 hours at this average temperature. The tubes can be cycled up to about 1800°F TMT for short periods of time (approximately 1 to 2 minutes) in an upset condition. This type of cycling shortens the tube life and must be avoided. An allowance is put into the design life for cycling the tubes.

In order to monitor coke laydown and determine what parts of the coil it is occurring in, each pass is equipped with five TMT measuring points. One is at the radiant section inlet to the pass; one is at the middle (where the pass goes from the center chamber to the outer chamber); and one is at the outlet of the pass. These are connected to a selector switch in the field that sends one temperature on each pass into the control room. This switch is kept on the outlet point during normal operation. The other points are monitored routinely and recorded. Each point has two thermocouple elements in case one burns out.

In addition, a fourth TMT is at the outlet of the pass at the floor. This thermocouple is connected to the furnace shutdown system. The fifth TMT for each pass is located on the bottom row of shock tubes in the convection section. These give an indication of coke build-up in exactly the same manner as those in the radiant section. The carbon steel tubes must not be subjected to more than 750°F.

If at any time during furnace operation it appears that coking of one pass is becoming greater than the other, then corrective action must be taken immediately. If it is not, then the coking may increase rapidly and result in the furnace having to be shut down due to poor product quality, severe pressure drop, high TMT, or possible plugging of a tube. The proper corrective action is to be sure the passes are balanced, or if necessary, to slightly decrease the heat input and/or increase the feed flow to the coking pass.

e. Abnormal Operation

In the event that a plug should occur in the tubes, each pass is provided with an SRV at the inlet, set at 350 psig, to protect the tubes from overpressurization. If the plug results in a loss of flow to the pass, the furnace shutdown system will stop the firing of the furnace to prevent damage due to overheating.

Another problem that can occur is incomplete vaporization in the convection section. Fireside fouling of the convection section, increased pressure in the tubes, or conversion too low are possible causes of this. The temperature at the outlet of the convection section (crossover) is used along with the pressure at that point to determine if the vaporization has been completed in the convection section. Corrective actions that can be taken if incomplete vaporization occurs are; reduce charge flowrate, increase conversion, or increase excess air.

Loss of feed to a pass of the furnace can be caused by misoperation of the furnace feed system, malfunction of the furnace feed flow control loops, or improper valving. The furnace shutdown system is provided to protect against these occurences which could result in damage to the furnace or unsafe conditions developing.

Other problems that may occur range from a pin-hole leak in a tube to severe tube rupture and fire. Operators should routinely observe the tube coils of the radiant section for pin-holes. These appear as small horizontal jets of fire. If one occurs, the furnace must be shut down and repaired.

In the event that a tube rupture occurs and a fire, snuffing steam is provided to the radiant and convection sections of each furnace. This can be used to smother out any fire while the furnace is being isolated.

The performance of the furnace is dependent on the quality of the furnace feed. There are a number of conditions in the feed that will result in undesirable furnace operation. In turn, the furnace can affect the operation of the remainder of the plant and the VCM product purity. The quality of the furnace feed must be maintained by the other sections of the VCM II plant.

If the furnace outlet temperature changes abruptly, it is an indication that the feed composition has changed. If the feed contains compounds that inhibit the cracking reaction (slow it down), then the temperature will increase and production will decrease. In order to offset this, firing will have to be increased to return production to the desired level. This will further increase outlet temperature. If furnace feed contains compounds that promote the cracking reaction (speed it up), then the temperature will decrease and production will increase. In order to offset this, firing will have to be decreased. Chloroprene is a known inhibitor. Carbon tetrachloride and chlorine are known promoters.

The presence of inhibitors in the furnace feed is undesirable, since they result in higher outlet temperature. The reactions that form impurities in the product are favored at higher temperature operation as is the secondary reaction of vinyl chloride to acetylene. The acetylene formed by this reaction is a direct precursor to mono-vinylacetylene (MVA), chloroprene (CLP), benzene, and butadiene (BD) which are all present in the furnace effluent gases. The BD and MVA end up in the finished VCM product as undesirable impurities.

In addition to inhibitors, certain impurities in the feed will result in off-specification product. Ethyl chloride (EC) is an example of this. Ethyl chloride in the furnace feed primarily ends up in the VCM product. It may result in the formation of other impurities such as BD. Other compounds in the feed may undergo reactions to form undesirable product impurities. Some examples of these are CLP →

MVA + HCl and 1, 1, 2 Trichloroethane (TCE) $\longrightarrow$ cis, trans dichloroethylene and vinylidene chloride (VDC).

f. Decoking

In order to remove the coke that builds up in the tubes of the furnace, it is necessary to shut down the furnace and decoke it periodically. There are two methods for removal of coke. These are: 1) steam air decoking, 2) jet blasting.

In the steam-air decoking method, steam is first used to remove coke by spalling and erosion. Next steam along with air is used to burn the coke from the inside tube walls. Connections are provided at the outlet for carrying the decoking effluent to the coke knockout drum. Blinding points are provided to isolate the furnace from the normal process. The effluent gases from decoking are quenched and partially condensed in the piping leading to the coke knock-out drum using water. In the drum, the liquid effluent is separated from any vapors. The vapors are vented. The liquid flows into the coke retention sump where coke is settled out using a flocculating agent. The water is discharged to the pigments ditch.

In order to get satisfactory steam-air decoking, the furnace must be fired and process temperature must reach about 1150°F at the outlet to achieve burning. The carbon steel tubes of the convection section must not be overheated during decoking. A TMT limit of 750°F and a cross-over temperature limit of 900°F are used. The procedure also involves cycling the tubes to cause coke removal. The procedure must be continued until coke is no longer being removed as determined by effluent color. The furnace must be inspected where possible to assure the completion of decoking. Inspection ells are provided at the outlet of each radiant pass. At the end of a steam-air decoking, the furnace process side must be completely free of coke deposits and water. All possible points where water can be trapped must be checked. The coil must be dried using dry nitrogen to a sufficient temperature to assure no moisture. Moisture left in the tubes will result in localized corrosion. If any significant quantity of water is left in the coil, it will be carried into the process and result in corrosion and failures.

In the jet-blasting method, a high velocity stream of inert gas, such as nitrogen, is used to carry small projectiles such as steel shot through the tubes. The coke is removed by erosion. The same connections can be used to jet-blast decoke as steam-air decoke. The coke knock-out drum and retention sump are not used in jet-blasting. The process is done in batch-wise steps. Pressure drop through to coil is used to determine when the coke removal is complete.

g. Start-up and Shutdown

The furnace system is usually started up last, after the VCM section has been put on recycle and the quench system has been heated up. A consumer for the HCl should be ready about four hours after feeds are put into the furnace and it is started on its heat-up.

The start-up procedure for the furnaces involves the Flame Management System. This system requires that the lighting off of burners in the furnace be done in a safe manner. After the burners have been ignited, EDC furnace feed flow is started to the furnace, and the firing rate is brought up. The ratio of feed flow to fuel gas flow must be such that the feed is being vaporized soon after it is started. This is necessary since the material from the furnaces goes to the quench tower. It can only get out of the quench tower as a vapor. The quench tower and quench dopp kettles do not have enough volume to accumulate liquid for a long period of time. The quench tower should not be flooded as this may result in damage to the packed section when vapor flow does commence.

Once the EDC charge is being vaporized, the fuel gas and feed flow may be increased to the desired values. The only restriction is on the rate at which the outlet temperature is brought up. It should be limited to 100 - 200°F per hour to avoid thermal shock to the retractory. On start-up after outages where the tubes have not been cleaned, the most important consideration is tube plugging. While in the start-up mode, the furnace shutdown system cannot protect against this occurrence. If flow cannot be established in a pass, it will be indicated by failure of the crossover and outlet temperature to begin rising as well as the flow meters. This results from the fact that these thermowells are outside the firebox. If there is no flow to carry heat to them, they will not heat up.

The shutdown of the furnace or furnaces can occur in two ways: 1) Controlled shutdown and 2) Shutdown system trip. Anytime it is desired to shut down a furnace for any reason, it may be done by reducing fuel gas flow and thereby rates. The other sections of the plant or complex can make necessary adjustments to compensate for the reduction in HCl co-product.

If the furnace shutdown system causes a trip to occur as a result of abnormal conditions, then there will be an abrupt drop in HCl co-product and feed forward flows to the quench system and the absorber-stripper system. It may result in an automatic shutdown of the OHC reactors.

If this occurs, the entire plant must be stabilized as quickly as possible to a safe and acceptable state of operation. The VCM Process Section is put on recycle. Necessary adjustments must be made to the quench system, the EDC purification section, etc. The object is to put the remaining plant into an operating or recycle operating mode from which it can be returned to full operation as conveniently as possible.

Whenever a furnace is shut down, the feeds must be stopped as soon as possible due to the limited liquid volume in the quench tower. To prevent tube plugging due to the thermal shocks and lack of flow, it is necessary to put a nitrogen purge on the tubes.

The safety shutdown features of the furnace shutdown system must be tested on a regular frequency. Whenever a planned furnace shutdown occurs, it should be accomplished by simulating a shutdown condition to the system and observing the results.

h. Furnace Shutdown System

The furnace shutdown system is provided to stop gas firing of one or both furnaces in the event that undesirable conditions develop on the furnace or in the area. In addition to stopping the firing of the furnace, in the case of a vapor detector shutdown, snuffing steam is automatically started into the firebox and the deluge below the furnaces is started. The system also monitors the operation and start-up of fuel gas burners. The undesirable conditions to be protected against are:

1) Loss of flow to one or more passes on a furnace while it is being fired resulting in tube rupture or damage, or refractory, or structure damage.

2) Ignition of a vapor cloud by the furnaces resulting in a fire or explosion.

3) Accumulation of fuel gas in the furnaces, either during start-up ignition or during normal operation which could result in an explosion due to fuel gas vapor cloud within the furnace.

The conditions that will cause a shutdown are:

1) High or low fuel gas pressure measured at downstream side of the flow control valve to each furnace.

2) Any damper, plenum or stack going fully closed.

3) Total flame failure.

4) Manual pushbutton in the field.

5) Power failure to the flame management system.

6) Loss of flow as determined by any two out of three inputs of the two furnace feed flows and one tube metal temperature per pass.

7) Any two vapor detectors as designated to the furnace vapor detector shutdown system sensing a LFL of 40%.

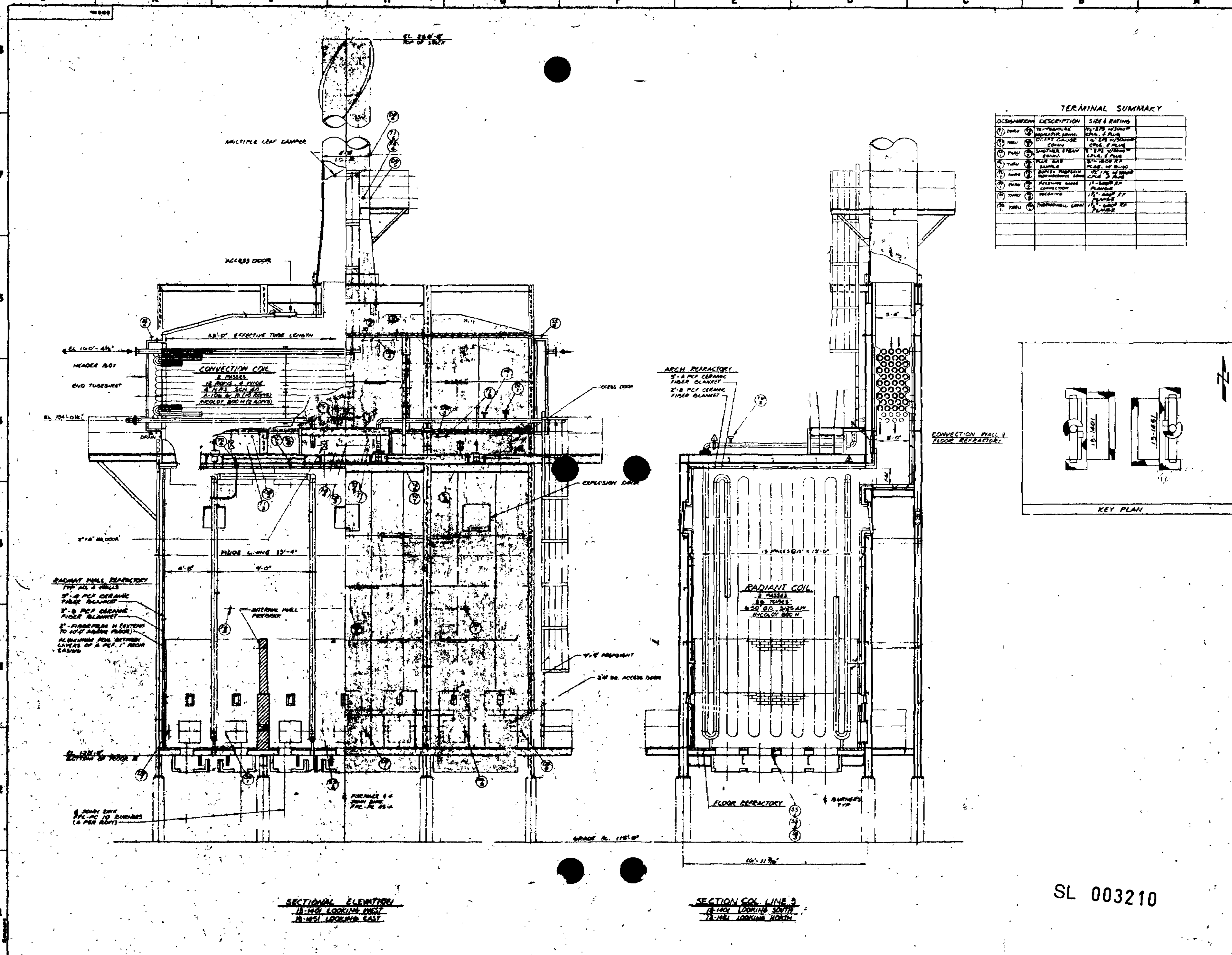
8) Manual pushbutton in the control room on the vapor detector panel.

9) Manual pushbutton in the control room on the furnace operator's panel.

There are two levels of shutdown associated with the furnace system. The first level is a shutdown of the fuel gas firing of either furnace. In this case, shutdown means that: (1) All of the maxon valves are closed. (2) All of the pilot solenoid valves are closed, (3) Turning off all of the 28 Fireeye amplifier circuits, (4) Closing the pilot gas supply valve, (5) Closing the main fuel gas, (6) The Flame Management System is put into a logic state that requires that it be taken through a start-up sequence in order to restart the furnace.

The first level of shutdown is managed, as described above, by the Flame Management System. This level of shutdown is caused when any of the input items, which are connected to the Flame Management System, indicate that a shutdown is necessary. In addition, this level of shutdown may be invoked from the control room by PLC III.

The second level of shutdown is an extension of the first level. It is invoked by PLC III as a result of vapor detector inputs indicating that



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a shutdown is required. In this case, both furnaces are shutdown, exactly the same as described above. In addition to this, several other things are done which are managed directly by PLC III. These are starting snuffing steam to both furnaces and starting deluge valve #1.

The logic for the furnace shutdown system is provided by several devices. First, the Flame Management System logic for each furnace is provided by two programmable logic controllers located in cabinets in the field. Each cabinet contains one Modicon 484 PLC and a number of relays associated wth the system. There is also one cabinet for each system that houses all of the Fireye amplifiers for that furnace. The functional indicator lights and switches for each system are provided on a field-mounted operator's panel. Second, the remainder of the shutdown system logic is provided by PLC III. The functional indicator lights and switches are provided in the control room on OIP-4 and OIP-6A.

A detailed description of all components of the furnace shutdown system and its operation is provided in the Safety Control System Manual. This should be referred to for further information.

3. Quench System

The VCM quench system is designed to perform three very important functions in the VCM production process. First, employing direct contact cooling, the quench tower abruptly cools the hot furnace effluent gas to its dewpoint temperature. Rapid cooling of the effluent gases is necessary to minimize undesirable side reactions such as coking and the formation of DCE (1,1 - dichloroethane), which result from the reverse reaction of VCM and HCl. Second, the quench tower removes carbon and tars produced in the cracking process from the furnace effluent gases by forcing the quench vapors overhead through a packed section. The accumulated waste material is then discharged to the quench dopp kettle system. The removal of carbonaceous and tarry material is imperative, since they would otherwise be carried forward into the VCM process and EDC purification sections, fouling reboilers and plugging process lines. Third, the quench condenser condenses as much of the overhead quench vapor stream as practical, the resultant quench liquor being used for reflux to the quench tower and liquid feed to the absorber stripper. Insufficient condensation of the quench vapor stream will result in an excessively high vapor feed rate to the absorber-stripper system, possibly causing flooding problems in the absorber.

Equipment included in the quench system are the quench tower, quench condenser, quench liquor tank, and the quench liquor pumps. The quench dopp kettle system is operated as an integral part of the quench system, but will be discussed as a separate system. The quench system is shown on process drawing 56A-10014 and P & I drawings 56A-10063 and 56A-10064.

The furnace effluent gases, consisting of a mixture of VC, HCl and EDC, along with small quantities of coke, tars and other impurities, exit the furnaces at a temperature of approximately 900°F (design outlet temp at 55% conversion). Cooling of the effluent gases is effected in a packed tower having a liquid level in the bottom. Transferred from each furnace pass outlet to the quench tower by way of "transfer piping", the furnace effluent gases enter the quench tower through nozzles submerged in a liquid bed consisting primarily of EDC. Upon entering the liquid bed, the effluent gases are immediately cooled by simultaneously boiling off the liquid. The submerged quenching step is important for two reasons: one, it provides an effective method of rapidly cooling the effluent gases; and two, it prevents carbonaceous material from passing upward through the packed section and forward into downstream process equipment.

As the quenched gases travel upward through the packed section, they are contacted countercurrently by an external reflux stream (quench liquor reflux). The quench liquor reflux stream is actually a recycle stream resulting from the subsequent partial condensation of the overhead gas stream leaving the quench tower. Distributed evenly over the packed section, the quench liquor flows downward through the packing contacting the upflowing gases. This "scrubbing" action removes any residual carbon particles entrained in the gas stream and provides additional cooling of the gases. The quench liquor reflux stream also serves to replenish the liquid lost in the bottom of the tower due to vaporization in the quenching step. There is, in addition, enough quench liquor reflux so that a small purge of carbonaceous and tarry material collected in the bottom of the quench tower can be carried to the dopp kettles.

All of the carbon and tars, produced by way of side reactions in the cracking furnace, accumulate in the liquid bed in the bottom of the quench tower. They are removed from the quench tower by purging the liquid bed batchwise to the dopp kettle system. The quench tower liquid, serving as a carrier for the suspended carbon and tars, drains through "dump" lines to the two dopp kettles. The dopp kettle system recovers most of the usable organic material from the dump stream and returns it to the VCM process prior to disposing the carbonaceous and tarry material for incineration.

Batchwise dumping of the quench tower liquid to the dopp kettles is controlled by the quench tower dump control system. By monitoring the tower level, the dump control system opens and closes air operated dump valves located on the dump lines to the dopp kettles as pre-set liquid levels are reached. For instance, as the quench tower liquid bed level rises to the pre-set high value, the dump control system opens the dump valve to one of the two kettles, draining liquid into the dopp kettle and lowering the quench tower level. When the pre-set low level is reached, the dump control system closes the dump valve. The dump control system automatically alternates dumps between the two kettles, repeating the dump cycle. During the time in which the dump valves are closed, the quench tower level rises gradually. The rate of level rise, and therefore, the dump frequency, is regulated by the amount of quench liquor reflux being recirculated back to the quench tower. The reflux rate is adjusted to obtain a maximum dump frequency without flooding the dopp kettles. A high purge rate out of the quench tower reduces carbon and tar concentration which lessens the chance of plugging in the tower inlet nozzles. Dump cycles of 15 - 20 minutes can usually be maintained.

Maintaining the quench tower level within acceptable operating limits is very critical to the operation of the VCM unit. Should the liquid level fall below the inlet nozzles, the furnace effluent gases will not be sufficiently cooled, thus greatly overloading the quench condenser and upsetting the absorber-stripper operation. If the liquid level rises too high, the violently boiling liquid will either damage the packed section or plug the packed section with carbon particles. For these reasons, the quench tower is equipped with dual level indicating devices, a float chamber and DP cell for monitoring its level. Both instruments are always in service so that there is a backup indication in case one of them should fail. Level indication from both devices is displayed in the control room.

The saturated vapor stream exiting the top of the quench tower is near its dewpoint. As process conditions vary from the design case, the overhead vapor temperature will change slightly. Downstream of the quench tower, the quench vapor stream is partially condensed in two air-cooled heat exchangers operating in parallel as a single partial condenser. Of the three major components entering the quench condenser, approximately 98% of the EDC, 70% of the VCM, and 22% of the HCl, are condensed at the design process conditions. Leaving the quench condenser, the condensate and remaining vapor drain to the quench liquor drum.

A temperature controller regulates the degree of condensation and cooling taking place in the quench condenser by controlling the temperature of the liquid-vapor mixture leaving the condenser. The controller does this by changing the blade pitch on two of the four condenser fans, thus varying the amount of air pulled through the exchangers for cooling. The amount of condensation occurring in the quench condenser is most important since it determines the ratio of the vapor and liquid feed rates to the absorber-stripper. As previously mentioned, a high vapor feed rate could possibly cause flooding problems in the absorber. Less likely is flooding in the top of the stripper caused by an extremely high liquid feed rate. One other consideration to keep in mind is that as the furnace conversion rate changes, the condensing load on the quench condenser also changes. As the conversion rate is lowered, the condensing load on the quench condenser is increased due to the increase in the EDC concentration of the quench vapor stream. The temperature controller also helps guard against process upsets as ambient conditions vary.

The quench liquor drum serves as both a liquid-vapor disengaging vessel and a surge volume for quench liquor. As the vapor-liquid stream from the quench condenser enters the quench liquor drum, the liquid separates by gravity while the remaining vpors flow along the top of the drum. The vapor stream exits the opposite end of the drum and is fed to the bottom of the absorber. This vapor stream is commonly referred to as "secondary quench gas".

Liquid accumulating in the quench liquor drum is transferred by the quench liquor pumps to two locations: The quench tower and the stripper. Quench liquor reflux is flow-controlled back to the quench tower at a rate sufficient to maintain the desired dump frequency. The quench liquor stream pumped forward to the top of the stripper is also flow-controlled to help provide a steady load on the stripper. Because both liquid outlet streams from the quench liquor drum are flow-controlled, the drum level has to be maintained within operating limits by making gradual adjustments to the quench liquor feed to the stripper.

The most common problem associated with the operation of the quench system is maintaining consistent dumps from the quench tower to the dopp kettles. Normally, to establish a good dump frequency, the quench liquor reflux rate is adjusted to give a steady level rise in the tower. However, there are many other factors that can influence this level rise, including such things as furnace rate changes, flooded dopp kettles, malfunctioning dump valves, and plugged dump lines. Whenever a rate change is made on the furnace, the quench tower reflux has to be readjusted since the vaporization rate changes in the quench tower. If a dopp kettle is operated with a high level, the dump control system may not be able to complete the dump cycle since the kettle will be unable to accomodate the entire dump load and thus prevent the tower level from reaching the pre-set low level point. There are times when a dump valve may not close fully, inhibiting a level rise in the quench tower until the dopp kettle is flooded. It is also possible for the dump lines to plug with carbon, tars, or packing material, preventing the quench tower liquid from draining to the kettles. Should a problem develop with the quench tower dump frequency, all of the above factors should be investigated as possible causes.

There is always the possibility that one or both of the quench tower level measuring devices will indicate the incorrect level. This is especially possible in the quench tower where there is violent boiling occurring, foaming, and plugging of nozzles. A sightglass is provided to check the accuracy of the level indicators.

Other indications of possible quench tower level problems include the quench vapor temperature below the packed section and the tower overhead temperature. A sudden drop in the liquid bed level will immediately raise the temperature of the vapors rising above the liquid bed due to a lack of liquid for quenching. In this situation, there will be very little change in the liquid bed temperature. Over a period of time, the overhead temperature will gradually increase if the liquid bed is not brought up to its normal operating level.

A problem that could be of severe consequences if not attended to immediately is the loss of one or more quench condenser fans. This immediately reduces the quench vapor condensation rate, thereby increasing the quench vapor feed to the absorber. It is essential that there is sufficient quench condenser cooling capacity to meet the process requirements, not only to maintain stable operation of the absorber-stripper, but also to provide enough quench liquor reflux to the quench tower. If the fan (or fans) cannot be restarted and the remaining fans in operation cannot meet the cooling requirements, furnace feed rates will have to be reduced to lower the load on the quench condenser.

As in most situations, the loss of an operating pump is serious. It is even more critical in the quench system where the quench liquor pumps are depended upon to deliver the necessary liquid for quenching the extremely hot furnace outlet gases.

The quench system is normally started up after the VCM process section has been put into operation (on recycle) and prior to a furnace start-up. Putting the quench system into operation in this manner alleviates operating personnel from having to concentrate on lining out the quench system while at the same time bringing up a furnace. Starting up the quench system involves heating up the quench tower and establishing a steady tower dump frequency. To accomplish this, the dopp kettles must also be started up at the same time; however, it is not necessary to start up the entire dopp kettle system. The quench system is shut down in the reverse order from which it is started. During just a furnace outage (both furnaces), the quench system is normally shut down, although it can remain in operation if it is desired.

One of the more critical control schemes associated with the quench system is the dump control system. Basically, the dump control system incorporates a programmable logic computer (PLC) to activate the dump valves at the proper times. The automatic dumping mode can be changed from both to one kettle, or done manually by operating hand switches located inside the control room. There is a series of five switches used to alter the operating mode of the dump control system. First, a "level select" switch is used to designate which level measuring device, the float chamber or the DP cell, will be used to provide the level signal to the dump system. Then associated with each dump valve are "auto-manual" and "open-close" switches. In the "auto" position, the dump valve is operated by the dump control system. In the "manual" position, the dump valve is operated by its corresponding "open-close" switch. To take a dopp kettle out of service, its dump switches are put in the "manual" and "close" positions. Also associated with each dump valve is an alarm light that lights up when the valve is in the open position.

To isolate the furnace and VCM process sections from each other during an emergency situation such as a major fire, or leak, or tube rupture, in the furnace area, a manual block valve is installed on the quench condenser outlet line. Whenever this isolation valve is closed, the furnaces must be immediately shut down and the quench liquor reflux FCV and furnace feed FCV valves closed.

Other indications of possible quench tower level problems include the quench vapor temperature below the packed section and the tower overhead temperature. A sudden drop in the liquid bed level will immediately raise the temperature of the vapors rising above the liquid bed due to a lack of liquid for quenching. In this situation, there will be very little change in the liquid bed temperature. Over a period of time, the overhead temperature will gradually increase if the liquid bed is not brought up to its normal operating level.

Due to the physical arrangement of the quench tower vapor line and quench condenser that would allow liquid to be trapped in the vapor line, a drain line is provided to drain any liquid in the vapor line to the quench liquor drum. The drain line has a seal loop which prevents vapors from bypassing the condenser and entering the quench liquor drum.

The quench liquor drum is protected from overpressure by SRV set at 175 PSIG. It should also be noted here that the SRV's protecting the furnace passes relieve to the quench vapor line. The quench tower is protected by three SRV's set at 170 PSIG. These SRV's are located on the vapor line near the quench condenser. At least two of these valves must be in service at all times to provide proper protection. The block valves beneath the SRV's are to be locked open except for those times when one SRV is taken out of service for maintenance.

4. Quench Dopp Kettle System

The VCM Quench Dopp Kettle System is designed to serve two purposes: one, it recovers most of the usable organic material (primarily EDC) dumped from the quench tower with the carbon and tar waste and recycles this material back to the VCM process, and two, it expels the remaining concentrated carbon and tar waste into facilities used for its disposal. Better than 95% of the material dumped from the quench tower is recovered in the dopp kettle system by being boiled overhead into either a dopp vapor recovery system or returned to the quench tower. The low pressure vapor recovery system is normally used in lieu of returning the dopp kettle vapors to the quench tower for one reason; it allows the dopp kettles to be operated at lower temperatures in order to reduce the inherent formation of 1,3-butadiene (BD) in this system. Butadiene, produced in more significant quantities at higher temperatures and pressures, is one of the major impurities that ends up concentrating in the VCM product. For this reason, its formation in the VCM section must be minimized as much as possible.

Improper operation of the dopp kettles and its vapor recovery system can result in a number of undesirable consequences, including the loss of usable organic material from the VCM II plant, high impurity levels in the VCM product, and reduced VCM II plant yields and efficiencies.

Equipment comprising the quench dopp kettle system includes the two dopp kettles, an overhead entrainment separator and condenser, the overhead surge drum, and the dopp kettle overhead pumps and filters. The VCM II plant VC tar buggy is also considered as part of the dopp kettle system. The quench dopp kettle system is illustrated on process drawings 56A-10014 and P & I drawings 56A-10065 and 56A-10066.

Carbon and tars suspended in a liquid organic stream enter the two dopp kettles through individual dump lines from the quench tower. A significant portion of the stream, primarily EDC and lighter boiling compounds, are reclaimed from the dump stream by being boiled overhead in the dopp kettles. The remaining carbonaceous and tarry matter, along with some residual EDC, is periodically drained from the bottom of the kettles into a portable pressure vessel (tar buggy).

Waste material from the dopp kettles gravity drains through flexible organic hoses to the VCM II VC tar buggy. The kettle drain lines are equipped with air-operated valves used when filling the tar buggy. These valves are operated by hand switches located near the kettles and by a remote switch that is used to close the drain valves in case of a spill or hose rupture.

The dopp kettle dumping process is a batchwise operation with the dumps being alternated between the two kettles. When the tar buggy is full or when the kettle is empty, draining is discontinued, and the buggy is hauled to the Plant B waste treatment unit where its contents are unloaded to be incinerated.

Overhead vapors from the dopp kettles first enter an entrainment separator where any liquid or carbon particles entrained in the vapor stream are removed and returned to the dopp kettles through a drain line. Leaving the entrainment separator, the vapor stream flows into the air-cooled dopp kettle overhead condenser. Condensate and any non-condensables exiting the condenser gravity-drain to a surge drum.

Due to the physical arrangement of the vapor piping between the entrainment separator and the condenser that would allow liquid to be trapped in the vapor line, a drain line is provided to drain any liquid in the vapor line to the surge drum. The drain line has a seal loop which prevents vapors from bypassing the condenser and entering the surge drum.

Any vapors in the condenser outlet stream are equalized to the vapor space of the surge drum through disengaging holes in the inlet line standleg. Leaving the surge drum, the vapors are vented through a pressure control valve to the incinerator header. The vapor flow is regulated by a field-mounted pressure controller to maintain the dopp kettle system pressure at a steady value. To protect against over-pressure in the system, the dopp kettles and the overhead surge drum are equipped with SRV's set at 170 PSIG and 150 PSIG, respectively.

Liquid in the dopp kettle overhead surge drum is pumped to either the bottom of the absorber or the quench tower. In either case, the liquid flow rate is regulated to maintain the surge drum level within operating limits.

As mentioned earlier, in addition to its normal flow route, the dopp kettle overhead vapors can also be returned directly back to the quench tower. This flow scheme is used for heating up the quench tower during the quench system startup. The vapor stream enters the quench tower below the packed section and above the liquid bed.

To provide the necessary heat for boilup, the steam jacketed dopp kettles consume 175 PSIG steam. Field-mounted pressure controllers control the steam chest pressure of each kettle at a value sufficient to boil EDC overhead. Condensate from the kettle jacket is collected in the plant's low pressure condensate header. Each dopp kettle is also equipped with an agitator having scraper blades attached to its outer frame. The purpose of the blades is to scrape the kettle walls, preventing a buildup of carbon and tars on the walls which would otherwise restrict heat transfer.

Because the quench tower dumping process is a batch operation, there is a resulting fluctuation in the continuous dopp kettle system operation. The boilup rate of the dopp kettles fluctuates as the EDC content changes in the kettles. The EDC concentration in the kettles is highest immediately following the completion of another dump cycle. The cyclic boil-up rate results in a fluctuating surge drum liquid level, making control of the drum level very difficult. Since the liquid outlet stream from the surge drum is flow-controlled, the flow rate has to be averaged at some value to maintain the level fluctuations with acceptable limits.

One of the more common problems associated with the quench dopp kettle system is flooded dopp kettles. Operating the dopp kettles with extremely high liquid levels will upset the quench tower dumping operation. Flooded dopp kettles are usually the result of insufficient steam chest pressure and/or excessive liquid load dumping from the quench tower. To warn of a high liquid level, each kettle is provided with a high-level switch that sounds an alarm in the control room. Other indications of a high level are an extremely high steam draw rate and a lower than normal kettle overhead vapor temperature.

The dopp kettle system start-up is divided in that the dopp kettles are normally put into operation as part of the quench system start-up, whereas the vapor recovery system can be put into service after a furnace start-up. As discussed in the quench system start-up, the dopp kettles are used to heat up the quench tower prior to a furnace start-up by returning the dopp kettle overhead vapors directly back to the quench tower. The vapor recovery system is actually not needed to operate the VCM section as long as the dopp kettle vapors are equalized back to the quench tower. It should be put into service prior to the start of the EDC cracking reaction, and especially when the plant is experiencing product purity problems with butadiene.

G. VCM PROCESS SECTION

1. Absorber-Stripper System

The material in the quench liquor and vapor streams that leaves the quench system is principally VCM, HCl, and EDC. These must be separated by the VCM process section to produce VCM product. The process section consists of a purification train composed of the absorber-stripper, the product still, and the neutralizers. An absorber-stripper distillation system is used in the VCM process section to separate HCl from VCM and EDC. The absorber column's primary function is to produce an HCl stream free of VCM and EDC. The primary duty of the stripper column is to remove HCl from the EDC and VCM. The HCl is sent overhead from the absorber to be used in other parts of the plant. The EDC and VCM are sent to the product still system for purification of the VCM.

The smooth operation of the absorber-stripper system is essential to the proper operation of all HCl consumers, particularly the OHC section. Upsets in the HCl flow can result in reactor shutdowns which affect the onstream time of the entire VCM II plant.

Failure to remove EDC and VCM from the HCl co-product will result in both a yield loss and additional processing difficulties. VCM in the HCl feed to the OHC reactors will react and form TCE, which is an undesirable component in crude EDC. Large quantities of EDC remaining in the HCl will result in fouling of the HCl preheater and plugging of the mixed feed orifices on each OHC reactor. Any VCM that leaves the absorber with the HCl is not available to be sold as product, and the cost and energy of producing that vinyl chloride is wasted.

Any HCl leaving the bottom of the stripper must be removed in the neutralizers. The neutralizers work best when processing a stream of only a few parts per million HCl. Larger quantities of HCl will result in short neutralizer life and possibly even off-spec product.

Although physically divided into two columns, the absorber-stripper operates as one distillation column. Due to the relative height and diameter that would result, it is mechanically impractical to construct the absorber-stripper as a single column. However, from an operating viewpoint, the absorber-stripper can only be operated as one distillation column. Any change in operation in one column is reflected almost immediately in the operation of the other column. Adjustments in one column's operation should not be made without considering the impact on the operation of the other column.

The absorber-stripper system consists of the 62-tray absorber column, the 40-tray stripper column, the absorber bottoms pumps, the pre-saturation (presat) cooler, the presat pumps, the upper intercooler (UIC), the UIC pump, the lower intercooler (LIC), the LIC pumps, the absorber condenser, the HCl K. O. drum, the HCl condensate educator, the stripper reboiler, the HCl economizer, the primary Lean Oil (L. O.) cooler, the secondary L. O. cooler, and the L. O. pumps. The system is shown on P & ID's 56A-10059, 56A-10060, 56A-10067, 56A-10068, 56A-10069, and 56A-10070.

Due to the extent of this system, this write-up will be divided into the following sections:

a. Description of System and Flows

b. L. O. Circuit

c. Operation of the Absorber

d. Operation of the Stripper

e. System Pressure Control

f. Abnormal Operation and Corrective Actions

g. Start-up and Shutdown

The VCM refrigeration system is closely related to the absorber-stripper system. The details pertaining to its description and operation are contained in the section of this manual on the VCM Refrigeration System. Also, the Process and Storage Refrigeration System supplies refrigeration for the absorber condenser. The section of this manual on that system should also be referred to for operation and description of that system.

a. Description of System and Flows

The main feeds to the absorber-stripper are quench liquor and quench vapor from the quench system. Quench vapor flows from the quench liquor drum into the bottom of the absorber beneath the bottom tray. Quench liquor is pumped to the top of the stripper. Additional feeds to the absorber can be the condensate from the quench dopp kettle and condensate and vapor from the VCM shift storage vent compressor. These streams are each fed to the bottom of the absorber below tray #1. Refer to the sections of this manual on each of these respective systems for more information on operation in these modes.

EDC free of VCM (and called Lean Oil - L. O.) is fed near the top of the absorber column at tray 60 as the absorbing oil. The overhead from the stripper enters the absorber beneath the first tray. Both quench vapor and stripper overhead vapor are composed mostly of VCM and HCl and a minor quantity of EDC. As the L. O. flows down the column, all of the VCM and EDC, and some of the HCl are absorbed from the gas stream flowing up the column. This absorption generates heat that must be removed from the column. The first heat removed is the heat of saturating the L. O. with HCl. This is done in the presat section of the absorber, trays 57-62. The presat section has a recirculating stream that is pumped through a heat exchanger (the presat cooler) outside of the column. This exchanger removes the heat of HCl absorption by cooling the material to about 56°F with freon 22 and returning it to the column. Next, as the presaturated L. O. flows further down the column, heat of absorbing VCM is removed in the upper intercooler section of the column, trays 18-20. The upper intercooler has a recirculating stream that is pumped through a heat exchanger (the upper intercooler, UIC) outside the column. This exchanger removes the heat by cooling the material to about 56°F with freon 22 and returning it to the column.

Finally, the L. O., partially laden with VCM and HCl, nears the bottom of the absorber column where heat of absorbing VCM is again removed in the lower intercooler section of the column, trays 6 to 9. The lower intercooler has a recirculating stream that is pumped through a heat exchanger (the lower intercooler, LIC) outside the column. This exchanger removes the heat by cooling the material to about 56°F with freon 22 and returning it to the column.

The L. O., now laden with VCM and containing some HCl, called absorber bottoms, is pumped from the bottom of the absorber to the top tray of the stripper. Absorber bottoms and quench liquor are mostly EDC and VCM and a minor quantity of HCl. A thermosyphon reboiler is used to supply heat to the bottom of the stripper. This heat causes some of the column underflow to be vaporized and flow up the column.

This stream of rising vapor strips most all of the HCl and some of the VCM out of the combined liquid streams flowing down the column. The stripper overhead vapor flows on to the absorber as earlier described. The bottoms liquid flow from the stripper is essentially free of HCl and overflows into the product still feed drum. Refer to the section of this manual on the product still system for further details on this system.

HCl free of VCM and with trace EDC flows out of the top of the absorber to the absorber condenser. The absorber overhead flows through the tube side of the absorber condenser, where it is cooled by freon 22 evaporating at about 10°F on the shell side. Most of the EDC vapor and a small quantity of HCl are condensed in this exchanger as the gas is cooled.

From the absorber condenser, the liquid-vapor mixture flows to the HCl knockout drum. Condensate separates from gas in the knockout drum. The condensate is mostly EDC with a high concentration of dissolved HCl. The knockout drum provides a surge capacity for collecting condensate. Flooding and carryover from the absorber, due to extreme pressure or flow variations, will also be caught by the knockout drum. Liquid collected in the drum is level-controlled out to either of two locations. A portion of the L. O. from the discharge of the L. O. pump upstream of the FCV is diverted to the HCl condensate eductor. The flow of L. O. to the eductor is set manually with an armored rotameter. As the L. O. is pumped through the eductor, it creates a suction on the side port of the eductor. The eductor pulls the condensate from the bottom of the HCl knockout pot. The combined condensate and L. O. flow to the bottom of the absorber and enter through the same nozzle as quench dopp kettle overheads.

HCl flows from the overhead of the knockout drum on to the shell side of the HCl economizer. The HCl is heated in the economizer by the hotter product still bottoms on the tube side. Piping is provided to bypass HCl around the economizer for maintenance purposes. Downstream of the HCl economizer is the absorber pressure control valve. The HCl passes through the PCV and enters the HCl distribution system. The HCl distribution system supplies the HCl to other parts of the plant. Refer to the section of this manual on the HCl Distribution System for continuation.

b. Lean Oil Curcuit

Lean Oil is a recirculated stream of EDC that flows from the top of the absorber, down the absorber, down the stripper, out the bottom of the stripper to the product still, down the product still, out the bottom of the product still, and back to the top of the absorber. The stream leaving the product still is composed of L. O. and recycle EDC. Product still pressure forces the flow through the tube side of the furnace feed economizer where the hot product still bottoms is cooled by heating the furnace feed. Product still bottoms is then further cooled by flowing through the tube side of the HCl economizer.

Following the HCl economizer, the procudt still bottoms flows on to the primary L. O. cooler. Product still bottoms is on the shell side of the primary L. O. cooler and cooling tower water is on the tube side. At the exchanger outlet, the flow splits into the L. O. stream and the EDC recycle stream.

Part of the product still bottoms bypasses the primary L. O. cooler and recombines with the EDC recycle flow for temperature control of the recycle EDC stream. The L. O. flows on to the suction of the L. O. pumps. The L. O. is flow-controlled on the pump discharge at a flow rate that is dependent upon VCM production rates. The lean oil is cooled to its final column feed temperature on the tube side of the secondary L. O. cooler by freon 22 evaporating at about 46°F on the shell side of the exchanger. The L. O. outlet temperature is controlled by adjusting the freon level control valve. Variation of a few degrees in L. O. temperature will not adversely affect absorber operation.

c. Absorber Operation

In a conventional distillation column, cooling and condensing are provided by reflux. Reflux is usually a composition very similar to the overhead vapor flow, but it is in a liquid state. Reflux provides cooling by absorbing heat and vaporizing. The absorber-stripper also requires cooling to eliminate heavier components in the overhead, (heavier is relative to the HCl product, that is VCM and EDC), but it is supplied in a different manner. Essentially, the same amount of cooling is required to condense VCM out of quench vapor and stripper overhead vapor, whether or not it is in the form of liquid HCl (same composition as the column overhead, but in a liquid state), or L. O. (EDC liquid), EDC is used because it does not have to be cooled to as low a temperature as it takes to condense HCl. It is more expensive to cool to low temperatures.

VCM is condensed from the vapor flowing up the absorber by the lean oil flowing down the column. The heat that the condensing VCM gives up is transferred to the L. O. stream and elevates the temperature of the L. O. Since L. O. is subcooled, little of the L. O. vaporizes as the VCM condenses.

The cooling mechanism of the absorber-stripper is more involved than this description indicates. However, the principle remains the same: EDC acts as an absorbent and heat transfer agent in order to condense VCM from the column overhead vapors. One problem that results from using EDC instead of HCl as reflux is that when the EDC L. O. first enters the column, it is not in equilibrium with the HCl. This results in the L. O. becoming saturated with HCl and heating up. This problem is handled in the presaturation section at the top of the absorber.

Trays 57-62 comprise the L. O. presaturation section of the absorber. The L. O. combines with a recirculating stream of HCl-saturated EDC, called presat recirculation, flowing down from trays 61 and 62. As the combined liquid flows down the column, it contacts HCl gas flowing up the column. HCl absorbs into the liquid, and, since the liquid stream is below its boiling point, the down-flowing liquid increases in temperature. Liquid leaving tray 57 flows onto an accumulator tray. From here the warm HCl-saturated EDC is pumped through a freon exchanger and cooled to near 56°F. A portion of the liquid is returned as described above to tray 62 of the absorber. The remaining liquid leaving the exchanger, a stream equivalent to the fresh L. O. fed to tray 60, is level-controlled by the accumulator tray level onto tray 56 and flows on down the column.

The presaturation section prepares the L. O. to condense VCM out of the rising vapors further down in the column. By saturating the L. O. with HCl, it moderates the temperature rise associated with VCM absorption. For a given temperature and pressure, there is a fixed maximum concentration of HCl in the EDC L. O. The purpose of the top five trays of the absorber is to saturate the fresh L. O. fed to the column with HCl. As the HCl-laden L. O. flows down the column, it contacts rising VCM-HCl vapor. When VCM is condensed into the liquid, som of the previously absorbed HCl vaporizes. The heat required to vaporize the HCl is supplied by some of the heat liberated by the condensing VCM. The remainder of the liberated latent heat of condensation raises the temperature of the liquid stream going down the column. The more HCl in the liquid when it leaves tray 57, the more VCM that can be absorbed in the liquid stream without elevating the temperature. The temperature of the presaturated L. O. stream is important because it also determines the amount of VCM that can absorb into the liquid. When the presaturated L. O. is warmer than design, the amount of VCM that can be absorbed is reduced. The amount of L. O. required is directly related to the amount of VCM being produced, since this is the amount of VCM that must be condensed in the absorber. L. O. flow should be set based on both VCM production and furnace conversion. L. O. flow is often expressed as some multiple of VCM production, that is GPM of L. O. per ton per day of VCM. This ratio is only a convenience, since a number of items must be defined for a value to be absolutely correct. Since L. O. flow is directly tied to production, the ratio of presaturation recirculation flow to lean oil flow cannot be changed by adjusting L. O. flow, but rather by adjusting presat flow.

Fresh L. O. is not fed to the top of the column, but rather onto the third tray from the top. Feeding the fresh L. O. to this point allows it to first mix with presat recirculation flow already containing HCl before contacting the HCl gas flowing through the column. The recirculated presat EDC is immune to further absorption of HCl and acts as a cooling diluent. Also, the amount of EDC in the HCl overhead is a function of the top tray temperature. If fresh L. O. were fed to tray 62, there would be a large increase in temperature on the tray which would force more EDC vapor into the overhead and more duty on the absorber condenser. Instead, the presat recirculation flow, which has been cooled and saturated, is fed to tray 62. This minimizes the EDC in the HCl.

The amount of HCl absorbed in the L. O. is a function of three parameters: Fresh L. O. feed temperature, column operating pressure, and presat recirculation flow to L. O. feed ratio.

The amount of VCM that can be absorbed in the L. O. is a function of four parameters: HCl content of presaturated L. O., column operating pressure, presaturated L. O. temperature, and total fresh L. O. to the column.

Based on these variables, HCl-saturated L. O. will absorb a given amount of VCM from the vapors rising up the column. All of the VCM could be absorbed in the L. O. if the flow was set high enough or the inlet L. O. temperature low enough. However, it is not economically practical to design a system with such a large flow or such a low temperature. A better approach is to withdraw the downflowing liquid and cool it to a lower temperature, thereby resetting the column temperature profile to a cooler temperature. A modification of this approach is to add a cooling diluent to the downflowing stream, as was done in the presat section. A portion of the downflowing liquid is withdrawn from the column, cooled to near 56°F, and returned to the column a few trays above its withdrawal point. Such a system is referred to as a pump-around. Liquid is pumped around in a loop consisting of an exchanger and a few column trays. This stream acts as a heat transfer agent in this section of the column. The liquid flowing down the column mixes with the liquid being pumped around. The net liquid and gas are cooled in this section of the column. The recirculated liquid is cooling the condensing VCM and diluting the temperature increase of the liquid as VCM transfers to the liquid phase. The concept is the same as if cooling coils were located on the tray itself.

There are two such pump-around intercoolers on the absorber: the UIC, and the LIC. Trays 18 to 20 comprise the UIC. The material that flows down the column from tray 18 enters an accumulator tray from which a portion overflows to tray 17. The remainder of the material is drawn off and goes to the suction of the UIC pumps. From there it is pumped through the UIC exchanger where it is cooled to about 56°F with F-22 and it returns to the column on tray 20. Trays 6 to 9 comprise the LIC. The material that flows down the column from tray 6 enters an accumulation tray, from which a portion overflows to tray 5. The remainder of the material is drawn off and goes to the suction of the LIC pumps. From there it is pumped through the LIC where it is cooled to about 56°F with F-22, and it returns to the column on tray 9.

The temperature of the material leaving either intercooler section tray and flowing down the column can be adjusted by varying the flowrate of the recirculating stream. Whenever the flow rate is adjusted, within limits, the temperature of the recirculating stream remains the same exiting the cooler, since the freon level-control valve on the cooler adjusts the freon flowrate. If the pump-around flow is adjusted to a flowrate that is too great, then the cooler will no longer be able to cool the stream to the same temperature. Pump-around flowrates must be adjusted smoothly and slowly to prevent upsets to the freon side of the coolers and, thereby, to the refrigeration system and upsets to the column temperature profile.

d. Stripper Operation

As has already been discussed, the absorber-stripper is really one distillation column. The stripper is the portion of the column below the feed point which is referred to as the stripping section in a conventional distillation column. The stripping section removes components lighter than the bottoms product steam. In the stripper, HCl that is absorbed in the lean oil and other condensed liquids is removed by applying heat to the reboiler on the bottom of the column and boiling up VCM and EDC. The temperature of the stripper bottom is set by the column pressure and the EDC, VCM composition. This composition is a function of furnace feed and conversion rates and the L. O. flowrate. The greater the percent of EDC, the higher the boiling temperature of the stripper bottoms. This temperature must be kept from going too high, since the higher it gets, the more difficult it becomes to separate the last traces of HCl. The composition, and thus the temperature, may be adjusted by recycling VCM to the quench liquor tank from the product still reflux pumps via the rework system. Furthermore, as the temperature of the bottoms increases, the chest pressure, and thus temperature of the steam in the reboiler, must increase in order to transfer heat from the steam to the bottoms. This is undesirable, since the higher the temperature at which the reboiler operates, the greater the tendency for fouling. The stripper reboiler is normally run on 45 PSIG steam with a chest pressure in the range of 25 PSIG. If the temperature of the bottoms increases too much, it becomes impossible to transfer sufficient heat to the bottoms. The reboiler is also provided with 175 PSIG steam so that sufficient heat may be transferred in the event of an operating upset or on start-up. There are two feed points for quench liquor feed to the stripper: One to tray 38 or combined with absorber bottoms on to tray 40. The choice of quench liquor feed tray is a function of the quench liquor composition and feed tray material composition.

The stripper is primarily controlled by its temperature profile rather than a specific temperature in the column. In the top part of the column, the temperature drops off rapidly due to the increasing presence of HCl. This is called the 'Break'. The steam to the stripper reboiler and the cooling to the absorber are adjusted manually to maintain the break in the top of the column. If the temperature break travels down the column, excessive HCl will exit in the stripper bottoms.

The material leaves the bottom of the stripper by overflow to the product still feed tank. This controls the level in the reboiler at a fixed point and reduces the chances of level upsets that could flood the reboiler and cause fouling.

e. System Pressure Control

The setting on the absorber pressure control valve controls the pressure from the discharge of the furnace feed flow control valves to the suction of the product still feed pumps. This valve maintains a constant pressure at the top of the absorber column. Pressure readings at other points in the front end of the VCM section depend upon the pressure control valve setting and the pressure drop at different flow rates through the system. Constant pressure is necessary for stable operation of the absorber-stripper. Proper set pressure is also important. If the control pressure is set too low, the capacity of the absorber-stripper will be reduced. A low PCV setting also reduces the residence time of the charge in the furnace tubes. Short resident time causes higher furnace outlet temperature which promotes faster coking and higher impurity formation. (Refer to furnace system). A control valve setting that is too high may cause lifting an SRV as a result of a pressure or flow upset. A high control valve setting also imposes a higher pressure at the furnace convection section, radiant section crossover. A high pressure at this point can result in failure to achieve complete vaporization prior to entering the radiant section, which can result in faster coking in the radiant section. Adjusting the pressure control valve too quickly will also adversely affect plant operation. Quickly raising the HCl economizer outlet pressure can affect the plant in the following manner: Momentarily stop or reduce the HCl flow out of the VCM section, which can result in automatic shutdown of the OHC reactors; decrease furnace feed and cause erratic furnace production, or even cause activation of the furnace shutdown system; upset the temperature profile on the absorber-stripper and result in high HCl in the product still feed.

Quickly lowering the pressure control valve setpoint releases a large, stored, or absorbed volume of HCl. Plant operation can be affected in the following manner from a too rapid decrease in system pressure: Flood the absorber-stripper due to the increase in vapor traffic; damage trays in the absorber-stripper by physically blowing the trays out of position; lift the bed in the quench tower; cavitate the product still feed pump due to boiling in the product still feed tank.

Downstream of the absorber pressure control valve, the HCl co-product goes to the HCl distribution system.

f. Abnormal Operation and Corrective Action

During the operation of the absorber-stripper, there are a number of problems that may arise. One of the most likely among these is column flooding. Flooding can be caused by excessive vapor flow going up the column, by excessive liquid flow going down the column, or by a combination of both. The most likely point for having high vapor flow is in the bottom of the absorber where upsets in the quench system, such as loss of condenser fans, will cause high vapor feed flow to the column. An increase of only about 25% in vapor and liquid rates at the same time may cause flooding on trays 10 through 17.

The most likely points for high liquid flows are in the intercooler and presat sections of the absorber. High liquid flow can occur, since the recirculating flow can be greatly increased. In order to indicate the potential of flooding, each pump-around section is provided with a differential pressure (DP) measurement that spans from the vapor space of the tray below the accumulator to a point above the top tray in the pump-around section. The pump-around must be operated at recirculating flowrates that do not cause too much differential pressure and possible flooding. The trays in the pump-around sections are 2 pass with 24" tray spacing, which increases their liquid handling capacity without flooding.

Another likely place for high liquid flow is on the top trays of the stripper. The top 4 trays of the stripper are provided with a differential pressure measurement to indicate possible flooding. The trays of the stripper are 2 pass, which increases their liquid handling capacity without flooding. The most probable point of flooding in the stripper is in the bottom 10 trays. An increase of as little as 10% in liquid and vapor rates at the same time may result in flooding due to downcomer back-up. In the event that any differential pressure measurement anywhere in the column indicates likely flooding or if flooding occurs as indicated by loss of absorber bottoms flow, level dropping in the product still feed tank, erratic HCl overhead flow, erratic stripper overhead flow, or highly disturbed temperature profile, then the corrective actions of reducing vapor and liquid flows must be taken immediately. This is done by reducing plant production rates by reducing fuel gas to the furnaces, reducing L. O. flow, reducing recirculating flows on the pump-arounds, and reducing steam flow to the stripper reboiler. These changes must be done quickly and smoothly and only to the extent required. If the changes that are made are too great, they can result in worse problems than the flooding, such as large quantities of HCl leaving in the stripper bottoms.

There are a number of problems that may arise that are associated with the temperature profile of the absorber-stripper. In the stripper the temperature break may begin to rise up or descend through the column. This is an indication that there is an imbalance between steam to the stripper reboiler and cooling in the absorber. The situation is corrected by making adjustments to L. O. and steam to the reboiler in order to move the break in the desired direction. When the break moves down in the stripper, it may result in excessive amounts of HCl passing out of the bottom of the stripper. This results in excessive NaOH usage in the neutralizers, possible off-specification product, or possible high pressure on the product still. The adjustment must be tempered so as not to upset the column further and not to allow the HCl to get out of the column. It is also pointed out that the break does not have to go much below its normal operating position in the column to cause excessive amounts of HCl to go out of the bottom. The pH of the stripper bottoms is measured routinely to determine the amount of HCl leaving the column.

The profile in the absorber has a number of breakpoints with inverse profiles due to the pump-arounds. First among these is the presat section temperatures. The amount of HCl absorbed by the L. O. in the presat section can be determined by monitoring the presat cooler inlet temperature, which is essentially the temperature of material leaving tray 57. If the inlet temperature is running hotter than desired, insufficient HCl is being absorbed in the presat section due to insufficient cooling. This situation can be corrected by reducing the presat cooler outlet temperature, reducing the secondary L. O. cooler outlet temperature, or by increasing the presat recirculation using the presat recirculation flow-control valve. However, caution must be exercised when increasing presat recirculation. Opening the FCV too fast may result in a momentary reduction in flow through the level-control valve regulating flow down the column. Depriving the absorber of down-flowing liquids will result in an upset. The temperature of material leaving tray 57 is set by the ratio of presat recirculation flow to fresh L. O. feed. A higher ratio of presat recirculation to L. O. feed will result in a higher concentration of HCl in the L. O. flowing down the column. The upper limit on this ratio is the ability of the presat cooler to accomodate the heat load and the ability of the column to handle the liquid flow without flooding. There is nothing gained by increasing the recirculating flow if the presat cooler cannot maintain the outlet temperature at the desired value.

The inverse temperature on the presat section is formed by the hotter temperature of the material leaving tray 57 and the cooler material on tray 54. The temperature on tray 54 indicates if presaturated L. O. has been sufficiently presaturated with HCl and if it is being cooled enough in the presat cooler.

The temperature of tray 54 down to tray 37 is nearly the same, then it increases rapidly from tray 37 down to tray 22, due to the increasing amount of VCM present. This temperature break will move up in the absorber if the VCM moves up, due to insufficient cooling in the UIC or insufficient cooling or presaturation of the L. O. leaving the presat section.

The temperature of the material leaving tray 18 of the UIC and tray 6 of the LIC may be monitored by the inlet temperature to the respective intercoolers. This temperature, in both cases, indicates the amount of VCM that is being condensed from the vapor flowing up the column. If this temperature is too high, it is an indication that insufficient cooling is being provided to condense the amount of VCM present. This can be corrected by lowering the intercooler outlet temperature, or increasing the recirculating flow. The same precautions apply to these corrective measures as described above for the presat.

The inverse temperature profile above the UIC trays is formed by the hotter material on tray 22 and the cooler material on tray 20 where the UIC recirculation returns to the column.

The inverse temperature profile above the LIC trays is formed by the hotter material on tray 11 and the cooler material on tray 9 where the LIC recirculation returns to the column. The insufficient cooling of the LIC, in particular, may be related to the previously described imbalance of steam to the stripper reboiler and cooling in the absorber. Too much steam on the reboiler will result in higher VCM vapor up-flow in the absorber, since VCM is the main component stripped in the stripper after the HCl. This is, in essence, an artificial recirculating loop that can be set up by VCM flowing out of the stripper into the bottom of the absorber, being condensed, and flowing back to the stripper via the absorber bottoms. For this reason, the minimum cooling and steam rates which satisfy the stripper bottoms HCl content requirements and the temperature profile requirements are the desired rates. Any higher rates waste energy and increase the potential of flooding the column.

One of the most serious problems that can occur during the operation of the absorber-stripper is complete or partial loss of refrigeration. The refrigeration system consists of two units, each capable of supplying about 60% of the cooling required by the absorber-stripper at 750 TPD VCM rates. Whenever a partial or complete loss of refrigeration occurs, then plant production rates must be brought to match the available cooling capacity. This is done by reducing fuel gas to the furnaces until the desired rate is achieved. At the same time, L. O. and pump-around flowrates must be reduced to demand only the cooling capacity available. Steam to the stripper reboiler must also be reduced to match the system demands. If the loss in refrigeration is partial, these cuts must be done rapidly enough to prevent overload of the refrigeration unit that is still in operation. If the refrigeration loss is total, then the rates must be cut to zero. If one or both of the refrigeration units can be restarted in a short period, then the rate cut can be done by cutting fuel and furnace feed without shutting down the furnaces; if not, the furnaces must be shut down. Once refrigeration is restored, the rates may be increased to match the cooling available.

The OHC section is most affected by such rate reductions. One or both reactors might have to be shut down as a result of these rate cuts, or the reactors might automatically shut down as a result of imbalances and upsets that can occur during rate adjustments. For these reasons, the restarting or continued operation of the furnaces in the VCM section after a refrigeration upset is strongly dependent on having HCl consumers.

Insufficient cooling of the L. O. occurs at times due to bypassing of the F. F. economizer or the HCl economizer, or due to fouling of primary L. O. cooler. If insufficient cooling is a problem, then plant rates must be reduced to match the cooling available.

The pumps on the absorber-stripper system are all provided with spares, with the exception of the UIC. A common spare is provided for the UIC and the LIC, which provides sufficient operating reliability. This is due to the fact that in the rare case where the spare is needed for both UIC and LIC, it is possible to use the pump on the LIC and shut down the UIC pump-around. Rates must be cut in this event to match the available cooling, but the plant does not have to be shut down.

Loss of refrigeration can occur on the absorber condenser, which receives its refrigerant from the Process and Storage (P & S) Refrigeration system. The loss of this refrigeration is unlikely, since there are two units, each capable of supplying all cooling for the absolutely necessary loads to which the P & S system is connected. In the event that limited P & S system cooling is available, the absorber condenser comes at the top of the priority list on the P & S units. The next item is the EDC tank farm, since it can be sent directly to the incinerator if no cooling is available for it. The other loads are discretionary, including the EDC reactor section vent condenser. The absorber-stripper system can be operated without the absorber condenser, but it is very undesirable, since it results in greater amounts of EDC in the HCl, which can cause fouling of the HCl preheaters and the plugging of the mixed feed orifices at OHC. Excessive amounts of EDC in the HCl feed also result in higher impurity formation in the OHC section.

Whenever there is greater EDC in the overhead from the absorber, the amount of EDC condensate entering the HCl K. O. drum will be greater. Liquid settles in the drum due to change in direction and velocity of the entering gas, and the presence of a mesh pad near the top of the drum. An increasing level in the knockout pot may require additional L. O. flow to the eductor. At times when the eductor is unable to adequately remove condensate from the knockout drum, the condensate can be level-controlled to the quench dopp kettle overhead surge drum. In order to line up the condensate directly to the quench dopp kettle overhead surge drum, it is necessary to switch the action on the HCl knockout drum level control valve. This change is accomplished by reversing the controller action in the field. This is not a good mode of operation due to HCl losses that will result in the vent from the quench dopp kettle overhead surge drum.

Since the motive fluid to the eductor is manually set in the field, the eductor will always pull the same volume of liquid. If more condensate is being removed from the drum than is being condensed, the field-mounted level indicator controller responds by recycling some of the eductor outlet material to the eductor suction. A check valve at the knockout drum outlet prevents filling the knockout drum with lean oil.

g. Start-up and Shutdown

The absorber-stripper is normally started as a part of putting the VCM purification section on recycle. Its operation at that time is only a simulated form, since no HCl stream is available. The complete start-up of the system comes at the same time as the furnace start-up. The absorber-stripper is included in the purification section being put on recycle, any time the furnaces trip off or are shut down for short periods. The purification section is put on recycle by returning EDC from the bottom of the product still to the quench liquor tank via the L. O. pumps and by returning VCM via the VCM rework system to the quench liquor tank, either from the product still reflux pump or from shift bullets via the rework pump. These two streams serve as dummy feeds to the absorber-stripper to replace the feeds that come normally from the furnaces via the quench system.

The ratio of these two streams is set such that the composition will be similar to that at normal operation so that the temperature of the stripper bottoms will be normal. Nitrogen is fed into the bottom of the stripper to provide a vapor up-flow and to keep the system pressure up. Nitrogen can also come from the furnace system initially as a result of purging furnace tubes. The use of nitrogen must be limited, due to its cost and due to the possibility of it going from the absorber overhead to the plant scrubber. This can possibly cause VCM to go to the scrubber which is environmentally undesirable and cannot be allowed to occur. The plant scrubber is equipped with a stack analyzer to detect VCM. The L. O. circuit is left in its normal operating mode when the purification section is put on recycle.

The starting of the absorber-stripper as a part of starting the VCM purification system on recycle is done by first establishing the L. O. circulation. Heat is then started to the stripper reboiler to provide a heat load on the system. Once a heat load is applied, the refrigeration system may be started up. The pump-around (presat, UIC, and LIC) may also be started. Steam is put on the product still reboiler to begin heating the product still. VCM is introduced to the quench liquor tank from the rework system when it is desired to start the product still.

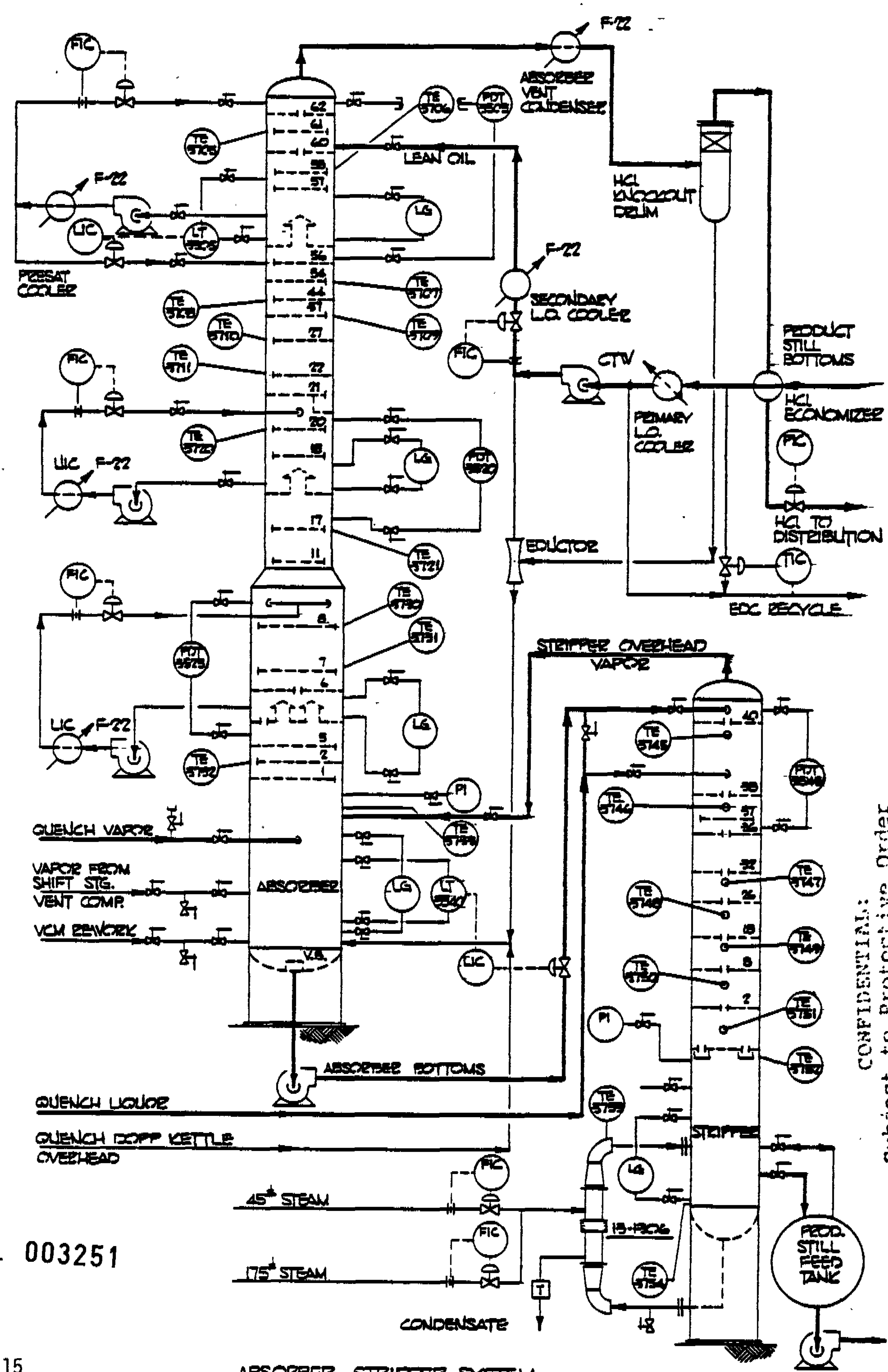

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FIG. VII-15

ABSORBER - STRIPPER SYSTEM

This is essentially all that can be done to start up the absorber-stripper until the furnaces are started.

2. Product Still System

The second phase of the VCM purification train in the process section is the removal of EDC (and certain other light and heavy impurities) from the crude VCM product. This separation is achieved utilizing the 50 tray product distillation column and its associated equipment. The above purification process is a very necessary and critical step in the effort to produce high purity VCM. The consequences of poor or improper operation of the product still system can be severe, ranging from the production of out-of-spec VCM to the fouling of its reboiler. In either case, depending upon the seriousness of the problem, shutdown of the furnaces and the entire VCM process section may be necessary.

Equipment comprising the product still system includes the product still feed drum and pumps, product still, product still condenser, and the product still reflux drum and pumps. The product still system is illustrated on process drawings 56A-10016, and P & I drawings 56A-10070, 56A-10071 and 56A-10072.

The crude VCM-EDC mixture pumped from the product still feed drum is flow-controlled to one of four trays in the product still. Multiple feed points are provided to compensate for changes in the feed composition caused by fluctuations in the VCM to EDC ratio in the bottom of the stripper. Periodically, the feed rate is adjusted to maintain the level in the feed drum within operating limits. It must be understood that besides vinyl chloride and EDC, the feed stream also contains a small amount of HCl carried forward from the stripper along with trace quantities of light and heavy organic compounds (with respect to EDC) produced in the cracking process.

Vinyl chloride fed to the product still is boiled overhead by a single thermosyphon reboiler consuming 175 PSIG steam. Steam flow to the reboiler is regulated by the product still temperature controller. The condensate leaving the reboiler is collected in the plant's high pressure condensate header.

Overhead vapors exiting the product still are condensed in a vertically-mounted cooling tower water-cooled condenser. Included in the overhead vapor stream are small quantities of HCl and light organic compounds carried forward in the product still feed stream. Most of these impurities are either condensed along with the vinyl chloride or dissolved in the condensate. Leaving the condenser, condensate and any noncondensables drain through a control valve into the product still reflux drum. The liquid in the reflux drum is then pumped back to the column as reflux or forward to the neutralizers as crude VCM product.

The reflux stream is flow-controlled to maintain the required reflux ratio (reflux flow/crude product flow). Operating at the correct reflux ratio is imperative to produce in-spec product and to minimize energy consumption. Besides the normal reflux point located at the top tray of the column, two additional reflux points are provided at lower trays. The lower reflux lines are used to supply reflux to the column in the event that the top tray becomes plugged with corrosion products restricting the normal reflux flow path. Plugging at the top of the product still is the result of high moisture levels in the product still system.

The crude VCM product pumped from the reflux drum is regulated by the reflux drum level controller to maintain the drum level. This material is referred to as crude product because it contains residual amounts of HCl that must be removed before it can be considered final product grade VCM. Prior to entering the VCM storage bullets, the crude product is processed through the neutralizer system to remove the remaining HCl.

As the separation process transpires in the product still, EDC, heavies, and any remaining lights are expelled from the bottom of the column. Leaving the product still, the bottoms stream undergoes a three-stage cooling process before dividing into two streams, namely the lean oil stream and the recycle EDC stream. The bottoms stream is first cooled in the furnace feed economizer where it serves to preheat the furnace feed stream. Secondary cooling of the bottoms stream occurs as it flows through the HCl economizer where it heats the HCl stream leaving the absorber. All or part of the bottoms stream is cooled for the third time in a water-cooled primary lean oil cooler. The bypass flow around the cooler is regulated by a temperature controller maintaining the temperature of the recycle EDC stream. Downstream of the primary lean oil cooler, the remaining bottoms stream splits, part of the stream flowing to the lean oil pumps and the remaining material joining the bypass flow around the cooler to form the recycle EDC stream. The lean oil stream undergoes additional cooling prior to entering the absorber. In effect, lean oil is circulated in a recycle loop from the bottom of the product still through the absorber-stripper and back to the product still. The recycle EDC stream represents that portion of the furnace feed that was not converted to VCM and HCl. This material undergoes EDC purification so that it can again be used as furnace feed, and for this reason is referred to as "recycle EDC".

The liquid level in the product still reboiler pot is controlled by a level controller regulating the recycle EDC stream flowing to the LP-EDC reactor gas separator. Restrictions to the product still bottoms flow upstream of the level control valve will upset the operation of this level control system. As noted above, the bottoms stream is circulated through a series of three exchangers prior to dividing. Obstructions in any one of these exchangers caused by fouling, foreign deposits, etc., could possibly restrict the bottoms flow sufficiently to over-range the capability of the level control valve. Once this occurs, level control of the product still is lost. Bypasses are provided around these exchangers for use in the event that plugging does occur. Care should be exercised in bypassing these exchangers so as not to upset other sections of the plant. Reliable level control of the column re-boiler pot is essential to prevent reboiler fouling caused by flooding (high level) or loss of circulation (low level). It should be emphasized that the product still reboiler operates at higher temperatures than other column reboilers in the VCM II plant and therefore becomes more susceptible to fouling caused by level upsets than other reboilers.

Control of the product still temperature is essential to produce the desired overhead product purity. The control temperature is a function of two factors; one, the composition of the feed stream; and, two, the operating pressure of the column. In all cases, the resultant temperature profile must be sufficient to prevent VCM from dropping out the bottom of the column and EDC from contaminating the overhead product stream. A good product still temperature profile is easily recognized by the fact that the top 20 trays of the column are operating at essentially the same temperature and, likewise for the bottom 10 or so trays with a gradual and smooth reduction in temperature between these two areas. This type of profile insures the presence of only VCM in the top of the column with little or no VCM dropping out the bottom of the column.

The product still pressure control scheme is somewhat different than what is normally installed on distillation processes, but it accomplishes the same purpose. The reason for this unusual pressure control system is due to the fact that the product still condenser operates as a total condenser, thus eliminating any vent flow from the condenser that is normally throttled to maintain the column pressure. With the absence of any vent flow from the condenser, the column's overhead pressure is determined by the vapor pressure of the condensing overhead vapors. In turn, the vapor pressure is dependent upon the temperature at which the vapors are condensed. This condensation temperature is a function of the heat transfer rate between the process and cooling water streams. There are a number of factors that can affect the heat transfer rate, and, therefore, the overhead pressure; the more significant factors are the process and cooling water flow rate through the condenser, the cooling water temperature, and the condenser heat transfer area.

The only means of controlling the product still overhead pressure is to artificially change one of the factors governing the heat transfer rate in the overhead condenser to compensate for changes in the column pressure caused by variations of other factors. In this case, the product still condenser's effective heat transfer area is varied to control the overhead pressure. The heat transfer area is adjusted by regulating the liquid level held up in the condenser tubes. The tube surface area below the liquid level, thus, cannot be used by the condenser for heat transfer. A control valve on the condenser drain line throttles the condenser outlet stream to maintain the necessary liquid level in the condenser tubes. The higher the level, the less effective heat transfer area and the lower the heat transfer rate, and vice versa. The heat transfer area is regulated accordingly by the pressure controller to produce the heat transfer rate necessary to maintain a steady column pressure.

Whenever a large amount of inerts or non-condensables are present in the product still overhead vapor stream, the above control scheme is ineffective in controlling the overhead pressure. Because of this, a secondary pressure control valve has been installed on the vent line leaving the product still reflux drum. If inerts are present, they purge through the condenser and accumulate in the reflux drum, where they are vented to the vent header as required to maintain the pressure in the reflux drum. The set point of the secondary pressure controller is operated at a slightly higher pressure than the primary pressure controller to insure that none of the condensed material flashes in the reflux drum and so that the secondary control valve does not open until the primary control valve is wide open. Too much inerts in the system will result in the product still pressure increasing beyond control. The product still and reflux drum are protected from overpressure by dual SRV's set to relieve at 135 PSIG.

The product still system is designed to process 115% of the necessary feed rate needed to produce the design plant capacity (750 TPD VCM). The additional 15% capacity was added to be able to rework off-spec product during normal plant operations. Depending upon the contaminant in the VCM product, off-spec VCM is reworked to one of a number of locations throughout the VCM purification section. VCM product out-of-spec on EDC concentration is reworked through the product still. Although the VCM rework header ties into the product still feed drum, off-spec VCM needed to be reworked through the product still. The reason for doing this is because the material in the feed drum operates at a higher temperature compared to the rework material, thereby possibly causing a portion of the rework material to flash in the feed drum, and also possibly causing the feed pumps to cavitate.

In the event that both product still feed pumps fail for some reason, material can still be fed to the product still from the feed drum by bypassing the feed pumps. This procedure is an alternative to having to shut down the furnaces and the VCM purification suction during this situation. A 6-inch line has been routed from the suction of the pumps to its discharge to bypass the pumps. The significant pressure difference between the product still and the feed drum makes this possible. Feeding the product still in this manner can be enhanced by either raising the pressure on the absorber or lowering the product still pressure beyond their normal operating pressures. Changing the pressure on the absorber or the product still will also require a corresponding change in control temperatures.

Frequently during furnace outages or emergency furnace shutdowns, the product still is kept in operation by operating the VCM purification section on recycle. This involves using both the VCM and EDC rework headers to recycle material back to the front end of the purification section. Caution must be exercised when operating the product still in this manner to maintain an acceptable VCM to EDC ratio in the product still feed drum, so as not to upset drastically the operation of the product still and the absorber-stripper.

Start-up of the product still system is one of the first steps in putting the VCM distillation train into operation. In most cases, the product still is started up by first establishing a cold recycle loop between the product still and the absorber-stripper. Material fed to the product still leaves the bottom of the column where it is both circulated back to the absorber via the lean oil header and to the quench liquor drum via the EDC rework header. Material in the quench liquor drum is then pumped forward to the stripper. Once the recycle loop is established, steam is admitted to the product still reboiler. Until the product still has heated up to temperature, the recycle EDC must remain blocked to the LP-EDC gas separator. During this time, a field-mounted LCV on the EDC rework header tie-in to the quench liquor tank is used to control the product still level. An alternative to starting up the product still in the recycle loop is to start it up on total reflux. In either case, once the product still is in operation, the absorber-stripper can be heated up and later the EDC and VCM purification sections can be tied together in a larger recycle loop in preparation for a cracking furnace start-up. During a total furnace outage, the VCM purification section may remain in operation if it is desired, by operating it on recycle. This must also be done whenever a spurious trip of both furnaces occurs.

To monitor the VCM product purity and help guard against producing out-of-spec product, frequent lab analyses are run on the VCM crude and VCM product streams. These lab analyses include tests for water, pH (HCl content), and VCM purity.

Normally, the water content of the crude runs less than 50 ppm. High moisture content in the crude indicates the leakage of water into the process at some point. The most probable location of such a leak would be the product still reboiler. Other possible sources are the quench dopp overhead stream and the furnace feed stream.

The pH of the crude depends upon the amount of HCl leaving the bottom of the stripper. For every part per million HCl in the product still feed, the HCl concentration in the crude increases approximately 3.8 times. The pH of the crude varies between 3.5 and 4.0, which correspond to about 1 to 2 ppm in the stripper bottoms. Any higher HCl concentration results in a lower pH crude which decreases the life of a neutralizer.

The crude and product streams contain trace quantities of light organic compounds. The impurities commonly include butadiene (BD), monovinyl acetylene (MVA), methyl chloride (MeCl), and ethyl chloride (EC). Due to the relative volatilities of these compounds, they cannot be removed in the product still. They are, however, minimized to meet product specifications by adjusting the cracking operation and furnace feed purity. Other possible contaminants in the VCM product include EDC and lights such as VDC, cis- and trans-dichloroethylene. In this case, the product still is being operated with too little reflux (low reflux ratio) or the control temperature is too high. Adjustments should be made to the product still operation as soon as possible to minimize the amount of out-of-spec material produced.

3. Neutralizer System

The VCM product stream leaving the product still reflux drum contains traces of HCl. This must be removed before the product is sent to storage and sold. The final phase of the VCM purification train in the VCM process section is the neutralizer system. The purpose of the neutralizer system is to remove this HCl by neutralizing it with caustic (NaOH).

The proper operation of the neutralizer system is necessary to produce in-specification product and prevent contamination of product in storage. Off-specification product must be reprocessed to remove the HCl. This results in extra costs and possible reductions in production totals, thus preventing the plant from meeting production requirements. Improper operation also results in short neutralizer life which leads to recharging cost, excessive consumption of caustic and large quantities of spent caustic to be disposed of.

The neutralizer system consists of the humidifier, the water addition drum, three product neutralizers, and two product filters. The neutralizer system and its operation is closely associated with the neutralizer wash system. The description of the neutralizer wash system and its operation is handled in a subsequent section of this manual. Three product neutralizers are provided so that two may be in service at all times and one may be out of service for recharging and maintenance. Two product filters are provided so that one may always be in service while one is out for filter element replacement.

The crude VCM product stream is pumped from the product still system via the product still reflux drum level control valve to the humidifier. In the humidifier the crude product stream is carried to the bottom of the vessel by a dip leg. This results in the product stream being vigorously mixed with an aqueous phase that is present there. The humidifier is lined with teflon to prevent corrosion that would result from the aqueous phase since it is strongly acidic.

In order to neutralize and remove the HCl from the crude product, the HCl is reacted with caustic (NaOH). The reaction, $HCl + NaOH \longrightarrow NaCl + H_2O$, can only be carried out in an aqueous phase. The HCl in the crude product is dissolved in an organic phase. The mixing of the organic phase and the aqueous phase in the humidifier results in the HCl being dissolved in the aqueous phase. This is because HCl has more affinity for the water than for the organic VCM product phase. The contacting of the product with the water also results in the product becoming wet. Too much water in the product will result in its being off-specification.

The wet product stream along with some acidic aqueous phase exit the humidifier at the top. The aqueous phase is heavier than the VCM phase and, therefore, it tends to remain in the bottom of the humidifier. After some time, it becomes completely saturated with HCl. Therefore, the aqueous phase is periodically drained from the humidifier to the neutralizer wash system, then fresh water is added.

The water addition drum is used to resupply the aqueous phase to the humidifier. High pressure nitrogen is used to pad water into the humidifier or "sop" it.

The effluent stream from the humidifier enters the bottom of one of three product neutralizers. It flows through a feed distributor nozzle that directs the flow down into an aqueous phase in the bottom of the neutralizer. This caustic, aqueous phase is heavier than the VCM product, so it tends to stay in the bottom of the neutralizer. After the

VCM phase separates from the aqueous phase, it flows up through a bed support plate and into a bed of solid caustic, NaOH Pels$^{(R)}$. After passing through the Pels$^{(R)}$ bed, the VCM flows through a fiberglass filter and out the top nozzle of the neutralizer.

The stream that enters the neutralizer is two phase; a wet product phase that must be dried, and an acidic aqueous phase that must be neutralized. In addition, the product phase may still have HCl dissolved in it that was not scrubbed out in the humidifier. The contacting of this stream with the caustic, aqueous phase in the bottom of the neutralizer serves to carry out the neutralization reaction and further, to remove the last remaining HCl in the product. The sodium chloride (NaCl) formed by the neutralization reaction also has more affinity for the aqueous phase than the organic VCM product phase, so it remains in the caustic aqueous phase.

Caustic, (NaOH), is a very good drying agent. The neutralizer also serves to dry the VCM product which had to be wetted to remove the HCl. The drying is a two stage process. The first stage takes place in the caustic aqueous phase in the bottom of the neutralizer. As the VCM product stream passes through this phase, it is scrubbed with the caustic phase. This tends to remove water from the wet product.

The amount of water dissolved in the product is dependent on the strength of the caustic and the degree of mixing. The stronger the concentration of caustic in the aqueous phase, the less water that will remain dissolved in the product. There is, however, no way to control the strength of the caustic or the degree of mixing in the bottom of the neutralizer. For this reason, and in order to assure the proper amount of drying of the product, it must be further contacted with caustic.

The second stage of drying takes place in the caustic bed. In this portion of the neutralizer, the product stream is contacted with solid caustic beads (Pels$^{(R)}$). This results in the last traces of water being removed from the product. As the water is absorbed by the Pels$^{(R)}$, it forms a liquid caustic solution. This solution tends to move slowly to the bottom of the neutralizer to replenish the caustic aqueous phase there. By this process the bed is slowly dissolved away.

Since the Pels$^{(R)}$ bed is slowly depleted, the effectiveness of the neutralizer is also slowly reduced. Furthermore, the neutralizer is only capable of handling a certain flowrate of VCM product with a certain concentration of dissolved HCl. VCM process section upsets that cause greater concentrations of the HCl or higher flow rates of product may result in breakthrough of HCl or water into the finished product stream leaving the neutralizer. For this reason it is preferable to run two product neutralizers in series. The three neutralizers are piped so that any one may be set up as the first in series and any other may be the second in series. The standard practice is to remove a depleted neutralizer from service and switch the one that was second in series into its place. The recharged neutralizer is placed in service as second in series. The depleted neutralizer is then recharged and stands ready for the procedure to be repeated when the next neutralizer must be taken out of service.

The product stream exits the top of the second neutralizer and flows to one of two product filters. In the product filter, any small entrained caustic particles are removed. After the filters, the product flows through a valve used for sampling and through dual product flowmeters. From this point, it flows to the shift bullet system for storage.

Several problems commonly occur during the normal operation of the neutralizer system. First of all is plugging, either of a neutralizer, or of the product filters. As plugging proceeds, the pressure drop through the system becomes greater. As the pressure at the inlet to the system increases, the product still reflux drum level control valve must open wider to increase the pressure. When this valve is fully open, it is possible to lose control of the drum level. In this case, it is necessary to switch neutralizers or filters to regain control. In this case where the system inlet pressure is high or in a case where a complete plug occurs, the humidifier and neutralizer upstream of the plug will be subjected to high pressure. The humidifier and neutralizers are protected by safety relief valves set at 300 PSIG. The filters are also designed for 300 PSIG. This is above the dead head pressure of the product still reflux pumps. However, subjecting the system to dead head of the pumps should be avoided, as it may result under some circumstances in SRV liftings and the release of large quantities of VCM.

A second common problem is poor performance of the neutralizer system resulting in out-of-spec finished product. This is commonly caused by channeling in the neutralizer caustic bed. Channeling will lead to very poor caustic utilization and poor neutralizer onstream time. High velocity is a cause of channeling. Reworking of product that results in excessive velocity in the neutralizers should be avoided. Poor performance may also result from improper "soping" or improper frequency of "soping".

The start-up of the neutralizer system is normally the last step in starting up the VCM process section on recycle. The shift bullet storage tanks are included in the recycle loop in this case. This is the procedure whenever the plant has been shutdown for an extended outage. The neutralizers are put into the recycle loop and flows established, so that any problems encountered, such as plugging, can be corrected prior to plant start-up. However, the performance of the neutralizers cannot be proven until the furnaces are started up and HCl, that must be neutralized, is present. While the VCM process section is on recycle, the "soping" of the humidifier is suspended.

Whenever the plant is shutdown unexpectedly, the VCM process section is put on recycle without the shift bullets by using the VCM rework FCV on the product still reflux. In this case, flow to the neutralizer system is simply stopped. When the plant is started back up, the flow may be resumed along with the "soping" and sampling. Whenever practical, the flow is resumed prior to start-up since plugging may result if the neutralizer is left sitting for too long.

Anytime it is possible that large quantities of EDC may get into the stream going to the neutralizer system, it should be isolated. If EDC contamination gets into the Pels(R) beds, it will result in contaminated product for long periods of time and usually results in the neutralizer being taken out of service and recharged to correct the problem.

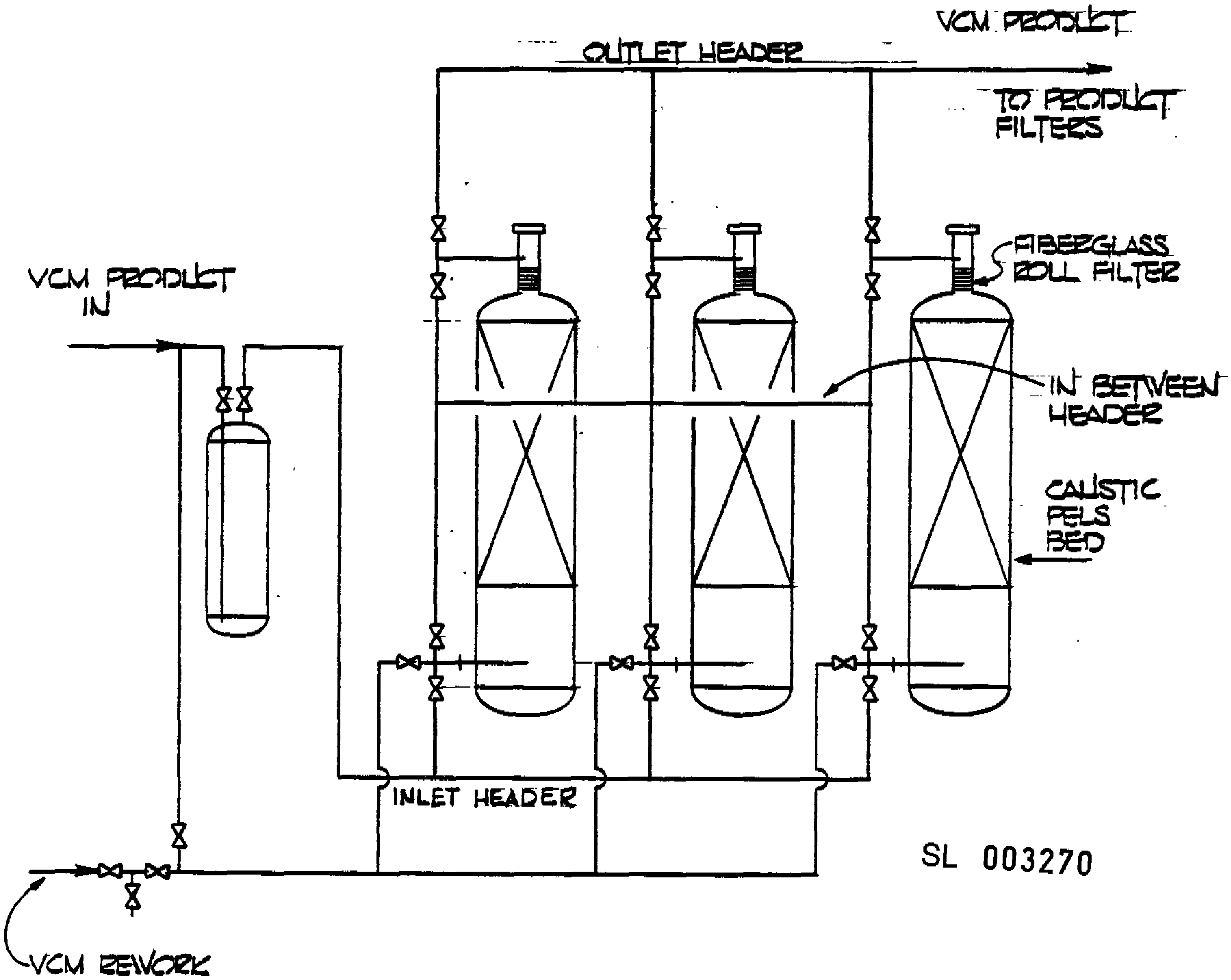
During the normal course of operation, neutralizers are taken out of service, recharged, and put back into service. This is done by first placing the third neutralizer into the series and taking the first in series off-line. The depleted neutralizer is then cleared, and re-charged. Any routine maintenance can also be performed at this time. The procedures for clearing a neutralizer for recharging must be strictly followed to prevent exposure to VCM and to prevent release of VCM to the atmosphere. The same applies to product filters, which are also removed from service routinely.

In order to measure the performance of the neutralizer system and to assure its proper operation, analyses are run on the crude and finished VCM product streams. The analysis of the finished product stream is also run to assure the product going to storage meets specifications, and if it does not, to take corrective action and thus minimize the impact on the storage system.

The crude product is analyzed for water, pH and iron. The water and iron should be minimal. If these are not it is a sign that water is leaking into the process and that corrosion is taking place in upstream equipment. Corrective action should be taken immediately to locate the problem and stop it. The pH should show the presence of the normal range of HCl concentration. If the pH is unusually low indicating an abnormally high concentration of HCl, it is a sign that the absorber-stripper is not operating properly. Corrective action should be taken or it may result in HCl breakthrough into the finished product.

The product from the first neutralizer is analyzed for water, pH and iron. This sample is necessary to indicate when the performance of the first in-line neutralizer is no longer satisfactory. Low pH, high water or high iron are signs that the neutralizer must be taken out of service. Before this is done corrective actions should be taken to try to keep the neutralizer in service and thereby fully utilize its caustic charge. The normal practice is to drain the neutralizer and humidifier and "sop" the humidifier with a charge of fresh water. The sample is then caught and run again to determine results.

The finished product stream is analyzed for water, pH, and iron, and in addition, a chromatographic analysis is run on it to determine the impurities in the product. The reasons for the water, pH, and iron test are the same as those described for the product from the first neutralizer. In addition, the pH test will also give an indication if caustic particles are being properly filtered by the product filters. The corrective action, should any of these tests be out of specifications, is the same as described above for the product from the first neutralizer. Care should be exercised in not allowing a problem to persist at this point for long periods of time, since it is affecting the quality of the product in the shift storage system.



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(DRAIN LINES, WASH LINES, PURGE CONN., ETC. NOT SHOWN)

NEUTRALIZER SYSTEM

FIG. VII-16

The chromatographic analysis of the finished product is run to determine the amount of impurities such as butadiene (BD), monovinylacetylene (MVA), ethyl chloride (EC), methyl chloride (MeCl), vinylidene chloride (VDC), or ethylene dichloride (EDC). The presence of any of these compounds in out-of-specification quantities is not an indication of the improper operation of the neutralizer system, but rather of other sections of the VCM II plant.

The presence of BD is an indication of problems in the furnaces, in the quench dopp kettles, or in the quench dopp condensing systems. The sections of the manual on these systems should be referred to for response to this problem. The presence of MVA, EC, or MeCl is an indication of problems in the furnace system or the furnace feed. The section of the manual on the furnace system should be referred to for the response to this problem. The presence of VDC, EDC, or other heavy compounds is an indication of problems in the product still system. The section of the manual on the product still system should be referred to for the proper response to this problem.

The neutralizer system is shown on the P & ID's beginning on 56A-10072.

4. Neutralizer Wash/Caustic Recovery System

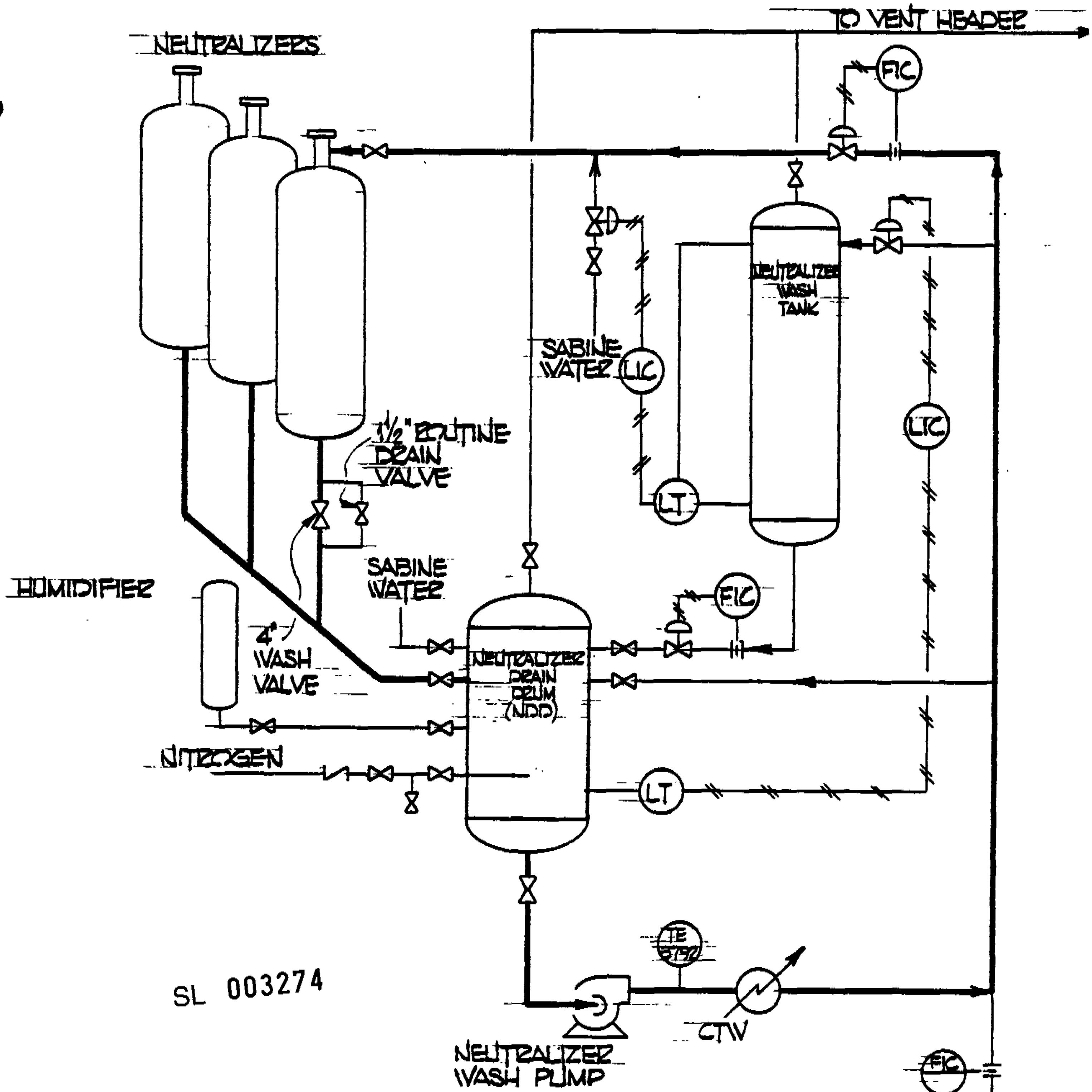
During the routine operation of the neutralizer system, the aqueous phase from the humidifier and neutralizer must be drained. After a depleted neutralizer is removed from service, it must be cleared for recharging. At this time it still has a great deal of spent caustic that must be washed out. The purpose of the neutralizer wash system is to provide an environmentally acceptable means of handling the material from both of these operations. It also provides a method which results in acceptable exposure levels to VCM. It does this by converting the caustic to a solution in a closed system. This solution can be used in the OHC aqueous system.

The proper operation of the wash system is necessary in order to keep from overheating the carbon steel and teflon materials of construction. Carbon steel should not be subjected to caustic solutions at over 150°F. The design temperature for the teflon liners is 225°F. The proper operation of the wash system is necessary to avoid creation of large quantities of caustic solution that results from the washing operation. The system must be operated so that it will always have capacity available when neutralizer system problems are encountered that necessitate draining.

The neutralizer wash system consists of the neutralizer drain drum, the neutralizer wash pump, the wash cooler, and the neutralizer wash storage tank. The system is shown on drawings 56A-10075 and 56A-10076.

The neutralizer wash system is used to handle the drain material from periodic draining of the neutralizers and the humidifier. The aqueous phase, saturated with VCM, from these vessels is drained into the neutralizer drain drum (NDD). It flows to the drain drum by the pressure difference, and enters via a distributor nozzle. A nitrogen purge is provided to strip VCM from the aqueous material. The nitrogen and VCM vapors flow out of the top of the NDD and into the plant vent header. Fresh water or material from the wash storage tank can be added to the NDD if needed to dissolve solids and to provide heat to help remove the VCM. The aqueous material from the NDD is pumped to the storage vessel where it is accumulated. From the storage vessel, the caustic solution is periodically pumped into the OHC section, aqueous system.

The neutralizer wash system is also used to wash spent caustic Pels(R) beds from depleted neutralizers that have been taken out of service. It takes a large quantity of water to wash the caustic from a spent neutralizer so that it may be recharged. The wash system provides a method of recirculating the wash water until all of the caustic is dissolved into solution. At the same time, the concentration of the solution is brought up. This minimizes the amount of waste caustic solution that is created by the washing operation. Fresh water is put into the top of the neutralizer along with the recirculation flow of wash water. The material flows down through the neutralizer and out the bottom to the neutralizer drain drum by gravity. As it passes through the neutralizer, it dissolves the Pels(R), heats up and becomes contaminated with VCM that was held in the bed. The material is stripped by nitrogen upflow in the NDD. The nitrogen and VCM vapors flow out of the top of the NDD to the ventheader. The hot wash water flows out of the bottom of the NDD to the wash pump. The wash pump sends the material through the recirculation cooler, cooled by cooling tower water, to remove the heat of solution. The material is then sent to the stor-



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NEUTRALIZER WASH SYSTEM

* PRIMARY WASH CIRCUIT SHOWN BY HEAVY LINES

FIG. VII-17

age vessel. A portion of the flow is also sent to the neutralizer as the recirculation. This recirculation flow is adjusted so that the heat up through the neutralizer is kept below 150°F. A portion of the material in the storage vessel is drained by gravity back to the NDD. This provides secondary stripping to further reduce the VCM contamination. The fresh water is allowed into the system until the storage tank is about 80% full; at this point, the fresh water is stopped. The storage tank is sized so that a full caustic bed can be converted into a 35% solution. After the water flow is stopped, the recirculation is continued until the bed is completely dissolved.

The wash material is sent to the OHC aqueous system where it is utilized to neutralize the aqueous effluent in place of cell liquor. The flowrate to OHC can be adjusted so that the cell liquor flow to the OHC aqueous system just barely drops to zero.

5. Shift Storage System

The purpose of the shift storage system is to provide tanks in which batches of VCM production can be qualified before they are moved on to bulk storage. These batches also serve as a method of checking the quantity of product made each day. In addition, they serve as holding tanks for batches that are found to be off-specification while the material is being reworked.

The proper operation of the shift storage system is necessary to insure that batches of off-specification product are not put into bulk storage. Transferring off-spec material to bulk storage can result in large quantities of bad product that then have to be reworked. This causes reduction in plant production and failure to meet production and sales commitments. Improper operation of the shift storage area can result in overpressurization of the tanks and large releases of VCM to the atmosphere, which is extremely unsafe and environmentally unacceptable.

The shift storage system consists of five shift storage bullets, each capable of holding one shift's production at 750 TPD VCM production rate. The five tanks are necessary to provide for sampling the tanks, resampling, reworking, and maintenance outages. The shift storage system also consists of two product transfer pumps and one product rework pump. The shift storage system is shown on the P & ID's beginning on 56A-10088.

The VCM product flow enters the shift storage system from the neutralizer system. It flows to one of the five shift bullets. As each shift bullet is filled with VCM, it is "topped-off" and the production is switched to the next shift bullet. After a tank is topped-off, a sample is drawn and sent to the main laboratory for analysis. The sampling procedure requires that the tank be recirculated to be sure it is completely mixed before the sample is taken. This recirculation, using one of the product transfer pumps, starts about one hour before the tank is topped-off and continues for about one hour afterward. This amount of time is necessary to insure good mixing. After the tank is analyzed by the main laboratory and proven to be in-specification, it is transferred to bulk storage using the product transfer pumps. Bulk storage consists of three storage spheres and two low temperature storage tanks. The storage manual should be referred to for further information on these tanks and their operation.

If a shift bullet is found to be out-of-specification, it may be reworked to the VCM process section to remove the impurity. If material is to be reworked, it is pumped back to the VCM process section using the rework pump. The rework pump delivers the material to the VCM rework system. The rework system can deliver the material to the desired system in the VCM process section.

There are several problems that may occur during the operation of the shift storage system. One is the possible misalignment of the shift bullets for sampling, reworking, or transferring. This is very undesirable, since it may result in contaminated material being pumped into a good shift bullet, or worse, contaminated material being moved to bulk storage. In order to reduce the chance of this occurring, each of the recirculation lines at each tank (transfer pump recirculation and rework pump recirculation) is equipped with a flow switch. Each time a sample recirculation or a rework recirculation is started, the flow switch will indicate to which tank the material is flowing. Also, the transfer lines between shift storage and bulk storage are equipped with flow switches that will indicate when flow is exiting or entering the shift storage system to or from bulk storage. The correct combination of flow switches will enable the operator to confirm that the line-up is correct. In addition, the computer system indicates at all times which shift bullet is lined up to the production line.

Another possible method of cross-contamination is by equalization of two or more tanks. This can happen as a result of opening incorrect outlet lines to the transfer pumps or to the rework pumps or by opening the tank vent lines incorrectly. If equalization is the result of opening outlet lines, then the level will begin dropping on one tank and rising on another. If the vapor lines are mistakenly equalized, it will only result in cross-contamination if there is a tank out-of-spec on low pH. This occurrence is virtually impossible to detect until it shows up by analysis, probably in bulk storage. For this reason, prevention is the only cure; whenever there is a tank with low pH material, its vent valve should be tagged closed to prevent accidental opening. If it is opened for pump-down, via the vent system, then the other valves on each tank should be tagged closed.

Anytime a tank of contaminated material is in one of the shift bullets, extra special precautions must be taken. Each time the contaminated material is manipulated, the lines that were used must be flushed with good material into the bad tank. Checks should be made that all special valves, such as those for floating long transfer lines, are closed when the bad material is handled.

Another problem that can arise on the shift bullets is that of overfilling and overpressurization. As each tank is filled during the normal course of operation, the vapor space contains inert gas, such as nitrogen. This will not condense as the vapor space is compressed. If the pressure becomes too great, it will result in the 150# SRV on the bullet, lifting. This is a very dangerous and undesirable situation.

For this reason, each shift bullet is protected by dual independent high pressure switches. These are set to alarm well below the SRV setting so that corrective action can be taken. The normal procedure is to vent the vapors to the shift storage vent compressor system. This system recovers as much of the VCM in these vapors as practical; and, then disposes of them to the incinerator system or the absorber-stripper system.

The most likely cause of a high pressure on the shift bullets is from filling. Overfilling the tanks will also result in a high pressure, even if the vapor space were to contain only VCM. This results from the fact that the pumps for sending material to the shift bullets all can dead head at above 150 PSIG. If the tanks are completely filled with liquid, then it will result in a liquid release through the SRV. This is an even more dangerous situation than a vapor release, due to the larger quantity of material that would escape. The pressure switches serve as a back-up alarm to prevent overfilling, but are not the best method to prevent overfilling.

Dual independent level alarms are provided to prevent overfilling of the shift bullets. One of the level alarms is the level transmitter; the other is a high level probe. These are set to provide a warning and a reminder to the operator of the high level. There is also a field-mounted level guage on each tank. This serves as a back-up to the level transmitter. It is used each day to check the transmitter reading by comparing the two.

The shift bullets are not normally started up or shutdown as other operating equipment. It is necessary from time to time to remove a tank from service for maintenance reasons. In this case, all of the liquid VCM is pumped from the tank and the shift storage vent compressor system is used to remove and recover the VCM vapors. The tank must be purged with nitrogen to remove final quantities of VCM. The best practice on a large tank of this type is to pressure it up and then depressurize it several times.

The sample that is taken on each shift bullet when it is topped-off is sent to the main laboratory for analysis. The tests that are run are for water, pH, iron, and chromatographic analysis for impurities. Possible impurities are butadiene (BD), monovinylacetylene (MVA), ethyl chloride (EC), and possibly other material lighter than VCM.

The shift bullet must meet all product specifications before it can be moved to bulk storage. The choice of where to move it in bulk storage depends on shipping requirements, such as, by tank car, by ship or barge, or by pipeline.

If a tank does not meet specification in either of the following two ways, it can be reworked to the VCM process section at the proper point to remove the impurities. These two ways are: 1) If it is out-of-spec on water, pH, or iron, or 2) If it is out-of-spec on heavies, such as VDC or EDC. The section of this manual on the VCM rework system should be referred to for further information on reworking. There is also some possibility that EC can be removed by rework, if the product still is operated so that the EC is forced out of the bottom, and the EDC recycle stream is going to the lights still. Refer to the product still system for further information on this.

As mentioned above, if a tank is out-of-specification due to very low pH, it may have to be pumped down to remove vapors using the shift storage vent system, in addition to reworking the liquid. This is necessary to get HCl vapors out of the tank to prevent contamination of new material. After the liquid is reworked, the vapors should be pumped out. Refer to the section of this manual on the shift storage vent system for further information.

If the EC cannot be removed by rework, or if the impurity is BD, MVA, or MeCl, which are impossible to remove in the purification section, then the only solution is to blend the material with other material of sufficient purity to result in product that meets specification. Blending with material in bulk storage is a very difficult operation that is undesirable, since it risks the possibility of contaminating large quantities of material. Another method is to rework the material to the purification section, or to blend the material in the shift storage bullets. This is a less risky practice, since results can be checked before the material is sent to bulk storage, but it may necessitate production rate reductions to accomplish. That is why the early detection of these impurities and the prevention of their formation is important. Refer to the section of this manual on the neutralizer system for further discussion of this.

The shift bullet area is monitored by vapor detectors that automatically turn on deluge water spray in the area whenever a VCM leak is detected in the area. In addition, since the storage area is a long distance from the control room, these vapor detectors can also cause the isolation and shutdown of the product transfer pumps, the rework pump, and the shift storage vent compressor. These are a likely source of a leak, due to seal failures or cracking of the pump bowls. For details on the operation of this shutdown system, refer to the write-up on the shift storage shutdown system.

6. Shift Storage Vent System

The purpose of the shift storage vent system is to provide for the removal and disposal of vapors from any of the shift bullets in the shift storage system and to recover VCM from these vapors. This is necessary any time a shift bullet is experiencing high pressure due to inerts or anytime it has to be cleared for maintenance. The shift storage vent system can also preform the same function for tanks in the bulk storage area. The VCM storage manual should be referred to for more complete information on this case.

The proper operation of this system is important to assure maximum recovery of VCM from the vapors and to avoid operating upsets on the systems to which the vent from the system is sent. The upset of the receiving system may result in the production of off-specification product or down time that causes undesirable venting of materials to the atmosphere.

The shift storage vent (SSV) system consists of the shift storage vent compressor, the shift storage vent compressor suction drum, the shift storage vent condenser, and the shift storage vent condenser receiver. It is shown on 56A-10091 and 56A-10092.

Vapors to be vented from a storage tank first enter the SSV compressor suction drum. Here, liquids that may be in the vent lines are prevented from reaching the vent compressor. The drum has a high level detector that causes the compressor to shut down in the event that a high liquid level is detected. The drum is also heated by external steam tracing to cause liquid VCM to be vaporized.

The vapors exit the top of the vent compressor suction drum and enter the two stage reciprocating vent compressor where they are compressed to a maximum of about 225 PSIG. It is necessary to compress the vapors if they are going to be sent to the absorber-stripper system. If the vapors are going to the SSV condenser, it is also necessary to compress the vent to get a better recovery of VCM in the condenser.

The vapors that exit the compressor are normally sent to the SSV condenser where they pass through on the tube side and are cooled to about 10°F by Freon 22 evaporating on the shell side. Freon is supplied by the Process and Storage (P & S) refrigeration system. The section of this manual on that system should be referred to for further information.

Any VCM that is condensed in the vent condenser exits along with the uncondensed vapors and travels to a vapor/liquid disengaging tee. Here, the liquid separates and falls by gravity into the SSV condenser receiver.

In the receiver, the liquid is level-controlled out of the bottom. The vapor space of the receiver is equalized to the disengaging tee to provide for gravity flow. The liquid leaving the drum via the level control valve flows by pressure difference to the VCM production line going to the shift storage system. This results in any recovered VCM showing up in the production tank where it can be qualified before getting back into storage.

The vent stream leaving the disengaging tee goes to the SSV system pressure control valve where the system pressure is set and the vent flow is measured. The system PCV is protected with an anti-back-upΔP to prevent backflow into the system.

The vent stream from the SSV system may be sent either to the absorber-stripper in the VCM purification section or to the vent header, which sends it to the incinerator.

Start-up of the shift storage vent system is done whenever there is a need to handle vents from the shift storage vent system or from the VCM bulk storage area. The receiving system for the vent from the shift storage vent system must be in service in order to start up. The system is started by first being sure that a shutdown is not being called for by the shift storage SDS or the vent header management system. (These will be explained subsequently). Next, all piping is properly aligned, and thereby a differential is established that will allow the flow to leave the system when it is started. Reset/start-up bypass is initiated next, and the compressor may be started. After the compressor is running, the system pressure control valve will allow material to leave the system as required to control the pressure at the setpoint. The flow can be sent through the SSV condenser if desired.

The vent from the shift storage bullets (or bulk storage systems) does not have to be compressed to send it to the incinerator. It is possible to send it directly to the vent header, due to the normal pressure difference in these two systems. For this reason, the SSV compressor and SSV condenser are equipped with bypass lines. It is more desirable to recover VCM from this vent stream rather than burning it. Thus, it is possible to send the vent stream through the SSV condenser without sending it through the compressor. This will give a satisfactory recovery of VCM if the vent is nearly pure VCM. However, if the vent does contain some inerts, the recovery of VCM will be much better if the vent in the condenser is operated at a high pressure. This can be achieved by sending the vent through the vent compressor.

The vent from the shift storage bullets (or bulk storage) can be sent to the absorber-stripper system. In order to do this, the vent must be compressed, since the absorber-stripper operates at a pressure higher than the shift storage system. When the vent is sent there, the recovery of VCM is complete; however, any inerts end up in the HCl stream, and, therefore, go to the OHC reactor system. These inerts result in a large reactor vent which causes a large ethylene loss. Therefore, it is undesirable to operate in this mode. It does serve as a back-up to sending the material to the vent header, but the economics must be considered each time before it is used.

Whenever the SSV system is used to vent vapors from a shift bullet that contained very low pH material, and it is suspected that the vapors contain HCl, then special precautions must be taken to prevent contamination of other bullets or new production. There are two ways of handling this vent. One possibility is to send it directly to the vent header bypassing the compressor, condenser, and receiver, and keeping them isolated during the procedure. The recovery of VCM from these vapors is not practical, since the recovered liquid will contain HCl and the SSV receiver will return this to the current production and cause it to be off-specification.

The other possibility is to send the material to the absorber-stripper, not employing the SSV condenser and receiver, and keeping them bypassed and blocked off during the operation. This does result in the recovery of the VCM in the vapors, but, as previously pointed out, it also results in a large ethylene loss in the OHC section if the vent contains any nitrogen.

In either case, all equipment and lines must be purged with nitrogen to be sure the HCl vapors are removed prior to returning to normal operations. During either procedure the vent lines from all other shift bullets should be blocked and tagged to prevent cross-contamination via the vapor spaces of the tanks.

The shift storage vent system can be shut down as a result of several different occurrences. First of all, the compressor is protected by a shutdown system that protects the compressor against damage due to pumping liquid. There are several different parameters used to detect possible liquid going to the compressor, or the possibility of condensing liquid directly in the head of the compressor during the compression stroke. Caution must be exercised whenever the vent compressor is used, since there are several possible ways of getting liquid into the conpressor. If the material going to the compressor suction is nearly pure VCM, it is possible for conditions to develop which can cause condensation to occur in the suction line. The compressor is protected against this case by the shutdown system. The vapor pressure of the vent is calculated from the measured temperature. As long as inerts are present, the measured pressure will be greater than the vapor pressure and thus, as long as inerts are present, it is permissible to operate the compressor. If the measured pressure drops to within a few PSIG above the vapor pressure, then the vent is essentially pure VCM and the compressor is no longer needed. It is at this point that condensation in the suction line is most possible so the compressor is shut down. Conditions can occur at which the discharge temperature of the compressor may be such that condensation can occur directly in the compressor head as the material is compressed (if it is nearly pure VCM). To prevent this, the discharge temperature must be kept well above the dew point. The shutdown system will shut down the compressor if this temperature drops too low.

Second, the shift vent compressor will shut down as a result of a shift storage system shutdown. This occurs whenever a designated vapor detector senses flammable vapors in the area. It causes the shutdown and isolation of the transfer pumps, the rework pump, and the vent compressor. For more complete details on the operation of this system, the write-up on the shift storage shutdown system should be referred to.

Third, the shift storage vent compressor will shut down anytime the vent from the system is going to the incinerator and a shutdown of the incinerator occurs. This is done because the vent from the shift storage vent system contains some amount of VCM. It is even possible for it to be nearly pure VCM. When the incinerator shuts down, the vents in the vent header are diverted to the plant scrubber. It is undesirable for VCM vents to go to the scrubber, since it may result in flammable vapors in the scrubber effluent liquid or vent. VCM in scrubber effluent is also environmentally unacceptable. For these reasons, any time an incinerator shutdown occurs, the anti-back-up valve in the vent stream from the SSV system is closed. The write-up on the vent header management system should be referred to for further details on the operation of that system.

Finally, the SSV system is protected from backflow of vapors from the vent receiving systems by an anti-back-up valve. The backflow of vapors is more likely when the vent is being sent to the absorber-stripper, since that system operates at a higher pressure than the suction side of the SSV compressor. Thus, anytime the compressor shuts down while vents are being sent, the system would be open to backflow.

7. Refrigeration System

The purpose of the VCM refrigeration system is to provide for the sufficient cooling of four process streams circulating in the VCM purification section. By supplying low temperature refrigerant to the secondary lean oil cooler, the presat cooler, the upper inter-cooler, and the lower intercooler, the refrigeration system cools th associated process streams. It is emphasized that all of the above exchangers are integral parts of the absorber-stripper system, and therefore, adjustments to the VCM refrigeration system must be performed with the consequential effects upon the absorber-stripper in mind. The failure of the VCM refrigeration system to provide the necessary refrigeration load due to either upsets or poor operation of the system will inhibit the absorber-stripper from achieving its intended task.

The VCM refrigeration system consists of two York refrigeration units operating in parallel as a single system to provide approximately 720 tons of refrigeration. Each unit is rated to deliver 430 tons of refrigeration (60% of total load) using freon-22 as the refrigerant.

The VCM refrigeration system incorporates only one level of refrigeration, that being at approximately 46°F. Each of the refrigerated coolers are sized such that their process streams are all cooled to around 56°F using this level of refrigeration.

Included within each York refrigeration unit are the screw compressor, primary and secondary oil separators, freon condenser, two oil pumps, an oil cooler and filter, and a capacity control system. Equipment common to both units are the freon liquid receiver, the freon liquid supply and vapor return headers, a suction header pressure controller, the refrigerated coolers (evaporators) and their associated oil stills, and the oil transfer pump. The VCM refrigeration system is illustrated on P & I drawing 56A-10080.

To avoid confusion in the ensuing discussion concerning the operation of the VCM refrigeration system, this write-up is broken down into the following sections:

a. Refrigerant Flow
b. Lube Oil System
c. Capacity Control System
d. Safety Control System
e. Abnormal Operation

a. Refrigerant Flow

The refrigerant flow of the VCM refrigeration system is basically the same as the other refrigeration systems employed in the VCM II plant. Both refrigeration units employ an oil-injected, positive displacement, screw compressor.

Low pressure freon gas from the four process coolers (from here on referred to as freon evaporators) is drawn into the suction of each compressor through a Y-type strainer and check valve. The purpose of the strainer is to keep trash from entering the compressor, whereas the check valve is necessary to prevent the compressor from turning backwards when it is shut down with a high gas pressure at the compressor discharge.

The screw compressor utilizes two helical intermeshing rotors to provide compression. Freon gas drawn into the compressor flows through the inlet port and fills the interlobe space between the adjacent rotors (lobes). As the rotors revolve, the interlobe space moves past the inlet port sealing the interlobe space. Continued rotation progressively reduces the interlobe space occupied by the gases, causing the gases to compress. During the compression cycle, the outlet port is also sealed by the rotors. When the interlobe space becomes exposed to the outlet port, the gas is discharged at a much higher pressure.

The high pressure freon gas is discharged into the primary oil separator where most of the oil entrained in the freon gas during compression is extracted. From the primary oil separator, the freon gas flows into a secondary oil separator. The secondary oil separator removes most all of the remaining oil entrained in the gas stream. Oil accumulating in the separators is returned to the compressor.

Leaving the secondary oil separator, the high pressure freon gas flows through a check valve to a water-cooled exchanger where the freon gas is condensed. The freon condensate, still under compressor discharge pressure, gravity drains to a liquid receiver common to both refrigeration units. The check valve is installed on the oil separator outlet to prevent refrigerant backflow when only one refrigeration unit is operating.

The freon receiver provides the necessary surge room needed due to fluctuations in the refrigerant quantity required by the individual evaporators. It also serves to maintain a liquid seal upstream of each evaporator level control valve. The high pressure liquid freon is pressurized out of the receiver through a standleg extending up from the bottom of the receiver. Out of the receiver, it flows through a filter/dryer and a moisture indicator and then into the liquid freon supply header which carries the refrigerant to the four evaporators.

Prior to entering each evaporator, the liquid freon flows through a level control valve where its flow is regulated by a field-mounted level controller maintaining the proper level in the evaporator. It is recommended that the level in the evaporators be controlled at the minimum level at which the evaporator can meet its design requirement. The reason for this is to help prevent any liquid carry-over in the freon vapors leaving the evaporator. Although screw compressors can handle more liquid than other types of compressors, it has its limits at which time severe damage can be inflicted upon the compressor. To warn of high freon levels, each evaporator is equipped with a level transmitter and high level switch used to activate alarms on the local refrigeration panel and in the control room. Usually, the freon level is controlled such that the liquid freon just wets the top tubes of the evaporator.

The evaporator level control valve is the dividing point between the high and low pressure sides of the refrigeration cycle. As the high pressure freon liquid flows through the control valve, its pressure is reduced to that of the evaporator pressure causing a portion of the liquid stream to vaporize. This pressure reduction and subsequent partial vaporization step cools the remaining freon liquid down to the saturation temperature consistent with the freon pressure in the evaporator (Design: 46°F freon temperature).

The resultant cold freon stream flows into the shell side of the evaporator where the liquid freon absorbs heat from the process stream flowing through the tube side. As the liquid freon absorbs enough heat to reach its boiling point, it vaporizes and flows out of the evaporator along with the other freon vapors back to the suction of the compressors. Upon reaching the compressors, the refrigerant flow cycle is repeated.

Freon can be added to the system, if required, as either a liquid or a gas. The liquid charging valve is located on the line out of the receiver. The vapor charging valve is located on the compressor suction line.

b. Lube Oil System

Each VCM refrigeration unit has its own oil system that is essential for the safe and proper operation of its compressor. The oil system serves several purposes:

1) Provides lubrication for all vital compressor parts.

2) Cools the discharge gas to allow operation at high compression ratios.

3) Seals the mating zone of the two rotors to assure high compressor efficiency.

4) Provides hydraulic pressure to operate the compressor capacity control system.

Oil supplied to the compressor is distributed to four locations; the inboard bearing and shaft seal, the compressor oil injection port, the outboard bearing and balance piston, and the capacity control hydraulic cylinder. The oil injection port supplies the oil used for cooling the freon gas and for sealing the mating zone of the two rotors. All of the oil supplied to the compressor is eventually discharged from the compressor along with the high pressure freon gas.

Separation of the oil and freon gas is completed through the use of two oil separators. The freon gas and oil mixture leaving the compressor is discharged directly into the primary oil separator. Once inside the primary separator, most of the oil immediately drops to the bottom of the separator while the remaining gas stream flows upward through a 6-inch demister and then out of the separator into a secondary oil separator. The lower portion of the primary separator serves as an oil reservoir from which the compressor oil pump draws its suction. A sight glass and low level switch are provided to monitor the level of the oil reservoir.

The secondary oil separator is divided into two chambers. The gas stream enters the lower chamber where more oil is allowed to drop out of the gas. Flowing upward into the top chamber, the gas stream passes through a series of replaceable filter separator elements. The oil concentration in the freon gas leaving the secondary separator should be less than 15 PPM. Oil accumulating in the top and bottom chambers of the separator is returned directly to the suction piping of the compressor by way of high pressure oil float valves. Bullseyes on each chamber are provided to check for high oil levels.

Oil accumulating in the bottom reservoir of the primary oil separator is pumped back to the compressor oil manifold where it is distributed among the four oil supply points. The oil pressure at the manifold is controlled by two pressure regulators mounted in parallel on the oil pump recirculation line. The regulators control the oil pressure by relieving any excess oil back to the primary oil separator. Prior to reaching the oil manifold, the oil stream is circulated through a water-cooled exchanger for cooling and a filter to remove any trash that may be present in the oil system at this point. A field-mounted temperature controller controls the oil supply temperature at the desired temperature by regulating the amount of oil allowed to bypass the cooler.

As noted, the freon gas leaving the secondary oil separator contains a few parts per million of oil. The remaining oil is eventually carried forward in the liquid freon to the various evaporators, where it accumulates as the liquid freon is vaporized. Using one of three oil drawoff valves, the accumulated oil and some freon are gravity drained from the evaporator into its oil still.

Each evaporator has its own oil still to which the accumulated oil and freon mixture is intermittently drained. The oil still is equipped with a heater to vaporize any freon falling into the oil still back to the evaporator vapor line. A thermostat controls the oil temperature in the oil still by energizing and de-energizing the heater as necessary. The thermostat also activates a control valve on the evaporator oil drain line. As the oil temperature drops below the control point, the thermostat simultaneously energizes the heater and closes the control valve stopping the oil from draining into the oil still. Above the control temperature, the heater is de-energized and the control valve is opened re-establishing the draining process. A manual block valve on the drain line is throttled such that the drain valve is opened 50 percent of the time. When the level in the oil still reaches a high level, the oil transfer pump is used to return the oil to the primary oil separator. The oil transfer pump is common to all four oil stills.

Oil can be added into the system as needed by using the oil transfer pump. When the system is started up initially, or after an outage during which the oil was removed, the refrigerant circuit will have an oil-free refrigerant charge. Upon operation, the freon will absorb oil until it reaches an equilibrium condition. This will require the addition of oil to the lube circuit. Once the system reaches equilibrium, it will not be necessary to add oil unless oil leaks develop. Oil additions after initial start-up or after outages can be minimized by adding oil to the evaporator before the system is started.

c. Capacity Control System

Because the VCM refrigeration compressors are positive displacement compressors, it is not necessary to balance the load between the two compressors. They can be operated together at unequal capacities, as one can lead the other. Since the maximum compressor efficiency is at full load, the most economical mode of operation is achieved by operating one compressor at full load while the second compressor varies its capacity to handle load fluctuations. To operate the refrigeration system in this manner, the fully loaded compressor is operated in the manual mode, while the floating compressor is operated in the automatic mode.

The operating capacities of the two compressors are controlled by their own capacity control systems. As noted, the control system can be operated in either the automatic or manual mode by adjusting the capacity control switch. In the automatic mode, the capacity control system (pressure control module) regulates the compressor loading to maintain the refrigeration system's suction pressure. Both compressor control systems receive their setpoint from the refrigeration system's suction pressure controller. Operating both compressors in the automatic mode may cause the individual control systems to fight each other as they try to maintain the desired suction pressure.

In the manual mode, compressor capacity is varied by manually adjusting the capacity control switch to either the "Load" or "Unload" position. The compressor will continue to load or unload until the switch is released or the slide valve has reached the fully closed or open position. When the switch is released, it will return to the "Hold" position and the control system will maintain the resulting load.

The capacity control system has a built-in current limiting control system that automatically unloads the compressor should the amp draw exceed the compressor motor design full load amp rating. This safety control feature is in effect whether the compressor is operating in the automatic mode or manual mode.

Basically, the capacity control system varies the compressor loading by adjusting an internal gas recycle stream. Internal gas recycle is accomplished through the use of a slide valve located on the bottom side of the compressor rotor housing. During times in which the compressor is operating at full load, the slide valve remains closed. As the compressor is unloaded, the slide valve opens allowing gas to recycle from the opening created in the bottom of the rotor housing back to the inlet port area prior to the gas being compressed. Continued opening of the slide valve increases the recycle flow rate and decreases the amount of gas to be compressed. In principle, enlarging the opening in the bottom of the rotor housing effectively reduces compressor displacement.

Initiated by the capacity control system, axial movement of the slide valve is achieved using a hydraulic cylinder mounted on the compressor with its piston connected to the slide valve. Oil supplied from the compressor oil manifold is fed to one side of the piston, while oil trapped on the other side of the piston is simultaneously released to the compressor suction piping to allow the piston to move in the required direction. Solenoid valves located on the hydraulic oil inlet and outlet lines are activated by the capacity control system to adjust the slide valve position. The length of time the hydraulic control solenoids are energized determines the degree of loading or unloading, as the slide valve can be stopped anywhere between 10% and 100% of compressor capacity. This gives the compressor the ability to have infinite steps of capacity control with corresponding savings in power requirements.

d. Safety Control System

Each refrigeration unit has its own safety control system that assures safe and proper operation of the unit. The main function of the safety control system is to warn of deteriorating operating conditions and to shut down the unit whenever any abnormal conditions exist that could possibly damage the compressor and other unit components. Some of the conditions protected against include over-pressure or over-heating of the equipment beyond design limitations and loss of lubrication due to insufficient oil flow or oil cooling.

To protect the refrigeration unit from severe mechanical damage when detrimental operating conditions exist, the control system will shut down the compressor based upon the following:

1) High discharge pressure
2) High discharge temperature
3) Low suction pressure

4) High oil temperature

5) Low oil differential pressure

6) Motor overload

Prior to shutdown, a general trouble alarm will sound in the control room. For more information on the safety control system, refer to the VCM II Plant Safety Control Systems Manual.

It is emphasized that the cause of any compressor shutdown must be determined and corrected before attempting to restart the compressor. Each unit is an expensive piece of equipment that can easily be severely damaged by momentary carelessness.

e. Abnormal Operation

Probably the most serious problem incurred in the operation of the VCM refrigeration system is the unexpected shutdown of one or both refrigeration units. What makes this situation so critical is the fact that the operation of the absorber-stripper system is very dependent upon that of the refrigeration system. The VCM refrigeration system provides more than 95 percent of the absorber-stripper's cooling requirements. Refrigeration is required in the absorber-stripper system to remove the heat of absorption (via the presat cooler and the upper and lower intercoolers) inherent in the process and to cool the incoming lean oil stream (via the secondary lean oil cooler).

Upsets in the absorber-stripper system as a result of a loss of refrigeration capacity include:

1) Higher process stream temperatures leaving the presat cooler, secondary lean oil cooler, and upper and lower intercoolers.

2) Distruption of the absorber and stripper temperature profiles.

3) Higher vapor flow rates through the absorber, possibly causing the absorber to flood, or suffer mechanical damage to the trays.

4) Loss of VCM and EDC by way of the HCl stream leaving the top of the absorber.

The loss of one refrigeration unit will reduce the available cooling capacity to approximately 60 percent of that needed by the absorber-stripper at full VCM rates. This means that the absorber-stripper cooling requirement has to be cut by 40 percent as quickly and as safely as possible. This is accomplished by cutting the VCM production rate, reducing the presat and upper and lower intercooler recirculation rates, decreasing lean oil flow, and cutting back the steam flow to the stripper.

Following the loss of one refrigeration unit and prior to the time in which corrective actions are taken to stabilize the absorber-stripper system, the remaining refrigeration unit can be overloaded. If the capacity control system of the operating unit is in the automatic mode, the compressor will load up to the point at which the current limiting control system will prohibit the compressor from loading any further. In the manual mode, the compressor will only load up as the freon gas density increases (due to a rise in compressor suction pressure), again up to the point at which time the current limiting control system takes over.

Immediately after a compressor shuts down, the remaining unit will not be able to provide the refrigeration load being called upon by the evaporators. Although the evaporators will be provided with sufficient liquid refrigerant for a short time (by surge volume in the receiver), the compressor cannot compress all of the freon vapors being generated by the evaporators. As a result, the compressor suction pressure increases raising the refrigeration level in the system. The process streams circulating through the evaporators are then not cooled properly, initiating the upset of the absorber-stripper system. It is important to make sure that the high process temperatures are a result of high suction pressure, and not insufficient level in the evaporator. As the suction pressure increases, so does the compressor discharge temperature. However, the freon condensers operating in parallel and equalized to each other will condense the discharge gas down to its normal temperature. The lone refrigeration unit should continue to operate with a high suction pressure until the absorber-stripper refrigeration requirement is reduced. As this is done, the suction pressure will begin dropping to its normal value.

In a compressor overload situation, the compressor will probably first shut down on overload (high amps) if its current limiting control system fails to work properly. The second most likely trip feature will be that of a high compressor discharge temperature.

The loss of both refrigeration units requires that the VCM production rate be cut to zero. If one or both refrigeration units can be restarted within a reasonable time, the furnaces can remain in operation by only vaporizing the EDC feed; if not, they are shut down. Once the first refrigeration unit is started, production rates are increased to match the cooling available.

8. VCM Rework System

The purpose of the VCM rework system is to provide a means of returning off-specification material from the shift bullets to systems in the VCM process section for processing and purification. It also provides a method of recirculating VCM from the product still reflux drum to the quench liquor drum so that the process section can be operated on recycle when the furnaces are not operating. Whenever the process section has been shut down and cleared, the rework system can be used to return VCM to the vessels for start-up.

The proper operation of the rework system is necessary for the smooth operation of the process section. If the rework flow is erratic or interrupted, it will result in upsets that can cause production of off-spec product or down-time on the process section. The proper operation of the rework flow from shift storage is essential for production accountability, since all material reworked from storage goes through the product flowmeters twice.

The VCM rework system consists of a network of piping that is connected to supply VCM to 1) the quench liquor drum, 2) the bottom of the absorber column, 3) the product still feed drum, 4) the product still reflux drum, 5) the neutralizer system, and to be supplied VCM by 1) connection to the discharge of the product still reflux pumps and 2) connection to the rework pump in the shift storage system. A double block and bleed valving arrangement is provided at each connection to prevent cross-contamination.

The rework system is normally aligned to supply material to the quench liquor drum from the product still reflux pumps. In this mode, whenever an unexpected shutdown of the furnaces occurs, the recirculation of VCM can be started by opening the flow-control valve on the rework system from the reflux pumps. This flow is necessary to keep the VCM process section artificially supplied with VCM so that it can continue operation. This alignment also provides for the rework line to float on the quench liquor drum and thereby be protected from rupture due to thermal expansion.

If it is desired to start VCM rework from storage so that material can be brought back for reprocessing, or so that the neutralizer system can be put into operation (if the process has been on recycle as described above), then the rework pump in the shift storage area must be aligned to a shift bullet, and the pump started. The flow-control valve from the rework pump may then be opened (and the valve to the reflux pumps closed back if it was in service). The flow-control valve from the rework pump is protected from backflow by an anti-back-up trip circuit that does not allow the flow valve to be open unless there is a positive pressure and, thus, flow from storage to the rework system. There is also a recirculation line on the rework pump that sends recirculation material back to any tank that is desired. This line can be used for mixing a tank for sampling using the rework pump. It should be remembered that it takes about 5 times as long to mix a tank with the rework pump as it does with the transfer pump. Great care must be taken whenever the rework recirculation line is used, since sending contaminated material to the incorrect tank can cause cross-contamination. The rework recirculation line to each tank is equipped with a flow switch to detect to which tank the flow is going. These switches will result in an alarm each time the flow goes to a tank, thus enabling the operator to confirm the recirculation flow.

Whenever off-spec material is to be reworked from shift storage, the flow is started as described above. The rework pump should be aligned to the desired shift bullet. If it is desired to take a sample of the material being reworked, a sample point is provided across the rework pump for this purpose.

The destination of the material to be reworked depends on the type of impurity that has to be removed. Water or iron or very slightly off pH material is reworked to the neutralizer system. Material severely off-spec on pH is reworked to the bottom of the absorber or to the quench liquor drum. Material off-spec on EDC or other materials heavier than VCM can be reworked either to the quench liquor drum or the product still feed drum, although the rework of material to the product still feed drum usually results in flashing. The rate at which material is reworked is dependent on plant production rates. The total of rework plus production should not exceed about 825 TPD VCM, since this is the maximum that the plant was sized to take. There may be other factors that limit this to a lower rate. For this reason, rework should be brought on slowly and production samples checked as well as the general operation of the VCM process section watched closely during that time. One possibility for higher rework rates is on rework to the neutralizer system. If it is desired to send material directly to a neutralizer, the rework flow can be sent to a neutralizer in parallel to the normal product flow. This enables a much faster rework of material. It should be remembered that the flow through any neutralizer should not be allowed to cause too high a velocity, since it will result in channeling and short neutralizer life.

VCM REWORK SYSTEM

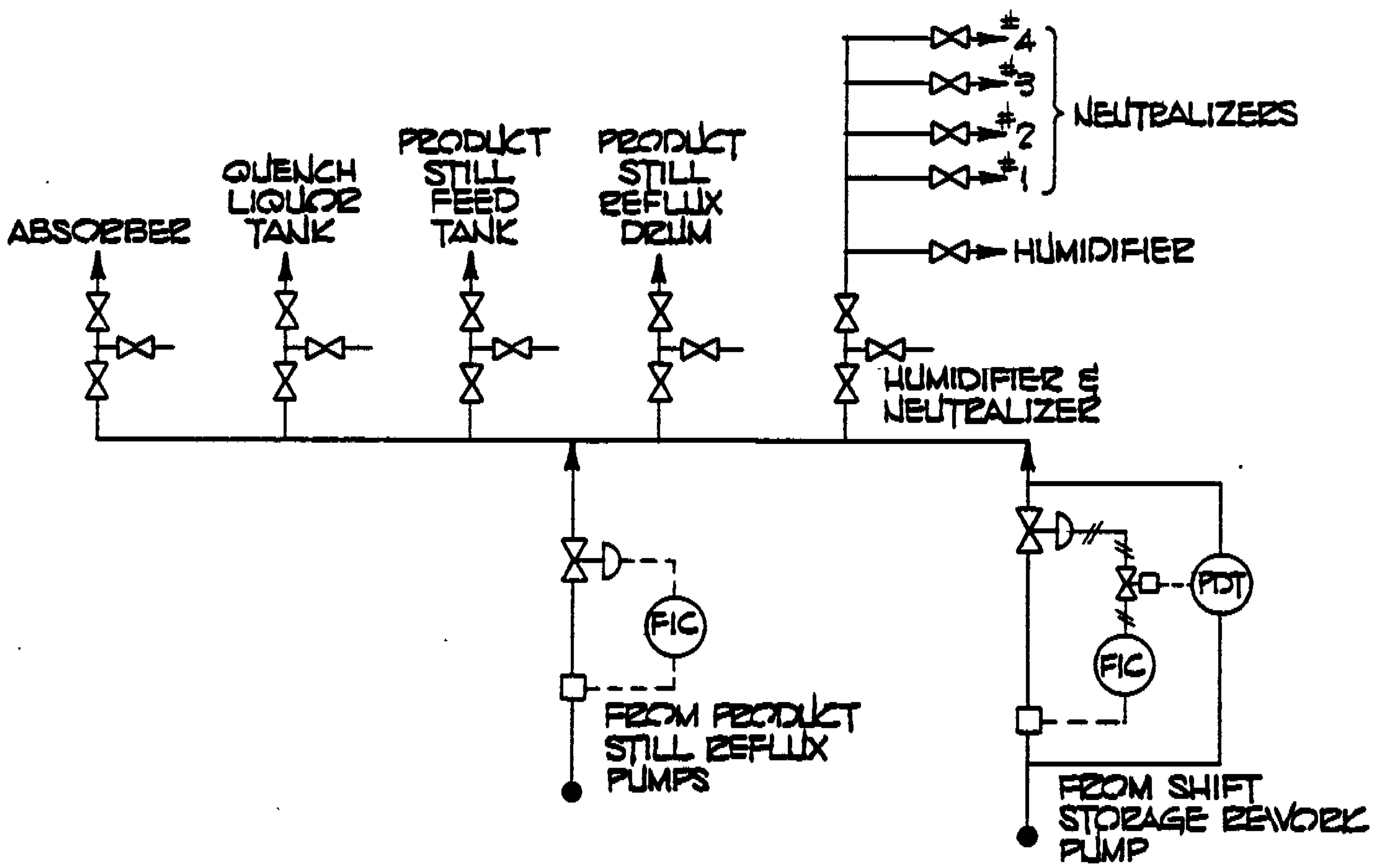


FIG. VII-18

H. INCINERATOR SYSTEM

1. Plant Vent Collection Systems

The purpose of the vent collection system is to collect all continuous and intermittent vents which can contain VCM, HCl, ethylene, chlorine or chlorinated organic compounds and route them to a control device. There are two control devices; the incinerator and the atmospheric vent scrubber. Each device has a main collection header; the incinerator vent header and the scrubber vent header.

a. Incinerator Vent Header

The incinerator vent header is 10" in diameter and comes from Plant B and low temperature storage along the east piperack. Vents from VCM-II tie in as it goes by the storage area, through the process area to the west piperack and to the incinerator. The incinerator header is shown on 56A-10108. Headers and vent piping that tie in from east to west are:

1) Vent from the crude OHC-EDC transfer pump sample point.

2) Vessel Clearing Drop (VCD) No. 36 This drop is for clearing equipment near the DH still feed pumps.

3) The crude EDC and DH bottoms storage tank sample point vents.

4) VCD No. 35. This clearing drop is for clearing equipment near the crude OHC-EDC transfer pumps.

5) The EDC vent compressor header. This is the compressed vent from all 9 EDC storage tanks and the DH feed tank.

6) VCD No. 34. This drop is for clearing of equipment near the EDC storage vent compressors.

7) VCD No. 33. This drop is for clearing of equipment near the furnace feed pumps.

8) Furnace feed storage tank sample point vent header.

9) Furnace feed pump sample point vent.

10) The VCM shift storage vent header. Vents enter this header from the following sources.

a) The high pressure VCM vent condenser, or if the vent condenser is bypassed, from the compressor, or directly from shift bullets, tank car loading, the spheres and VCM-I bullets if the condenser and compressor are out of service. This vent is considered to be discretionary and is automatically blocked if the incinerator taking VCM-II vents (#1, #2, #3, or #4) goes down.

b) The VCM compressor distance piece vent.

c) VCM product transfer pump and rework pump mechanical seal pot vents and sample point vent.

d) VCD 39 and VCD 37. A continuous nitrogen purge also goes into this header.

11) The OHC plant vent collection header. The OHC header supplies the largest continuous flow to the incinerator vent collection system. This stream also provides most of the fuel value for the incinerator. The two OHC reactor small pressure control valves are the source of the vent gases. Vents tie into the OHC header as follows:

a) No. 1 reactor small pressure control valve (PV-9491).

b) VCD #19.

c) The refrigerated vent condenser vent.

d) VCD #18.

e) No. 2 reactor small pressure control valve (PV-9591).

f) The refrigerated vent condenser vent bypass.

g) The aqueous surge drum vent.

h) VCD No. 15.

i) Chloral treatment product and DH still bottom sample point vents.

j) Steam stripper phase separator vent.

12) The EDC - VCM vent header. This steel header runs from the quench tower area to where it joins the incinerator vent header on the east-west piperacks. Only equipment that must operate at low pressure is tied into this header. The high pressure vent header ties into this header just before it joins the incinerator headers.

a) At the end of the header there is a continuous nitrogen purge.

b)-e)The lean oil pumps, the low intercooler pumps, the upper intercooler pump and the absorber bottoms pumps seal oil pots all vent to this header.

f) The quench dopp kettle surge drum vent is a continuous vent to this header.

g)-i)The quench dopp overhead pump, the quench liquor pump and the product still feed pump seal oil pots all vent to the EDC-VCM vent header.

j) The lights still condenser vent is the largest continuous vent to this header.

k) The seal pot from the product still reflux pump.

l) The product still condenser vent.

m) The neutralizer drain drum vent.

n) The heavies still vent.

o) The high pressure VCM vent header is the last vent to tie-in to this header.

13) The high pressure vent header. This is a 2" steel header that runs parallel to the EDC-VCM vent header. Only sample point vents and vessel clearing drops tie into the high pressure header. Since the clearing of vessels could easily overload the incinerator, the high pressure vent header is equipped with a flow control valve (FV-5002) and an orifice meter. When clearing equipment, a specific flow can be set and control loop 5002 will prevent overloading and tripping of the incinerator shutdown system. When the incinerator collection header trips to the scrubber, the high pressure vent header flow control valve closes to prevent VCM from being discharged to the atmosphere through the atmospheric vent scrubber. The flow control valve also closes if pressure downstream of the valve gets too high.

The following lines tie-in to the high pressure vent header:

a) There is a continuous nitrogen purge on the end of the header.

b) VCD #2.

c) VCD #3.

d) The furnace pass sample point and super valve purge header.

e) VCD #30.

f) Lean oil and lower intercooler sample point vents.

g) VCD #4, VCD #5 and the upper inter-cooler sample point vent.

h) The presaturation sample point vent.

i) The absorber bottoms sample point vent and VCD #6.

j) The quench dopp overhead sample point vent, the quench liquor sample point vent and VCD #25.

k) The heavies still feed sample point vent.

l) VCD #7 and VCD #8.

m) The lights still reflux and product still feed sample point vents.

n) VCD #29.

o) The product still reflux sample point vent and VCD #9.

p) The recycle EDC sample vent and VCD #10.

q) VCD #26.

r) VCD #11.

s) VCM product to storage sample point vent.

t) EDC reactor reflux sample point vent.

u) VCD #12.

v) VCD #13, VCD #27 and the heavies still bottoms sample point.

w) The heavies still reflux sample point vent.

14) HCl from the HCl distribution header small pressure control valve (PV-3591).

15) There are two RD's in the line from Plant B just inside the battery limits and two near the incinerator. All are set for 50 psig.

16) Waste storage tank vent. This vent consists of nitrogen, organic vapors and some HCl. It is a small but continuous vent if the tank is being-used.

b. Scrubber Vent Header

The scrubber vent header begins on No. 1 OHC reactor system as a 10" header, increases to 12" near No. 2 reactor and then crosses the plant on the east-west piperack on the way to the atmospheric vent scrubber. The scrubber header is shown beginning on 56A-10030 and 56A-10041. Vents that tie into the scrubber header are:

1) No. 1 OHC reactor primary vent valve (HV-9090). This valve is used only for short periods during shut-down, start-up and during extreme pressure surges on the reactor.

2) The large system pressure control valve (PV-9490) for No. 1 OHC reactor. This valve is normally closed but opens anytime vent flow exceeds the capacity of the small pressure control valve (PV-9491). Reactor feed upsets will usually cause the valve to open and rate changes may cause it to open.

3) The large system pressure control valve (PV-9590) for No. 2 OHC reactor. This valve operates just like PV-9490 described above.

4) The primary vent valve (HV-9190) for No. 2 reactor. This valve operates like the valve described in 1).

5) The liquid phase reactor vent compressor line. Flow through this line should not occur very often. This line is used only when liquid phase vent cannot be sent to the HCl header and when the incinerator is down or overloaded. However, there is a continuous nitrogen purge on this line. (Shown on 56A-10049).

6) The HCl distribution system vent line from the large pressure control valve (PV-3590). This valve is normally closed, but will open during start-up of VCM cracking furnaces and shutdown of OHC reactors. PV-3590 will open anytime there is a large excess of HCl being fed to the HCl distribution system.

7) The incinerator trip line (from HV-5000). This valve will open anytime the incinerator to which VCM vents are being sent (can be #1, #2, or #3 as well as #4) trips.

8) There is a rupture disc on the header just before the vent scrubber which will relieve at 14 PSIG.

Normal operation for the incinerator vent header is as follows. Vents from low temperature storage, VCM shift bullets, OHC, VCM-EDC and the other vents flow into the incinerator header and through FV-4003 into the incinerator. The valve to Plant B (FV-6016) and the valve to the scrubber header (HV-5000) are closed. The normal response to an incinerator trip for this case is for the incinerator shutdown valve (FV-4003), the high pressure vent header valve (FV-5002), the shift bullet vent shutdown valve (PDV-7427) and the low temperature vent valve (XV-6806) to close. HV-5000 will open to allow vents to go to the atmospheric vent scrubber.

The purpose in having the high pressure vent header flow control valve (FV-5002), the shift bullet vent shutdown valve (PDV-7427) and the low temperature storage isolation valve (XV-6806) close when the incinerator shuts down is to prevent VCM from being vented to the atmosphere through the atmospheric vent scrubber. These vents are considered to be discretionary and can be blocked for some period of time without causing problems.

A variation of the normal operation mode is when <u>all</u> vents from inside the battery limits area (shift and day tank storage, OHC, EDC and VCM) are being burned in incinerator No. 4 and vents from low temperature storage are being burned in one of the B-1 incinerators by blocking the low temperature storage vent to B-1 incinerator block 'valve. Closing the valve operates a position switch which separates the automatic closing of XV-6806 from incinerator No. 4 shutdowns and connects it to the shutdown system of the incinerator in B-1 in which low temperature storage vents are being burned. A switch (VCM-II vent switch) in the B-1 incinerator panel board must be set to the incinerator in which low temperature vents are being burned for this shutdown feature to work properly. When the low temperature vent to B-1 incinerator block valve is closed, XV-6806 does not close if No. 4 incinerator shuts down.

A second variation of the normal operating method is for all VCM-II vents to be burned in No. 4 incinerator along with VCM-I vents. This is the only case when the VCM-I vent jumper valve is to be open. No. 1, No. 2, and No. 3 incinerator block valves are to be closed. FV-6016, the low temperature to B-1 incinerator block valve, XV-6806, FV-5002, and HV-4015 are all open. HV-5000 is closed. The VCM-I vent switch on the B-1 control board must be in the No. 4 incinerator position. If No. 4 incinerator shuts down, then HV-5000 opens, FV-4003, the discretionary vents in VCM-II and FV-6016 all close. Valves also operate in VCM-I to divert their vent to a scrubber.

When the vent header is being operated as described in the normal operating case or either of the two variations, the operating mode selection switch (HS-4915) on OIP-4A must be in the "INC 4" position for the shutdown system to work correctly.

A second mode of operation is for most VCM-II vents to be burned in No. 4, but some excess vent be sent to one of the Plant B-1 incinerators. When vents are burning, FV-4003, FV-5002, PDV-7427 and XV-6806 are all open. HV-5000 is closed. The low temperature to B-1 block valve must be open and FV-6016 is open and set to control a certain flow of vents to one of the B-1 incinerators. The vent header operating mode selection switch must be set in the "Both" position. The VCM-II vent switch in B-1 must be set to indicate which incinerator is burning the excess vent from VCM-II. If No. 4 incinerator shuts down, then FV-4003, all the discretionary vents (FV-5002, PDV-7427 and XV-6806) and FV-6016 close. HV-5000 opens and vents the incinerator header to the atmospheric vent scrubber. If the B-1 incinerator shuts down, FV-6016 closes and the discretionary vent valves close (FV-5002, PDV-7427, and XV-6806). The No. 4 incinerator continues to operate on OHC and VCM-EDC vent header vents.

A third mode of operation is for No. 4 incinerator to be down and for all vents to be burned in one of the B-1 incinerators. For this method of operation, FV-4003 is closed, HV-5000 is closed and FV-5002, PDV-7427, XV-6806, FV-6016 and the low temperature to B-1 incinerator block valve are all open. The shutdown system is operated by shutdown of the B-1 incinerator in which vents are being burned. The VCM-II vent switch in the B-1 control panel must be set to the incinerator in which VCM-II vents are being burned. When that incinerator shuts down all the automatic valves go closed (FV-6016, XV-6806, PDV-7427, FV-5002) except HV-5000. It opens the vent header to the atmospheric vent scrubber. The vent header operating mode selection switch (HS-4915) must be set in the "INC B" position.

In addition to the incinerator trips, high pressure (PSH-5400) and a manual trip (HS-4910) will also trip the incinerator vent header shutdown system.

Care should be taken during start-up of the header to purge out all oxygen before introduction of any flammable vents. Also during shutdowns in which sections of the header are to be isolated by blinding, all continuous nitrogen purges should be turned off.

The incinerator vent header/incinerator flame management system is a two-part system. It is composed of the vendor supplied #4 incinerator flame management and shutdown system, and the vent header management system. The vendor supplied incinerator shutdown system is a hard-wired system typical of incinerator shutdown systems in Plant B-1. It is located inside the control enclosure in front of No. 4 incinerator. The incinerator shutdown system provides for the standard burner start-up and shutdown safety as well as for shutdown of the vent header if conditions for burning are not satisfied. The incinerator shutdown system is discussed further in the section on the incinerator (H-3) and in the Safety Control System Manual.

The incinerator vent header safety/shutdown management system is programmed into PLC-1. The vent header shutdown system diverts continuous vents to the proper scrubber and blocks off intermittent vents that might release VCM to the atmosphere when tripped. The shutdown system prevents operation of the header in an undesirable or unsafe manner even though vents may be sent to any of the four

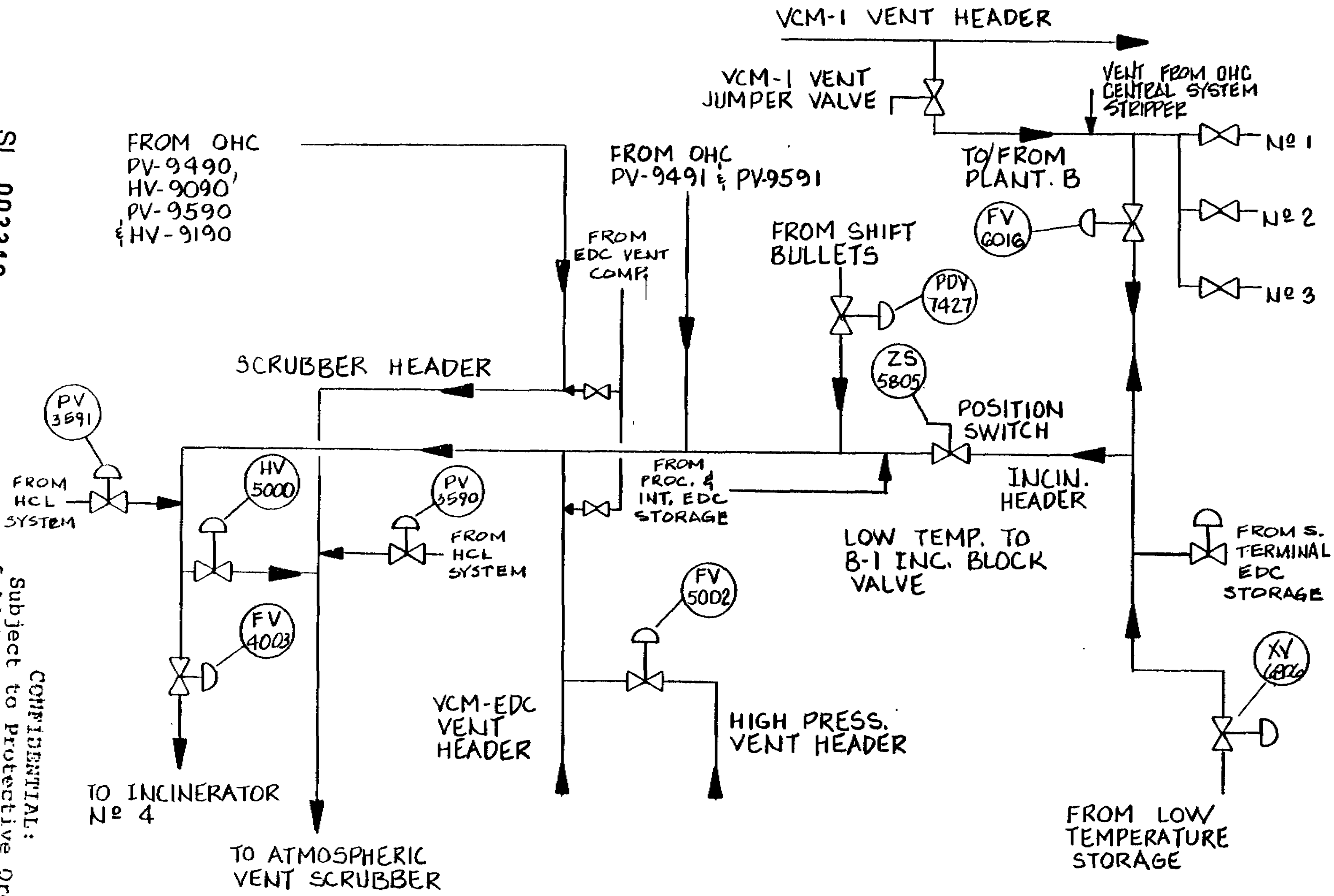


FIG. VII-19

VCM II PLANT VENT COLLECTION SYSTEM

incinerators in Plant B. The vent header safety/shutdown system assures that valves in the header are lined up as the mode switch indicates and the shutdown system also allows changing from one mode to another while in operation. See the writeup in the Safety Control System Manual.

2. Liquid Feed System

The purpose of the incinerator liquid waste feed system is as follows:

a. To collect chlorinated organic liquid waste from the VC quench dopp kettles and the lights still overhead purge.

b. To store these liquid wastes in the waste storage drum.

c. To pump the liquid waste to the incinerator.

The waste materials must be collected so that they can be disposed of by incineration. The incineration of liquid waste is described in the incinerator write-up which follows in this manual. The purpose of this section is to describe the equipment and system operation related to liquid waste collection and feeding of it to the incinerator.

The liquid waste feed system consists of the waste storage drum, the incinerator feed strainers, and the incinerator feed pumps.

The lights still overhead purge can be transferred to the waste storage drum continuously through a two-inch pipeline. Bottoms from the vinyl quench dopp kettles can be transferred to the waste storage drum batchwise in the tar trailer. Nitrogen pressure is used to pad bottoms from the tar trailer into the waste storage drum.

EDC dopp bottoms are sent to the waste treatment unit for disposal. The lights still overhead purge normally goes to the bottoms plant so usable chloride can be recovered. Vinyl quench bottoms will be sent to the B-1 waste storage tank when they can handle it. If B-1 cannot burn the vinyl quench bottoms, then it will have to be put in the waste storage drum for No. 4 incinerator.

Vinyl quench bottoms can be so thick that it has to be mixed with lights still overhead before it can be pumped to the incinerator for burning. Mixing should be done by first putting a level of lights still overhead into the tank and then unloading the tar trailer. As additional trailers are unloaded, lights still overheads should be added to control the consistency of the waste. Burning will be intermittent since there will not be enough vinyl quench bottoms to burn continuously.

Bottoms that have not been processed with ferric chloride as a catalyst (vinyl quench dopp bottoms) have been known to decompose and solidify when mixed with wastes that have been processed with and contain ferric chloride (EDC dopp kettle bottoms). For this reason EDC dopp kettle bottoms cannot be stored in the VCM-II waste storage drum. They must be hauled to the waste treatment area in B-1. The use of the VC quench dopp kettle tar trailer and the EDC reactor bottoms dopp tar trailer cannot be interchanged or substituted unless the rear manway is removed and the trailer washed out and dried.

Due to the concern about decomposition, a thermocouple was installed in the waste storage drum to detect the temperature rise and sound an alarm if a reaction occurs. If decomposition gets started, water has been proven to be an effective stablilizer for bottoms because it deactivates the iron. Water should be added directly into the tank. Caution must be exercised against putting water into the tank if the temperature goes above the boiling point of water as steam may be evolved rapidly, causing high pressure.

There are two large rupture discs rated at 29 psig on the tank for venting in case a large decomposition does occur. There is also a small rupture disc with an SRV set at a lower pressure (24 psig) than the two large discs to prevent blowing the large discs unnecessarily.

When the VC tar trailer is dumped into the waste storage drum, there may be some flashing. Also nitrogen may be blown into the tank through the tar trailer during unloading. These gases along with the nitrogen purge on the level transmitter are vented from the top of the tank to the incinerator header.

There is a continuous nitrogen purge to the level transmitter. Its purpose is to keep liquid waste from backing up to the level transmitter diaphragm. Solids buildup may plug the nozzle and interfere with operation of the diaphragm, giving incorrect level indication. The continuous purge also purges air from the tank vapor space that may accidentally be introduced from unloading tar trailers and reduces the possibility of forming a flammable mixture. A third benefit from the purge is that it helps keep moisture from backing up through the vent piping from the incinerator header into the steel waste storage drum.

Liquid waste flows from the bottom of the tank through one of the two screens into an incinerator feed pump. A scraper is provided on each screen to prevent plugging. It must be used frequently. Occasionally solids will have to be cleaned from the lower part of the screen. The frequency will depend on the feed rate to the incinerator and the amount of solids in the waste storage tank.

When liquid waste burning is shut down for a shift or more, the liquid waste line should be cleared into the incinerator or the waste storage drum, with nitrogen to prevent plugging of the line.

The waste storage drum and associated equipment are shown on P & ID 56A-10081.

3. Incinerator System

The purpose of the incinerator system is to burn hydrocarbons and chlorinated hydrocarbons so they can ultimately be discharged to the atmosphere. Hydrocarbons are burned to carbon dioxide and water vapor similar to the following reaction.

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

Chlorinated hydrocarbons are burned to carbon dioxide, water vapor and hydrogen chloride similar to the following reaction.

$$C_2Cl_2H_4 + 2\tfrac{1}{2}\ O_2 \longrightarrow 2\ CO_2 + H_2O + 2\ HCl$$

The burning is carried out in the primary and secondary combustion chambers of the incinerator. Waste materials and fuel gas begin mixing with air as the air and fuel leave the windbox and enter the primary combustion chamber. Natural gas is injected with wastes to provide a stable flame and to maintain the combustion chamber temperature. Combustion gases exit the incinerator and enter the primary scrubber where HCl is removed and the gases are cooled. The gases exit the primary scrubber and enter the secondary scrubber for trace chlorine and HCl removal.

The proper operation of the incinerator and complete combustion of waste materials is necessary for the operation of the VCM-II unit. If the incinerator is inoperable then other means of incineration such as the Plant B-I incinerators must be used or the plant must be shut down in accordance with the VCM Emission Control Plan.

The description of the incinerator system is divided into the following sections:

a. Liquid Burning System
b. Natural Gas System

c. Waste Gas System

d. Combustion Air

e. Combustion Process

f. Combustion Control

g. Safety Control System

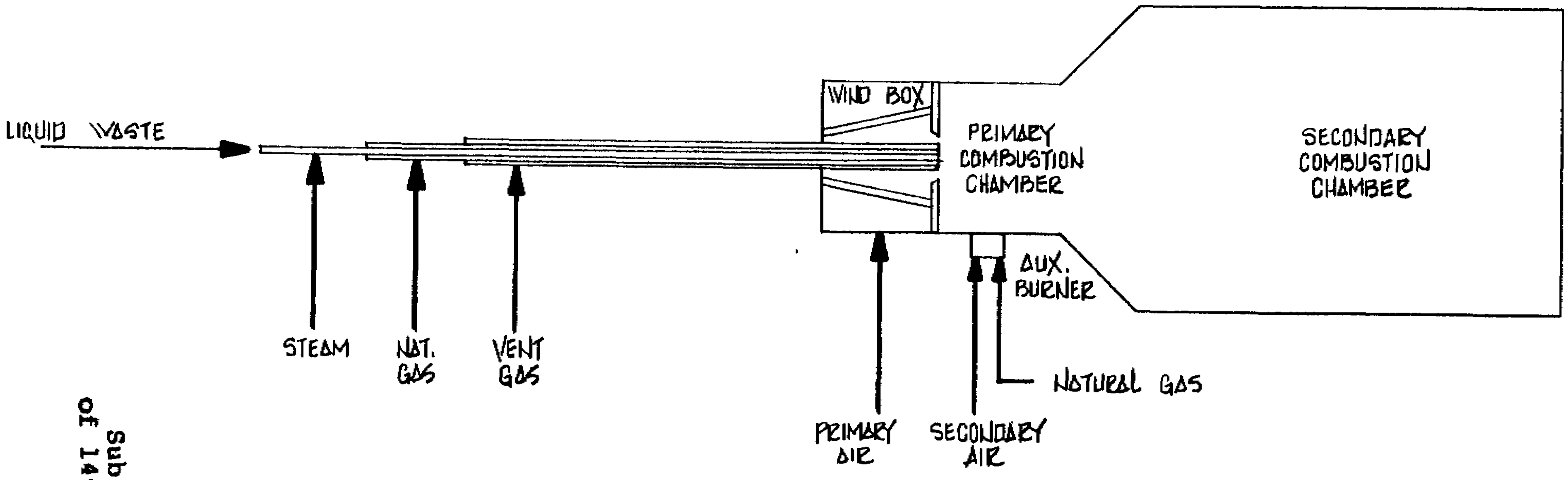
In addition, the sections on the primary scrubber and the secondary scrubber that follow also describe the operation of the incinerator system since they are very closely related to the incinerator operation.

The incinerator system consists of the liquid waste injector, the LV-48 vent gas and natural gas burner, the auxiliary burner, the windbox, the primary combustion chamber and the secondary combustion chamber. Auxiliary equipment like the combustion air blower and air controls, the flame arrestor and waste gas controls, the natural gas control valves and instrumentation, steam lines, the shutdown system and burner temperature controllers are all included in the system. The incinerator system is shown on P & ID's 56A-10082 and 56A-10083.

a. Liquid Burning System

Normal flow for liquid waste is from the incinerator feed pumps through the feed line and the shutdown valve (BV-4802) and through the center tube of the liquid waste injector.

Liquid waste must be atomized into small droplets if the burning process is to be complete. Each drop must be heated to the boiling point, and then boiled to dryness. Then the carbon and other residue must be



INCINERATOR No 4

FIG. VII-20

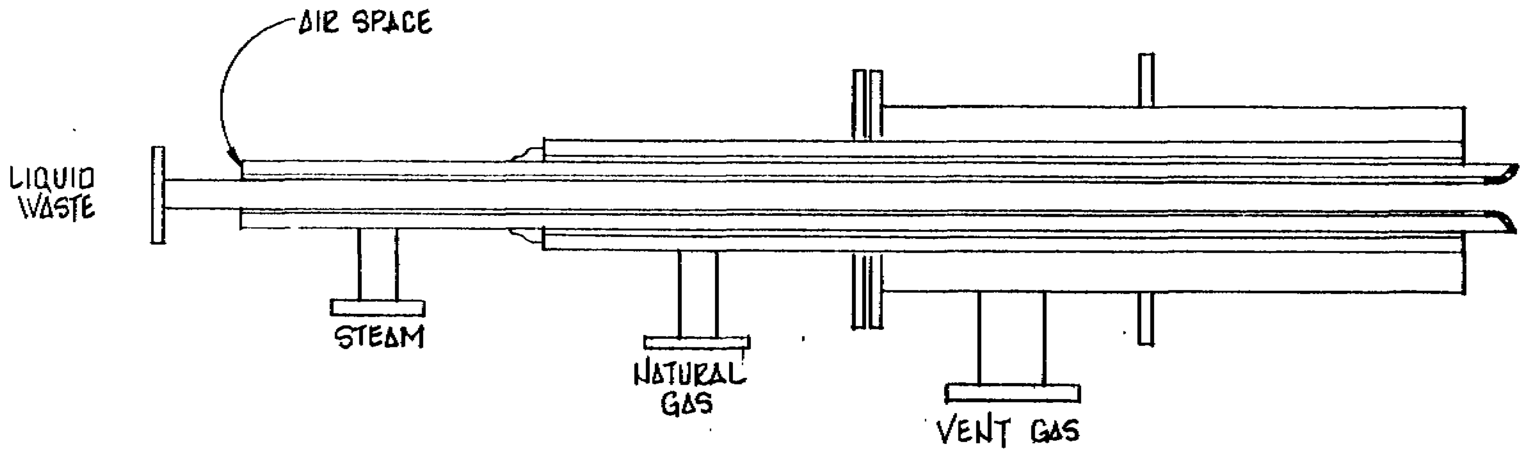
heated to its ignition point. After ignition, each particle must have time to burn. These processes occur much faster for a small droplet than for a large one. Complete combustion of liquid waste depends upon good atomization.

This atomization is achieved with steam supplied from the 175 psig header. It flows through a flow transmitter past a low pressure shutdown switch and into the waste liquid injector. Steam flows through an annular space in the injector to the atomizing tip (see the drawing). Atomizing steam is hot enough to boil lights out of the liquid waste and it is also hot enough to decompose heavies in the waste. Both of these actions cause plugging in the injector. Therefore, there is a hollow annular space between the liquid waste and atomizing steam in the injector to protect liquid waste from the high temperature of the atomizing steam.

The operation of the steam trap upstream of the orifice plate is also important to liquid waste atomization. Droplets of condensate in the steam erode the atomizing tip quickly to the point that good atomization cannot be achieved. Therefore, the trap must be maintained and insulation on the steam line must be kept in good condition.

b. Natural Gas System

Natural gas flows to the incinerator through a pressure regulator, past a low pressure shutdown, through an orifice plate, through a double block and bleed valve arrangement, past a high pressure shutdown switch, through a flow limiting orifice, through a



BURNER ASSEMBLY

FIG. VII-21

temperature control valve and into the burner assembly. Natural gas flows through an annular space in the burner tip. After leaving the burner tip it is in contact with and begins mixing with combustion air. Both air and gas flow through the orifice at the inlet to the primary combustion chamber and combustion begins.

Natural gas for the auxiliary burner comes off the main natural gas line between the two double block valves (BV-4804 and BV-4805). Auxiliary burner gas flows through a flow meter, a block valve (part of a double block and bleed for the auxiliary burner), a temperature control valve and into the auxiliary burner. The auxiliary gas temperature control valve is mechanically linked to the combustion air temperature control valve (TV-4604).

The auxiliary burner and TV-4604 and 4602 are used to control the combustion chamber temperature during curing and heat up-cool down cycles. The auxiliary burner also assures a stable and steady flame for the Fireye flame scanner during upsets in fuel flows to the main burner.

Ignition pilot gas is taken upstream of the double block and bleed arrangement so the ignition pilot can be lit without opening either of the double block valves. This insures that gas cannot leak into the combustion chamber through either burner before the ignition pilot is lit.

c. Waste Gas System

Waste gas flows from the incinerator header, through the orifice plate, through the double block and bleed valve-flow control valve arrangement, through the flame arrestor and into the burner assembly. Like natural gas, waste gas begins mixing with combustion air as it leaves the burner assembly and burning begins after the air and gas go through the orifice at the inlet to the primary combustion chamber.

d. Combustion Air

Combustion air is supplied by the combustion air blower. Air enters the blower through a silencer, flows past a low pressure shutdown switch, past an annular flow element, through the flow control valve and into the windbox. There is a set of vanes inside the windbox that gives a strong rotational motion to air and fuel gases. The rotational motion or vortex continues through the primary and secondary combustion chambers into the primary scrubber. Combustion air also goes to the auxiliary burner, the ignition pilot and to purges on the sight ports, Fireyes and the radiomatic pyrometer.

e. Combustion Process

The flame and the combustion reactions begin after fuel gases and air pass through the orifice of the primary combustion chamber. The flame ends a few feet downstream of the primary combustion chamber. But combustion reactions continue toward completion as long as the combustion gases are in the secondary combustion chamber. The degree of completion that is ultimately reached is determined by three variables: 1) the temperature, 2) turbulence inside the combustion chamber and 3) residence time inside the combustion chamber.

Residence time is determined by the feed rate to the incinerator, therefore, the operator has little control over residence time. Turbulence is determined by pressure drop across the combustion air vanes. This pressure drop is related to combustion air flow which is also a function of feed rates. Temperature can be controlled by the operator and should be kept as close to 2600°F as possible. The high temperature will destroy more of the chlorinated hydrocarbons and form less chlorine than burning at lower temperatures.

Excess oxygen is necessary to insure complete combustion of the organic compounds. Ten to twenty percent excess air is required for complete combustion. This excess will give two to four percent oxygen in the stack. If there is not enough oxygen the stack gases will become discolored and even turn black if the oxygen shortage is severe. An undesirable reaction that occurs during combustion is the reaction of hydrogen chloride and oxygen to form water and chlorine.

$$2\ HCl + \tfrac{1}{2}\ O_2 \longrightarrow Cl_2 + H_2O$$

The presence of excess oxygen promotes this undesirable reaction, but a high combustion chamber temperature, steam and auxiliary fuel all retard the reaction to form chlorine. Chlorine is difficult to scrub from the combustion gases and cannot be discharged to the atmosphere in significant quantities. Too much oxygen or combustion air will cause excessive chlorine formation and will cause excessive natural gas consumption.

f. Combustion Control

Combustion in the incinerator is controlled in the following manner. Natural gas is temperature controlled to the combustion chamber. If combustion chamber temperature decreases, then the natural gas TCV will start opening and send more gas to the combustion chamber. This control system works well as long as there is some excess air being fed, but it does exactly opposite of what is needed if there is a shortage of air. If there is a shortage of air and natural gas flow is increased, the combustion chamber temperature will drop causing even more natural gas flow. This condition can be recognized by the oxygen analyzer indicating low oxygen in the stack, by the stack being discolored or black and by combustion chamber temperature responding abnormally to natural gas or combustion air flow changes.

If combustion chamber temperature is above 2400°F and oxygen in the stack is 1% or greater, combustion air flow should be adjusted until there is little or no natural gas flow so that it is conserved. Natural gas is a major cost of operating the incinerator and should be minimized when possible.

When burning vents with a lot of inerts, there may be a problem maintaining combustion chamber temperature and maintaining enough excess oxygen. Controlling combustion chamber temperature at the minimum (2400°F) will help maintain the oxygen excess and reduce natural gas usage under this condition. If oxygen in the stack is still low, the addition of combustion air until the natural gas valve is near wide open will help the excess air problem.

Special consideration and procedures necessary for incinerator start-up will be explained in the section on the Primary Scrubber System since both are closely related and both started up at the same time.

g. Safety Control System

Shutdown features are provided to protect equipment and personnel if process conditions get too far out of control. All fuels (liquid waste, natural gas and vent gas) to the combustion chamber are blocked off when the shutdown system is tripped. Neither combustion air nor atomizing steam are affected. There can be either liquid waste or vent gas shutdowns in addition to a total incinerator shutdown. Shutdown features are listed and discussed below.

1) Flame failure
2) High Combustion Chamber Temperature
3) Low Combustion Air Pressure
4) Low Natural Gas Pressure
5) High Natural Gas Pressure
6) Low Combustion Chamber Temperature
7) Low Atomizing Steam Pressure
8) Low Vent Gas Flow

The flame failure feature shuts the incinerator down. The purpose of this feature is to block all fuel if the flame goes out. This prevents an accumulation of fuel inside the combustion chamber and an explosion if the fuel ignites from hot refractory.

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The high combustion chamber temperature feature shuts down the incinerator. This shutdown prevents overheating and the resulting damage to the refractory and brick inside the combustion chamber.

The low combustion air pressure shuts down the incinerator. It is intended to stop fuel flow to the combustion chamber anytime air flow is lost. The primary combustion air flow control valve (FV-4005) has a stop that prevents it from going completely closed. Therefore, it is not possible to stop combustion air flow by closing the flow control valve.

High or low natural gas pressure shuts the incinerator down. Both of these shutdowns are required by PPG's insurance carrier. The high pressure switch prevents feeding too much gas to the burner and the combustion chamber. The low pressure switch is designed to shut the incinerator down anytime the natural gas supply pressure gets too low to sustain a flame in the incinerator.

Low combustion chamber temperature will shut down liquid waste and vent gas burning only. The purpose of this shutdown is to prevent chlorinated hydrocarbon emissions when the combustion temperature gets too low for complete burning.

Low atomizing steam pressure shuts down liquid waste burning only. This shutdown feature is designed to prevent incomplete combustion of liquid waste due to poor atomization.

Low vent gas flow will shut down vent gas burning only. The purpose of this shutdown feature is to prevent operation with an unstable flame. It will also prevent air and fuel from flowing from the burner tip backward through vent gas piping if there is a malfunction and low pressure in the vent gas header.

A detailed description of the Incinerator Safety Control System is provided in the Safety Control System Manual. It should be referred to for more information.

Specific procedures for start-up and shutdown of the incinerator are provided in the S.O.P. Manual.

4. Primary Scrubber System

The purpose of the primary scrubber is to cool and scrub HCl from the incinerator combustion gases.

The HCl from the combustion of chlorinated hydrocarbons must be removed before the combustion gases can be emitted to the atmosphere. This is accomplished by passing the gases through the primary scrubber which has a packed contacting section using ceramic saddles.

The gases must be cooled to prevent damage to the scrubber and other downstream equipment. The cooling takes place in the quench section which is the area of the scrubber below the packed section. The gases enter the quench section from the incinerator secondary combustion chamber and pass up through the scrubber packed section and exit.

The primary scrubber, the primary scrubber effluent pumps and piping, and the Sabine River water piping are all part of the primary scrubber system. The Primary Scrubber System is shown on 56A-10083.

Sabine River water is used to scrub HCl from combustion gases. Sabine water is flow controlled to the top of the scrubber. Water flow is adjusted depending upon the scrubber gas exit temperature.

Combustion gases enter the bottom of the scrubber at about 2600°F and contact Sabine water as it comes out the bottom of the packed section into the quench chamber. Combustion gases are cooled to about 200°F in the quench chamber.

Combustion gases pass up through the packed section and HCl is scrubbed. Combustion gases exit the top of the primary scrubber containing traces of HCl and almost all the chlorine that was formed in the combustion chamber.

The Sabine water-HCl solution is pumped from the primary scrubber by the primary scrubber effluent pumps, through the primary scrubber level control valve to the waste treatment area in Plant B-I. It is very important to keep the level in the control range in the scrubber so that water never gets into the combustion chamber. If water contacts the hot refractory in the combustion chamber it not only damages the refractory, but the water can vaporize with explosive force and rupture the combustion chamber. An emergency overflow to a seal pot is provided to prevent a dangerously high level in the scrubber.

It is very important that Sabine water flow be maintained to the scrubber anytime the combustion chamber is above 200°F or anytime the burners are being fired. The scrubber is lined with pyroflex (an asphalt-like compound which begins melting at about 200°F. The scrubber packing support is made of graphite bars. The top of the scrubber has rubber and polyester coatings limited to operating temperatures of 200°F. All of these materials will overheat very quickly if Sabine water flow is lost. For this reason, fire water is tied in downstream of the Sabine water flow control valve (FV-4007) for use if Sabine water is lost. The fire water flow is insufficient to allow operation of the incinerator. It is to be used only in an emergency to prevent damage to the primary scrubber.

The feeding of basic or high pH Sabine water to the primary scrubber should be avoided. High pH will dissolve chlorine as combustion gases leave the top of the primary scrubber. Once dissolved, chlorine forms hypochlorite. As the scrubbing water dissolves hydrogen chloride further down in the packed column, hypochlorite reacts again to form chlorates. Both hypochlorite and chlorate will oxidize and destroy the Furan and polyester brick mortar and the other plastic parts in the primary scrubber. If brick mortar is destroyed, the pyroflex lining between the brick and the steel shell of the scrubber starts oozing out leaving the steel shell susceptible to HCl corrosion.

a. Start-up

Start-up of the incinerator scrubber system is discussed below:

1) Start the combustion air blower first. This is done first to purge any flammables from the combustion chamber and to prevent any combustibles from collecting there. It is also done before putting water on the primary scrubber so the air flow into the scrubber will prevent water from splashing back into the combustion chamber.

2) Start Sabine water to the primary and secondary scrubbers. Start the primary scrubber effluent pump and the secondary scrubber circulation pump. Put level control valves on both scrubbers in service.

3) Establish natural gas pressure up to the natural gas double block and bleed valves (BV-4803, 04 & 05).

4) Make an explosion meter check on the combustion chamber.

5) Put natural gas valve (TV-4601) in wide open position. Natural gas flow is sized to provide only enough fuel to fire the incinerator at minimum rate when the valve is wide open.

6) Put the combustion air valve (FV-4005) in the closed position. The stop that prevents closing the valve is adjusted to provide the correct amount of air for the natural gas flow. About 10 SCFH of air is needed for each 1 SCFH of natural gas.

7) Light the pilot and the auxiliary burner. When 1500°F is reached, light the main (LV-48) burner.

8) Adjust auxiliary air flow (RV-4604) and primary air flow (FV-4005) to heat the combustion chamber up at a rate of 100°F per hour until 800°F is reached. The heat-up rate can be increased to 175°F/hr. once 800°F is reached.

9) Put steam on the liquid waste atomizer at 1000°F to cool the atomizing tip.

10) At 1500°F light the main burner and adjust natural gas and primary air to heat the combustion chamber at a rate of 250°F/hr.

11) The heat-up rates given above are to be used only when heating up a dry combustion chamber which has already had the refractory cured. Specific curing instructions will be given anytime maintenance is done inside the combustion chamber.

12) When the combustion chamber reaches 2500°F, liquid waste or vent gas can be burned. But the following preparations must be made.

13) Put cell liquor on the secondary scrubber.

14) Purge all oxygen from the vent header and the flame arrestor before burning vent gases. Start vent gas burning slow and make air adjustments to prevent an oxygen shortage in the combustion chamber and a black stack when introducing vents.

15) Increase atomizing steam pressure, start the liquid waste pump prior to starting liquid waste burning. Adjust air and start liquid waste burning slowly to prevent a black stack.

b. Safety Control System

Shutdown features associated with operation of the primary scrubber are listed and discussed below. Activation of any of these features will shut down the incinerator.

1) Low Sabine Water Flow
2) Low Sabine Water Pressure
3) High Packed Bed Temperature
4) High Vent Temperature

The purpose of both low Sabine water flow and pressure is to prevent overheating of the scrubber internals and vent piping due to loss of water flow.

Scrubbers have overheated when water distributors and the packing failed, even though adequate water flow was maintained on the scrubber. The high bed temperature shutdown and the high scrubber vent temperature are intended to prevent overheating in this instance.

5. Secondary Scrubber System

The purpose of the secondary scrubber system is to remove traces of HCl and to remove the chlorine formed during combustion.

HCl and chlorine that are discharged to the atmosphere cause a fog or haze. This haze smells and irritates the eyes slightly. There are also government regulations which require that HCl and chlorine emissions be held within permit values.

Chlorine and HCl are removed by scrubbing with a solution containing sodium carbonate, sodium bicarbonate, sodium chloride and sodium hypochlorite.

Combustion gases flow into the scrubber below a packed scrubbing section. Gases flow up through the packing, past the liquid distributors, through a mist eliminator and to the atmosphere through the stack.

The secondary scrubber system consists of the scrubber, the secondary scrubber circulation pumps, circulation and effluent piping, Sabine water piping, cell liquor piping and the vent stack. The Secondary Scrubber is shown on 56A-10088.

The scrubber is constructed of a glass-reinforced vinyl ester resin to resist oxidation by the hypochlorite. The packing support and some of the liquid distributor parts are made from titanium. The mist eliminator is kynar mesh with titanium supports and frame. Packing is 1" CPVC intalox saddles.

The scrubbing solution circulates from the reservoir in the bottom of the scrubber to the circulation pump, through an orifice and back into the liquid distribution system in the top of the tower.

Cell liquor and Sabine water are added continuously to the reservoir in the bottom of the scrubber. Sodium hydroxide in the cell liquor reacts immediately with sodium bicarbonate in the bottom of the tower to form sodium carbonate. As the sodium carbonate solution contacts combustion gases, it reacts with HCl, chlorine and carbon dioxide to form salt, sodium hypochlorite and sodium bicarbonate. Water is added to the solution to dilute the salt and hypochlorite.

Water and cell liquor flows are adjusted to maintain a constant pH and hypochlorite concentration. pH is determined by lab samples and a continuous pH meter located in the circulation line. Hypochlorite concentration is determined by the main lab.

Sabine water contains some calcium, magnesium and iron as water hardness. This hardness precipitates when the water becomes basic and when it comes in contact with carbonates. The hardness will coat the inside of pipes and orifices and restrict the flow of the scrubbing solution. The scrubber may have to be acid-washed to remove the hardness from piping and packing periodically.

The oxygen analyzer for the incinerator system is located in the secondary scrubber stack.

The level in the bottom of the scrubber is controlled by purging a stream from the circulation line through a level control valve and to the sodium formate destruction effluent line from Plant B-I. If the level gets high in the secondary scrubber, there is an emergency overflow to the sewer. The scrubber should not be allowed to overflow routinely since this effluent is very corrosive to the sewers if use is continuous. Also chlorine is released to the atmosphere when this effluent becomes acidic.

6. Atmospheric Vent Scrubber System

The purpose of the atmospheric vent scrubber is to remove HCl from vent streams before these vents are discharged to the atmosphere. The atmospheric vent scrubber is used only during start-up, shutdowns or operational upsets.

The scrubber has a packed section using polypropylene intalox saddles. The vent gases enter below this packed section and pass up through it. Sabine water enters the top of the scrubber and flows down through the packed section contacting the vent gases counter currently and thereby scrubbing the HCl.

The scrubber is constructed of glass reinforced Furan resin. The packing support and water distributors are made of chemical porcelain. The mist eliminator is polypropylene.

This system consists of the scrubber, Sabine water piping, three scrubber effluent pumps and the piping associated with the scrubber effluent pumps. The Atmospheric Scrubber is shown on 56A-10087.

Normally the scrubber will be sitting ready to take vents on an emergency basis. There must be enough scrubbing water flowing to wet the packing (about 350 GPM) in order for the scrubber to be ready to take HCl. Since the vents fed to the scrubber will contain organics, the scrubber effluent will also contain organics. This water has to be treated in the Waste Treatment Unit (WTU) steam strippers. Since the scrubber effluent must be stripped, it would not be practical to feed 350 GPM of fresh Sabine River water through the scrubber on a continuous basis. Therefore, scrubbing water is circulated until vent streams are fed to the scrubber.

When on recycle, scrubber water flows from the bottom of the scrubber through one of the scrubber effluent pumps, through a flow meter (FE-5020), through the scrubber recycle control valve (FV-5020) and into the top of the scrubber through the Sabine water line.

Vent gases that will go to the scrubber are listed and discussed below.

a. No. 1 and No. 2 OHC Reactor Primary vent valves (HIC-9090 and 9190). These valves are normally open only during reactor start-ups and reactor shutdowns. Extreme pressure surges on a reactor may cause these valves to open but surges of this magnitude should be rare. Maximum load for the scrubber will occur from these valves when both OHC reactors are running at full rates and both shutdown systems trip.

b. No. 1 and No. 2 OHC Reactor large pressure control valves (PV-9490 and 9590). These valves open during rate changes and pressure surges on the reactors. But this vent should not contain a significant amount of HCl except during an OHC reactor shutdown system trip.

c. The liquid phase EDC reactor vent. This vent should go to the atmospheric vent scrubber only when the vent compressor is shut down and the incinerator is down at the same time. The EDC reactor vent does not contain much HCl.

d. The large HCl distribution system back pressure control valve (PV-3590). This source has the potential to fully load the scrubber with HCl. Vent from this valve is usually pure HCl. This valve will open anytime there are moderate pressure surges in the HCl distribution system and allow small amounts of HCl to go to the scrubber. The large flows from this source will come when VCM and both OHC reactors are running at high rates and both OHC reactors trip off. Rate reductions on the cracking furnaces will reduce the load on the scrubber.

Vent gas flows into the bottom of the scrubber up through the packing and mist eliminator, and through the stack to the atmosphere. As vent gas flows through the packing, HCl is absorbed into the scrubbing water and the water temperature begins to rise. This temperature rise is monitored by a thermocouple (TE-5615) in the bottom of the scrubber packed section. Temperature controller 5615 sends a signal to a signal selector (FY-5015). If there is no other or no larger signal being sent to the selector, then the signal from the TIC-5615 is sent to the Sabine water flow controller (FIC-5015) and water is added to control the scrubber temperature. If the recycle flow control valve FV-5020 is set on remote and automatic, the computer will reduce recycle flow by the amount of Sabine water flowing through FE-5015. If there is more than 350 GPM of Sabine water on the scrubber, then the recycle valve is completely closed.

While the scrubber is on recirculation, only one scrubber effluent pump will be running. One pump can handle about 850 GPM. Any of the three pumps can be started from OIP-4A. If Sabine water flow gets high enough to cause high level in the scrubber with only one pump running, then level switch LSH-5212 will start all three pumps. If the level continues to rise, an alarm sounds and eventually the scrubber will drain through the emergency overflow to the pigments ditch. When water flow to the scrubber is reduced, the pumps have to be shut down manually.

When the vent header management or either of the OHC reactor shut-down systems trip, a large amount of HCl can be put to the scrubber very quickly. The temperature-scrubbing water control arrangement will not respond fast enough to prevent a large HCl release to the atmosphere through the scrubber stack when a trip occurs. A manual loading station (HIC-5016) is provided to handle this situation. The MLS is set to provide 1500 GPM (the maximum required for two OHC reactor trips) of Sabine water. A set of contacts controlled by PLC-I prevents the MLS signal from getting into the Sabine water flow control loop until an incinerator or OHC reactor trips. When a trip does occur, the contacts make and the MLS signal is sent to the signal selector for the Sabine water flow control valve (FY-5015). The signal from the MLS is selected because it is larger than the signal from TIC-5615 and water is put on the scrubber. It is very important to keep FIC-5015 on automatic and remote so the scrubber water flow control system can work.

If all of the 1500 GPM of scrubbing water is not needed, then it should be reduced stepwise as soon as possible. All this water must be stripped in Plant B-I and extra water will unnecessarily increase the load on the waste treatment unit. As the MLS is reduced and the bottom of the scrubber heats up, the signal selector (FY-5015) will start taking the signal from TIC-5615. At this point, the Sabine water MLS reset (on OIP-4A) should be pressed. The reset opens the contacts in the signal from the MLS to the signal selector. Then the MLS should be set for 1500 GPM so it will be ready for the next shutdown.

The scrubber is a support facility for VCM-II and must be operable prior to starting up OHC, the cracking furnaces and LP-EDC.

I. PLANT EFFLUENT SYSTEM

1. Impounding Basin System

The purpose of the impounding basin system is to prevent organic discharges to the sewer each time the pad and pad drain lines are flushed with a large volume of water (from rain, the sprinkler system, etc.). It is not practical to retain and steam strip organics from all the water that falls on the pad and comes through the process pad drain piping. After this first water is caught and organics have been flushed into the impounding basin, any other water bypasses the impounding basin and overflows to the pigments ditch. Water in the impounding basin is pumped to the waste treatment surge pond in B-1 or to the pigments ditch if organic contamination is low enough.

The impounding basin holds 30,000 gallons of water. If the basin is empty (as low as the pumps will pump), then the first 30,000 gallons to fall on the process pad are caught. Additional water overflows from the inlet chamber to the pigments ditch (see flowsheet 56A-10084).

The impounding basin system consists of the inlet chamber, the basin, two impounding basin pumps and instrumentation. Water fed to the basin is collected from the trenches on the main process pad and on the furnace pad. Water from the other pads is not sent to the impounding basin.

If the impounding basin is not operated correctly, it could result in organic discharges to the sewer and violation of our NPDES permit. If the discharge was major, PPG could have to pay fines.

The normal state for the impounding basin should be for it to be sitting idle, nearly empty (as low as the pumps can pump), ready to receive water.

When a rain starts, water flows from the pad trenches through storm sewer piping to the inlet chamber of the impounding basin. As long as the level in the basin is lower than the overflow pipe in the inlet chamber, water drains into the impounding basin. When the level gets up to 4 feet, a level alarm will sound. A sample should be taken and the discharge of the pumps should be lined up to the surge pond or the pigments ditch, depending upon the organic content of the water. The discharge can also be routed into the inlet to the covered separator. As the basin continues to fill, a high level alarm sounds at 7 feet, and water from the process pad begins to overflow the inlet chamber to the pigments ditch. As the level in the impounding basin and the inlet chamber continue to rise, more water overflows to the pigments ditch.

2. Storage Area Lift Station

The purpose of the storage area lift station is to collect water from the pump pads in the storage area, the process and intermediate storage refrigeration unit and the control room laboratory sinks. The lift station pumps this water into the process sewer system. If the lift pumps or the level control system do not work, water will back up to a low point and overflow to a ditch. Eventually this water will drain to the pigments ditch.

This system includes the storage area lift station, two lift pumps and the level control system. Water is collected from the sources listed below:

a. The control room lab drains.
b. The EDC storage tank diked areas.
c. The furnace feed pump pads.
d. The EDC rework pumps (3) pads.
e. The DH feed pump pad.
f. The DH feed tank diked area.
g. The storage refrigeration unit pad.

Operation of the lift station is cyclic. Water drains into the sump and level builds up until a level switch starts one of the pumps. If the level continues to rise a second level switch starts the second pump. When the level drops below the point where the first pump was started, a third switch shuts down the pump (or both if both were running).

Water is pumped from the lift station into the process sewer. It drains through the process sewer into the covered separator. See Drawing 56A-10107 for a flowsheet of the storage area lift station.

Rainwater that collects in the dikes for the EDC storage tanks (DH bottoms tanks, and EDC tanks, furnace feed tanks and the DH feed tank dikes) can be drained to the ditch or to the storage area lift station. The dike drain valves are to be kept closed. When water collects in the dike it should be sampled to determine if there is organic contamination. If organic content is low the water is to be drained to the ditch. If organics are too high the water is to be drained to the lift station. In either case drain valves are to be closed when draining is complete.

3. Covered Separator System

The purpose of the covered separator is to collect organic contaminated water, to separate and recover any phase organics, and to send the contaminated water to the waste treatment unit in Plant B-1. See drawing 56A-10085 for a drawing and flowsheet of the covered separator system.

The covered separator is constructed of acid brick lined concrete and consists of two forebays and sandtraps, two main bays, and one pump bay. There is one organic pump and filter for the two main bays. There are two water pumps (covered Separator Pumps) in the pump bay. Water is collected from the curbed areas on the main process pad and from the storage area lift station. The curbed areas represent likely organic spill areas, i.e. process pump pads, dryers, filters, reboilers, dopp kettles, sample stations, etc. The water drains through the process sewer lines into one of the inlet bay/sandtraps in the covered separator. Some of the sand and some scum will be retained in the inlet bay. The rest will be carried into the main bay (one of two) along with the water and any phase organics. Organic-laden water from the impounding basin can also be routed into the inlet of the covered separator.

Phase organics and sand settle to the bottom of the main bay. The organic level is detected by level transmitters (LT-5270 & LT-5274). Organics are pumped from the main bay by the recovered organics pump. The suction can be lined up to either bay. Starting of this pump is manual. Organics are filtered to remove sand and then sent to the intermediate crude drum in OHC. If the recovered organics pump fails, organics must be removed from the main bay by a vacuum truck. Connections are provided on the pump suction lines. Operation with high level in either of the two main bays will cause organics to get into the pump bay and be pumped to the waste treatment unit surge pond.

Floating scum is removed from the inlet bay and the main bay by a vacuum truck. When sand builds up enough to interfere with the separation of water and organics, the process sewer must be lined up to the other inlet bay and main bay. Water and organics are sucked out of the used bay by vacuum truck or the organics pump (to the process sewer) and the sand is removed manually.

Water overflows the weir from one of the main bays into the pump bay. The level is detected by LT-5260 and as the level builds up, LSH-5262 starts one of the covered separator pumps. If the level continues to rise, LSH-5264 starts the second pump. When the level gets low, LSL-5261 and LSL-5263 shut the pumps down. If something happens to the pump(s), or if there is too much water for them to handle, the pump bay has an emergency overflow to the pigments ditch. Overflow to the pigments ditch may result in violation of our chlorinated organic effluent permits.

Water pumped from the covered separator goes through a flow meter (FE-5090) and to the surge pond in the Plant B-1 waste treatment unit. Water from the impounding basin and the atmospheric vent scrubber pumps both tie in to the covered separator water line to Plant B-1.

4. Sanitary Sewer System

The purpose of the sanitary sewer system is to collect and pump sewage to the Plant "C" sewage treatment facility.

The system consists of a sanitary sewer sump, two sanitary sewer lift pumps, and a level control system. Sewage is collected from restrooms and lavatories in the control room and in the maintenance building. The system is shown on P & ID 56A-10107.

There are level switches that start and stop one or both pumps automatically. There is also a pump alternator relay which prevents operation of the same pump all the time.

If problems develop with the level switches, the pumps can be operated manually. If the pumps fail to operate, a high-high level alarm is activated. Then a vacuum truck should be used to keep the level down in the sump. High level in the sump will cause sewer water to back up through the floor drains in the control room restrooms.