DESIGN OF A HIGH-CONTAINMENT POLYMERIZATION PROCESS

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INTRODUCTION

A recently designed plant for the production of suspension type polyvinyl chloride and vinyl acetate vinyl chloride copolymer incorporates several systems to reduce exposure of employees by limiting the release of vinyl chloride into the atmosphere to acceptable values. The plant, represented in simplified fashion in Fig. 1 is an adaptation of the classic batch polymerization process. The parallel recovery of vinyl acetate is not shown.

The reactors discharge slurry to a blowdown tank which is vented through a water scrubber to a large gas holder acting primarily as a surge tank in the suction of the liquid ring compressor feeding the monomer recovery condensers. The cold condenser vent is disposed of in an incenerator fitted with a tail gas scrubber. The gas holder and the incinerator are two departures from the old norm. These and some other departures are the subject of the paper. The reader will note that the paper discusses the containment of vinyl chloride without regard to whether a given regulation stems from OSHA or EPA rules; these rules in any case often overlap in their effect even if they differ in intent.

The protective measures taken in this design divide themselves, at least for purposes of discussion, into three classes. They are:

Systems permanently installed to protect personnel from vinyl chloride concentrations exceeding the standards:

- Breathing air network
- Gas chromatograph monitors
- Lower explosive limit (LEL) detector and alarm system

Systems to contain or reduce emissions connected with mechanical devices or maintenance operations.

- Gas holder in recovery system
- Fugitive emissions capture system
- Reactor safing procedure and the water displacement system
- Double mechanical seals

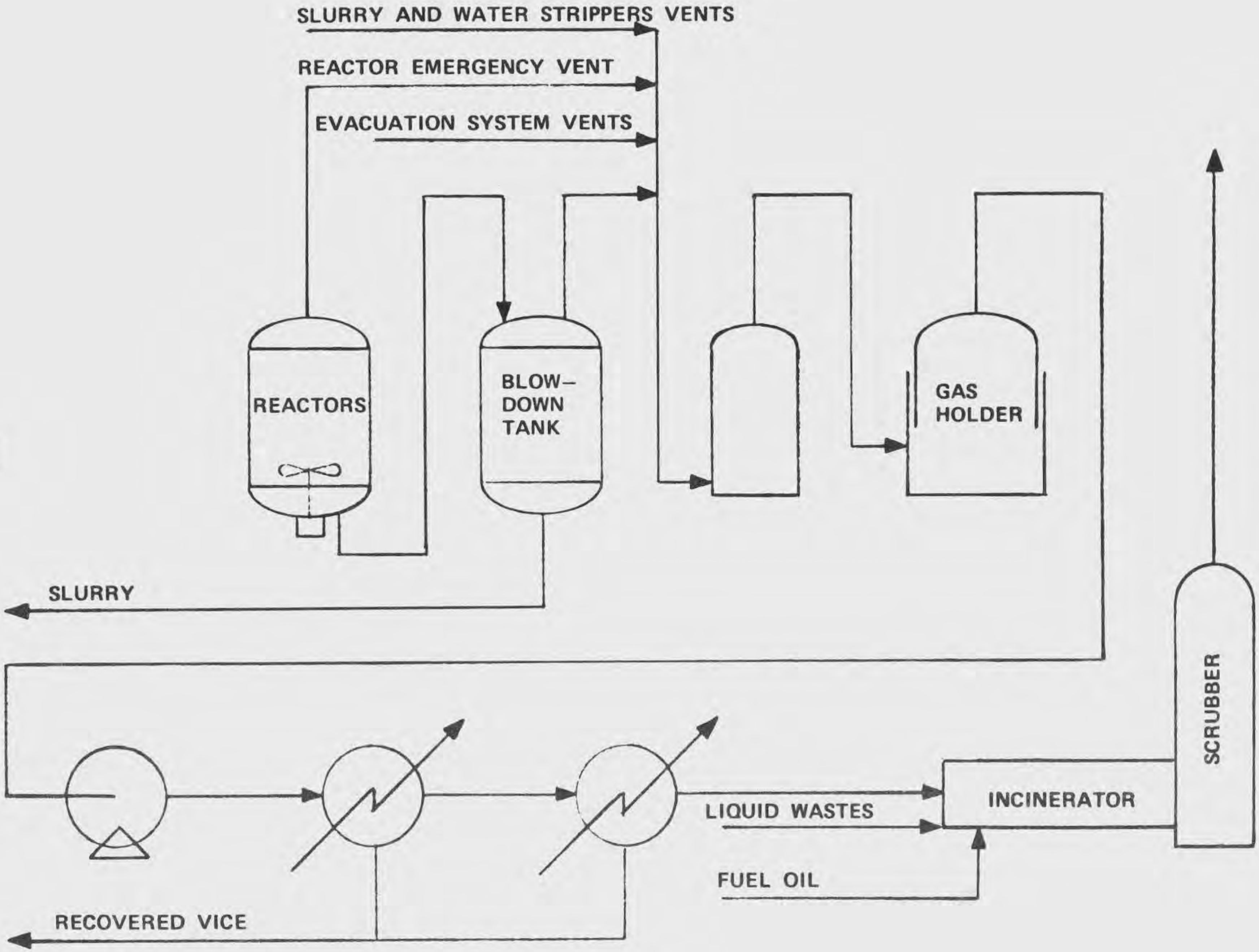
SLURRY AND WATER STRIPPERS VENTS
REACTOR EMERGENCY VENT
EVACUATION SYSTEM VENTS
REACTORS
BLOW-
DOWN
TANK
GAS
HOLDER
SLURRY
SCRUBBER
INCINERATOR
LIQUID WASTES
FUEL OIL
RECOVERED VICE

FIGURE 1

- Reciprocating shaft seals

Systems dealing with irreducible process vents.

- Steam stripping of slurry (and water)
- Incineration of the cold condenser vent

BREATHING AIR NETWORK

This system is by now standard in every installation handling vinyl chlorides. Air is taken in high, preferably well to windward (and not to leeward of some other plant's discharge) compressed in oil-free, spared machines, filtered, passed through active carbon adsorbers, and distributed at 70-100 psig to a number of quick-connect outlets. The outlets in this installation, provided with sintered bronze final filters, are located near vessels which must be periodically opened (reactors, filters) or where a serious leak may unexpectedly develop (large pumps). Hose lengths stored near the outlets are connected by the use of a reducer and half-face mask. In this installation the air reservoir is continuously monitored by a gas chromatograph set to alarm at ½ ppm. The carbon is changed periodically and safely disposed of.

GAS CHROMATOGRAPHS

Four gas chromatographic analyzers are installed to continuously monitor some 35 sample points throughout the installation. They indicate locally on a strip chart and store each reading in a computer for daily print-out. Alarms in the control room and lights near each sample point indicate excursions from the norm.

About half the sample points are in the polymerization and monomer recovery units, the rest are near likely sources of leaks. Two are in each incinerator stack and three are in the air intakes of the two control rooms.

COMBUSTIBLE GAS DETECTOR

Some 30 sample points throughout the plant are connected to catalytic oxidation type combustibles detectors, sometimes referred to as LEL or lower explosive limit detectors. Their distribution is similar to the chromatograph sample points. All are set to indicate a warning at 10% of the LEL and to sound a general alarm at 60% of the LEL. Those at the polymerization and the monomer recovery areas will also trip off the local deluge system, if in a five second grace period the operator does not defeat the action with a manual selector switch. The same switch can be used to start the deluge system if the automatic system malfunctions. In any case, when the polymer area deluge valve is tripped open, the ventilating fans are simultaneously shut down.

The detector at the control room air intake shuts off the air at a level of 60% of the LEL.

Besides all this, there is a detector at each (indoor) motor control center that close the ventilating louvers at a level of 60% of the LEL.

GAS HOLDER IN RECOVERY SYSTEM

Most of the unreacted monomer remaining in the PVC reaction mass (suspension process) is released in the blowdown tank when the slurry is tranferred from the reactor (at high pressure) to the blowdown tank (at low pressure, essentially atmospheric). The VCM vapor release from the blowdown tank is a batch operation and relatively large volumes of vapor are released in a short time, say ½ to 1 hour.

A vapor recovery system (since the vapor cannot be discharged into the atmosphere), sized to handle the instanteneous discharge would be too large and uneconomical. A gas holder, to act as a surge tank is, therefore, installed to collect these vapors and feed the recovery train at an average rate. The recovery train can thus be operated continuously. The recovery train typically consists of a compressor, followed by multistage condensation, followed by carbon adsorption or incineration.

A water scrubbed is provided upstream of the gas holder to minimize carryover of foam (solids) into the gas holder.

In addition to collecting reacted monomer discharge from blowdown tanks, the gas holder collects various VCM-containing vapor streams for recovery, thus avoiding atmospheric discharge of those streams. Other vapor streams are as follows:

1. Reactor Vent: EPA permits manual discharge of reactor contents to reduce the discharge to the extent possible of the vapor to atmosphere via a relief valve. This will be vented to the gas holder.

2. Slurry Stripper and Waste Stripper Vents:
   These strippers reduce the VCM content of the slurry or waste water to limits acceptable by EPA.

3. Displacement Water Tank Vent:
   This tank holds water which is used to purge reactors or any other equipment of VCM Vapors. The tank is maintained at gas holder pressure, slightly above atmospheric.

4. Fugitive System Vent:
   The fugitive vent collection and evacuation system discharges all vapors to the gas holder for recovery.

5. Monomer Charge Tank & Recovered Monomer Tank Vents:
The pressure regulating vent valve(s) discharged from these tanks are piped to gas holder to avoid atmospheric discharge.

Figure 2 is a sketch of the scrubber and gas holder

FUGITIVE EMISSIONS CAPTURE SYSTEM

The term "fugitive emission sources" as discussed in EPA guidelines, pertains to VCM discharges at loading or unloading operations; leakage from pumps, compressor and agitator seals, leakage from relief valves; manual venting of gases; opening of equipment for maintenance; leakage at sampling points; leak detection and elimination procedures; and emissions from in-process waste water.

Here, Fugitive Emissions System means essentially that system provided to minimize VCM discharges due to opening of equipment and/or piping for maintenance purposes.

According to EPA regulations, before opening any equipment for any reason, the quantity of VCM is to be reduced so that the equipment contains no more than 2% by volume VCM or 25 gallons of VCM vapor, whichever is smaller at standard temperature and pressure.

An evacuation and collection piping system is provided throughout the plant in all areas which process VCM. This system has a capability of reducing the pressure in the equipment or piping to 2 psia an thereby limits the applicability of this system to pieces of equipment or piping that have a maximum enclosed volume of approximately 170 gallons, calculated as follows:

$$25 \times \frac{(460 + 60)}{(460 + 60)} \times \frac{14.7}{2} = 172 \text{ gallons}$$

All equipment or piping which contains enclosed volume of 170 gallons or more will be evacuated by using a water displacement procedure similar to the one practiced during reactor "safeing" procedure. All vapors being vented to a gas holder for recovery. See Fig. 3 for a simplified arrangement.

Procedure for use of the Fugitive Emission Containment System is as follows: (up to 170 gallons)

1. All equipment and/or piping containing VCM is provided with blind flanged vent connections and necessary valves to connect it with the fugitive emissions evacuation system. When such equipment and/or piping is taken out of service for maintenance, it is first vented to gas holder, which brings the pressure in the equipment to near atmospheric.

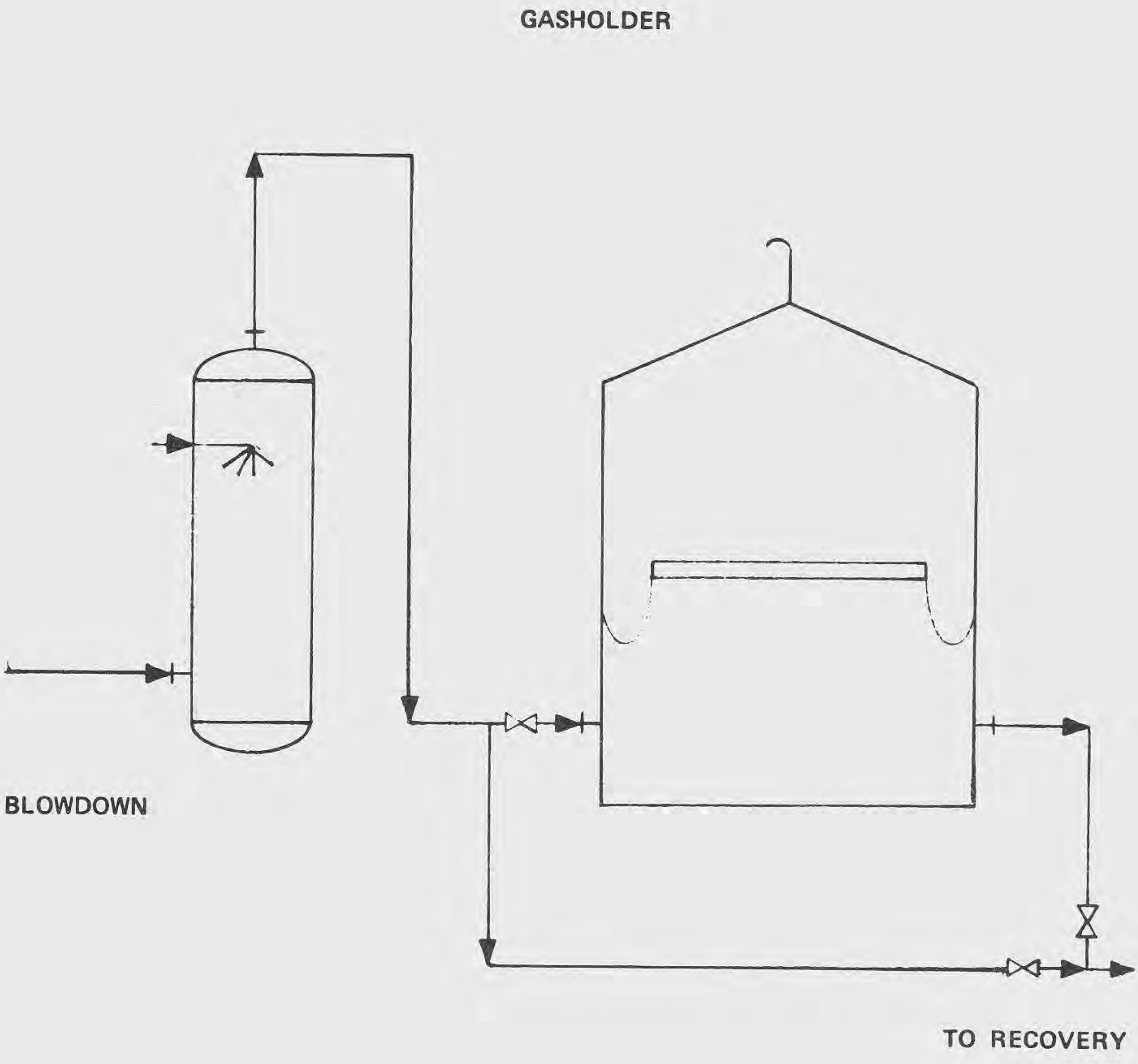

Figure 2. Scrubber and gas holder.

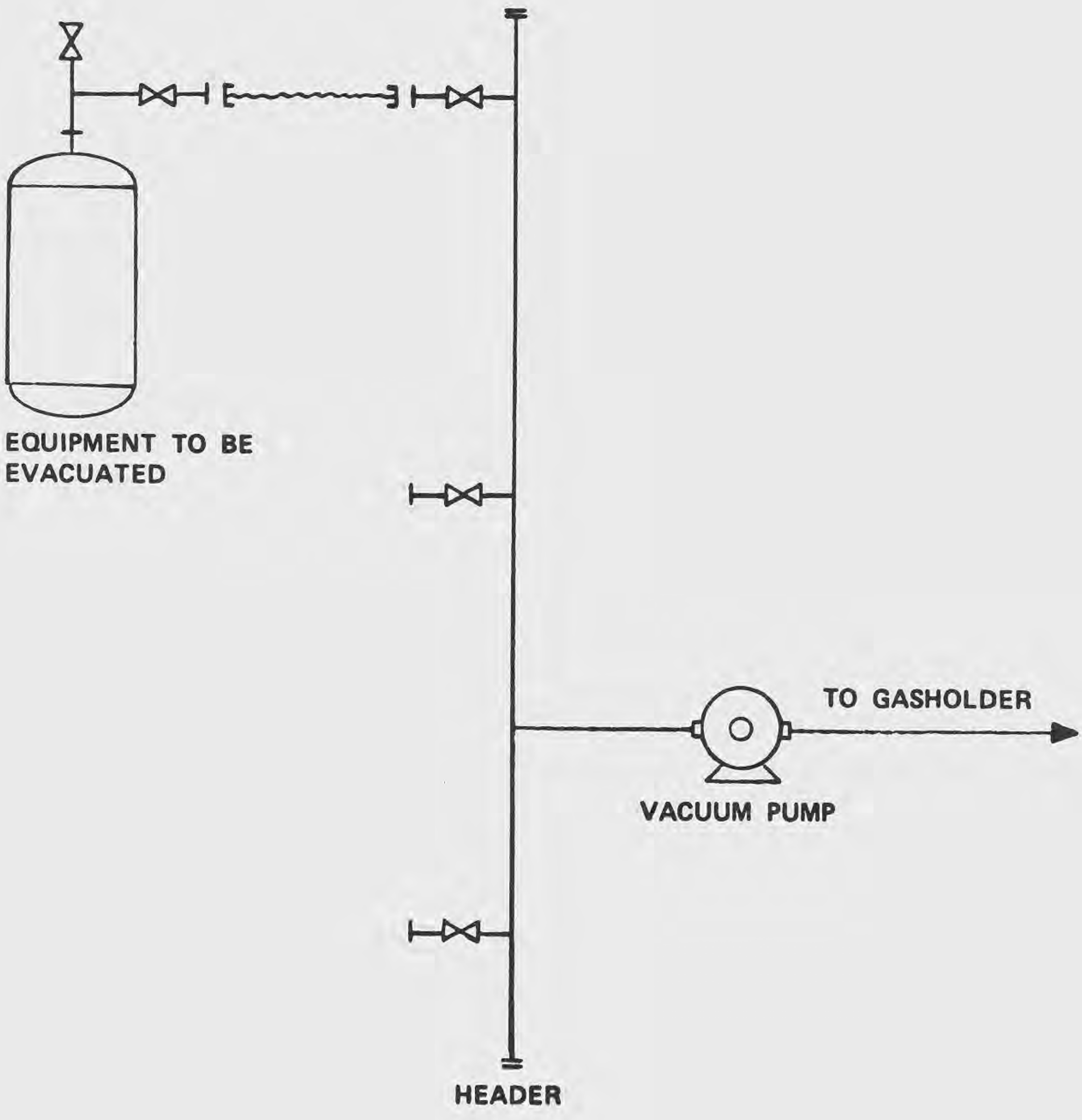

Figure 3. Capture system.

2. The equipment and/or piping is then connected to the evacuation system and evacuated to a pressure of 2 psia. The vapors are sent to gas holder for recovery.

3. The equipment and/or piping is then vented to atmosphere.

SUMMARY

0 to 25 Gallons System Volume at Standard Conditions

a) Vent to gas holder directly.
b) Vent to atmosphere directly.

25 to 170 Gallons System Volume

a) Vent to gas holder directly.
b) Vent to gas holder via vacuum pump.
c) Open to atmosphere.

Above 170 Gallons System Volume

a) Vent to gas holder directly.
b) Vent to gas holder using water displacement
c) Open to atmosphere and pump out the displacement water to the water stripping system.

REACTOR SAFING PROCEDURE AND THE WATER DISPLACEMENT SYSTEM

The reactor is rinsed, purged with water, and chemically cleaned with solvent to remove all monomer vapors and PVC resin sticking on reactor walls before personnel entry. The sequence of operation is as follows:

1. After the polymer slurry has been transferred to the blowdown tank, isolate the reactor from the blowdown tank.

2. Make sure that adequate amounts of displacement water and the solvent are available in storage tanks.

3. Fill reactor with displacement water while venting all vapors in the reactor to a gas holder.

4. Pump displacement water back to the water storage tank. This water is to be steam stripped for removal and recovery of VCM. Allow the reactor to be filled with N_2 or other oxygen-free inert gas. The inert blanket is required to minimize the explosion hazard due to the use of a chemical solvent in other steps of the operation.

5. Spray rinse the reactor with high pressure water using spraying valves such as Fetterolf valves. These valves use high pressure water at 200 psig or above to wash down loose PVC resin from the walls. Drain the rinse water.

6. Fill the reactor with heated solvent. Circulate the solvent for 8 to 9 hours with agitation.

7. Pump the solvent out under a nitrogen blanket and spray rinse the reactor with high pressure water jets.

8. Evacuate nitrogen to atmosphere by using steam jet ejectors or any other vacuum pumps, till the pressure in the reactor is reduced to about 2 psia.

9. Open the reactor to atmosphere. At this point the reactor should be safe for "personnel entry." A portable VCM monitor must be used to determine that VCM in the reactor is below OSHA guidelines.

DOUBLE MECHANICAL SEALS

Vinyl chloride emissions from seals on all rotating pumps in vinyl chloride service are to be minimized by installing seal-less pumps, pumps with double mechanical seals, or equivalent as provided in the vinyl chloride standards.

If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump or by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm. Similar requirements apply to rotating compressors and rotating agitators.

Water or non-freezing sealing fluids compatible with the process, and as 50/50 ethylene glycol/water mixture may be used. When water is used as the sealing fluid, freeze protection is required when the equipment is placed outdoors.

In mechanism under discussion, 50/50 ethylene glycol/water mixture was selected as the most suitable fluid. Small leaks of the mixture into the process were not considered detrimental.

For rotating pumps, double mechanical seals were provided with the seal fluid circulation system as shown in Fig. 4.

For rotating compressors double mechanical seals were provided with a centralized seal fluid system, because all compressors were located in one area. (Fig. 5)

Similar systems may quite obviously be applied to ganged pumps or, for that matter, to single pumps.

For agitators the seal system was similar to the system provided for pumps. However, the finned tube exchanger was not required since the

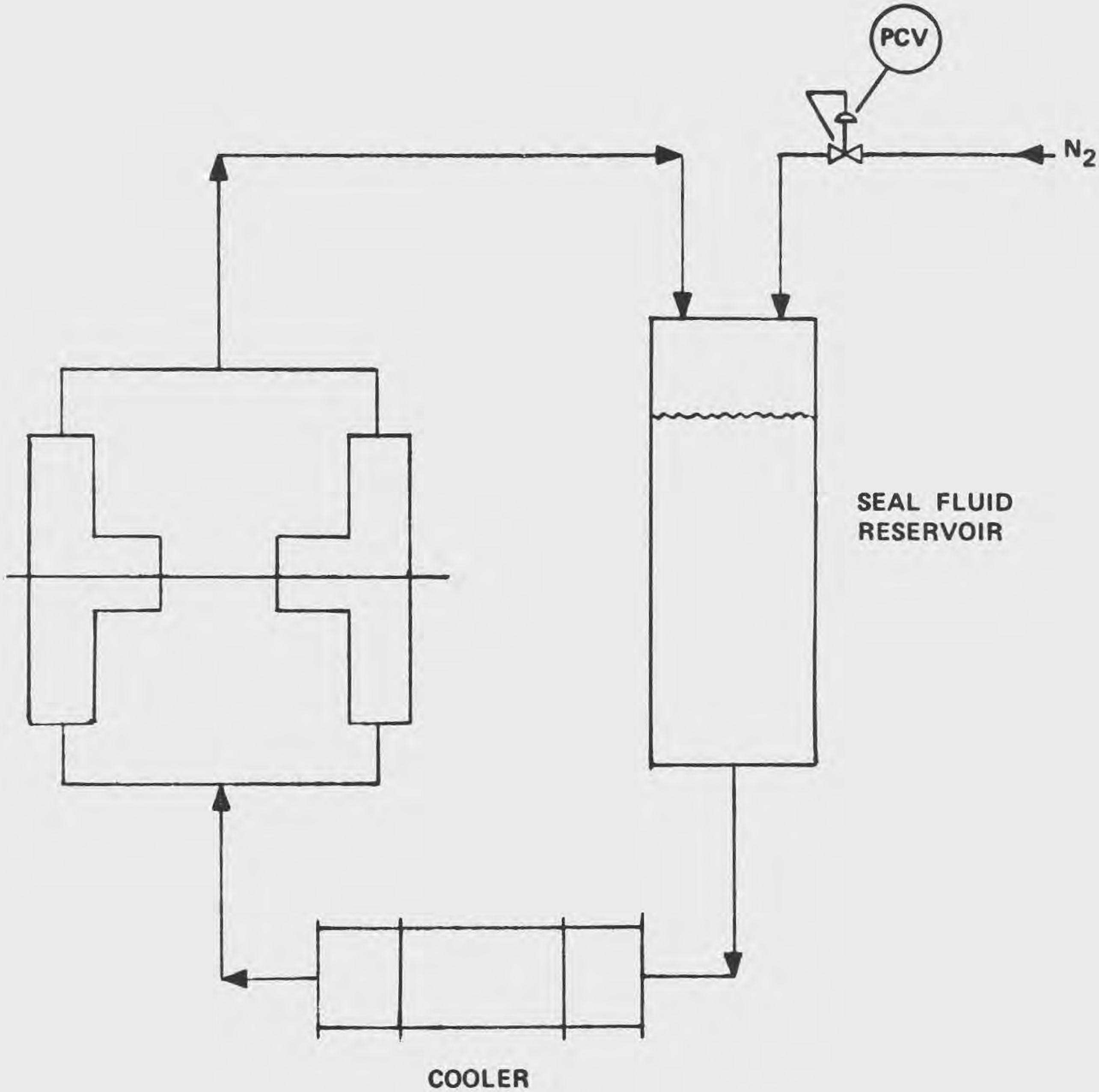

Figure 4. "Non-pumped" seal.

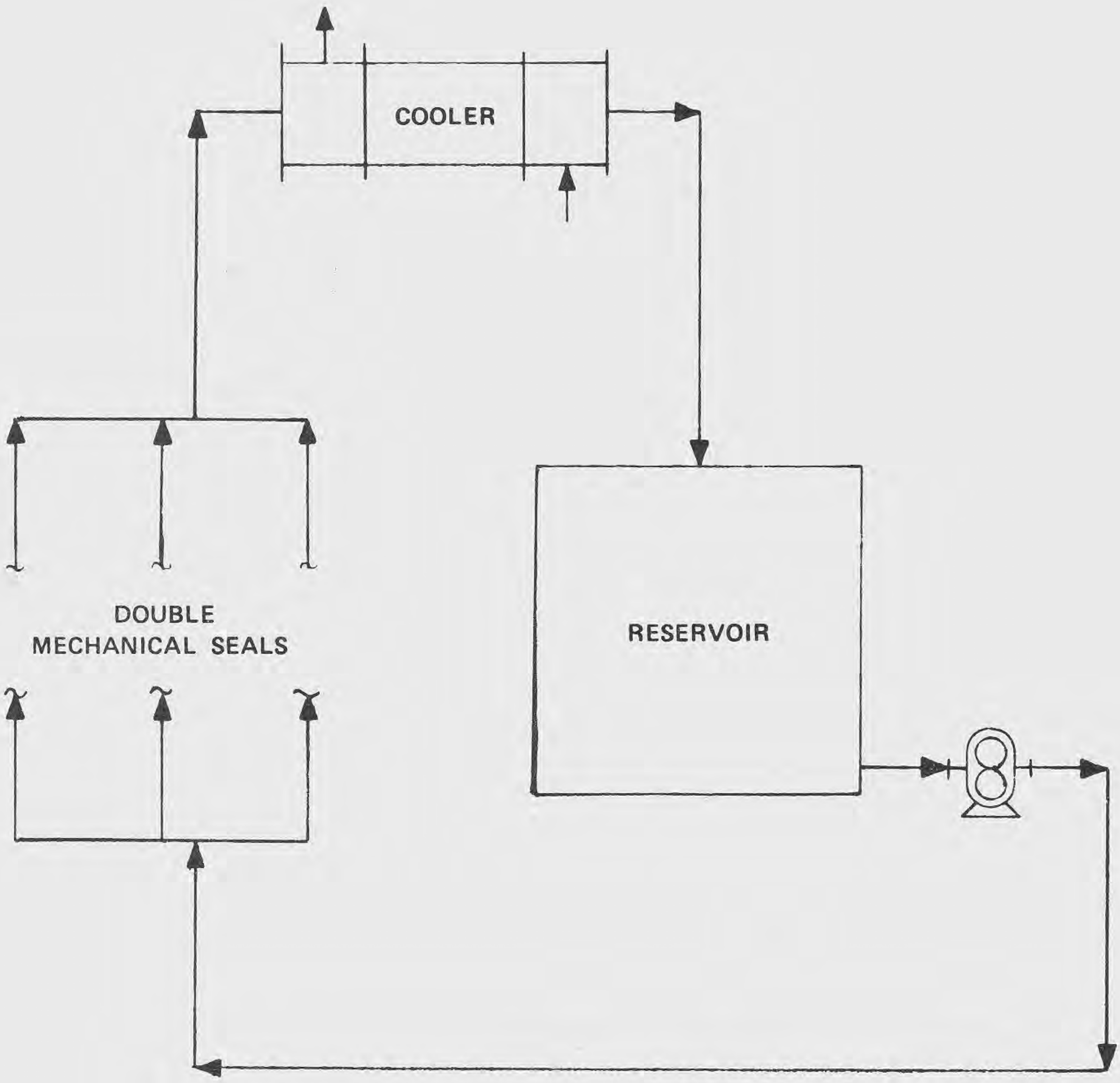

Figure 5. Ganged double seals - pumped system.

agitators did not operate continuously and the seal housings were provided with water cooled jackets.

RECIPROCATING SHIFT SEALS

Where reciprocating compressors are employed, the preferred method of sealing with leakage is the purged double distance piece.

Where a reciprocating shaft emerges from a cylinder three packed glands in tandem are employed. The spaces between are purged with inlet gas and vented to the gas holder. (Fig. 6)

STREAM STRIPPING OF SLURRY AND WATER

This design makes use of one of the several available proprietary processes for stripping the PVC slurry. These are adequately described in the literature and will not be enlarged on here.

A second stripper is employed to remove vinyl chloride from water blown down from various points in the plant. Chief of these are excess water from the displacement water tank and the excess scrubbing water ahead of the gas holder.

Condenser vents from both these strippers are fed to the gas holder.

INCINERATION

In PVC production, unreacted vinyl chloride monomer (VCM) is vented from the reactor to a VCM recovery system. A typical VCM recovery system consists of vapor collection, compression, condensation (often refrigerated), storage, and recycle. Non-condensibles, which are eventually vented to the atmosphere, are saturated with VCM at the final condensation temperature. These saturation levels of VCM generally exceed the environmental regulations. Therefore, to meet the regulatory criteria, a pollution control system is required.

Three systems presently in use in PVC production facilities to control VCM emissions are:

Three systems presently in use in PVC production facilities to control VCM emissions are:

1. Activated carbon adsorption and recovery

2. Destruction via thermal oxidation (incineration)

3. Solvent scrubbing of vent gas

We chose inceneration because:

1. It can consistently meet the EPA emission criteria of 10 ppm VCM.

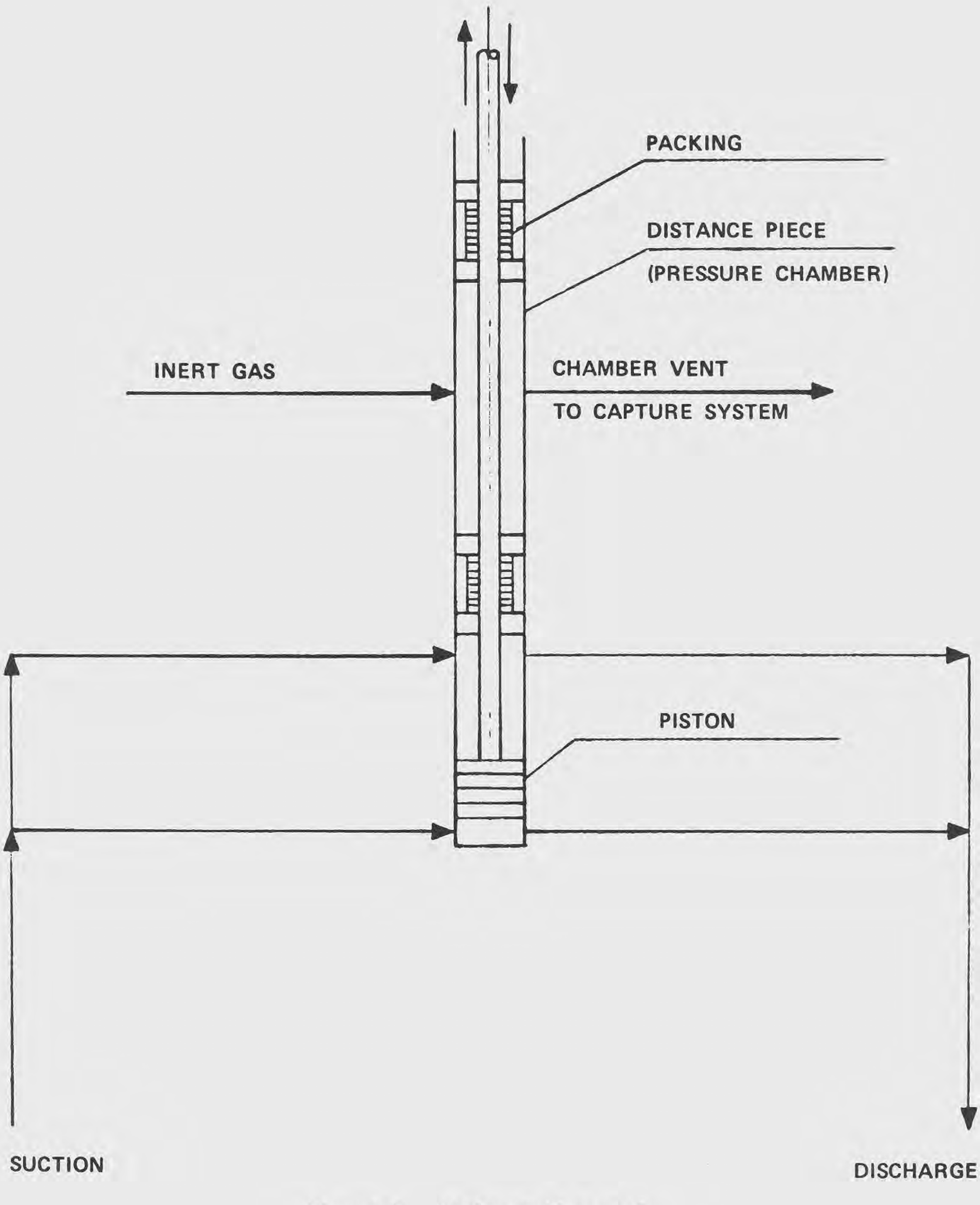

Figure 6. Reciprocating seal.

2. It can accept both gaseous and organic liquid wastes either simultaneously or alternately.

3. It helps to minimize build-up or non-reactive VCM containments (methyl chloride) which can occur when operating with a high degree of VCM recovery and recycle. Methyl chloride in the waste gases is destroyed along with VCM in the incineration process, whereas it is recovered and recycled in the activated carbon adsorption process.

4. It conserves energy; VCM is flammable and has a sufficiently high heating value, and the incinerator can be (a) made nearly energy self-sufficient when designed to oxidize both gaseous and liquid organic wastes or (b) designed to recover energy via a waste heat boiler if a separate fuel source is required to oxidize the waste gases.

There are, however, two limitations to the use of incineration as a pollution control method for VCM emissions from a PVC production facility, namely:

1. Reliability: Incinerators generally do not enjoy as high an on-stream time as the process facility they serve, thus necessitating a shut-down of the production unit during an incinerator outrage. This problem can be solved by installing two full size incinerators (one spare). Where one unit is operational, the other can be maintained in a "standby" condition, i.e., the unit is hot and ready to immediately accept wastes.

2. When incinerating chlorinated hydrocarbons, the combustion (oxidation) process generates the following objectionable by-products which cannot be discharged directly to the atmosphere:

   a) Hydrogen Chloride (HCl)
   b) Chlorine (Cl_2)
   c) Particulates
   d) Nitrogen Oxides (NO_x)

These noxious emissions can be reduced by the following techniques:

a) HCl, Cl_2, and Particulates - Scrubbing the incinerator stack gases with an alkaline solution or water is effective and is the usual control method. If water is used for scrubbing, the resulting acidic solution must be properly neutralized prior to discharge to the environment.

b) Particulates and NO_x - Proper design and control of the incineration process variables and parameters such as combustion temperature, present excess air and residence time of the wastes within the oxidation zone are effective in reducing formation of these constituents, and are the most commonly used control techniques.

Further reduction of emissions in the stack discharges, if necessary, can be achieved by additional equipment depending on the requirements of the particular vapor stream.

Finally, incineration is an effective and viable method of meeting present and anticipated future environmental regulations with regard to controlling VCM emissions from PVC production facilities.

In summary, the design described here provides:

- A breathing air network,
- Chromatographic and explosive limit monitoring,

and

- a gas holder connected to
- a fugitive emissions capture system,
- a water displacement system,
- double rotating mechanical seals, and
- double seals on reciprocating shafts,

and finally,

- slurry and water stripping and
- incineration to dispose of otherwise irreducible process vents.

We expect these design measures, coupled with strict attention to proper operation and maintenance, to result in a safe and environmentally acceptable installation.

* * *

DISCUSSION:

MR. JOHN T. TALTY: Any questions of Mr. Knox or Mr. Schroy?

MR. ARTHUR SPIEGELMAN: Mr. Knox, you indicated on one of those charts that in order to check the lower explosive limit, you had a sniffer that was picking it up at 60 percent, and that would activate the deluge system at that time and also mechanical fans.

MR. LEWIS C. KNOX: It shuts down the fans at that point.

MR. SPIEGELMAN: I have seen one where they operate the fans, too. Our experience with one particular plant, or I have actually seen that operation which failed to operate correctly, is that sniffers -- first of all, we would insist that they be inserted at 25 percent of the lower explosive limit, but even when it did pick it up, it did not function quickly enough. This was a plant up in Rhode Island, very close to a school, and the people in that locality opposed the plant when they put it in. We went up and took a look at it, and we would have agreed with you that would be the best way to handle this problem, was to knock the walls out of the building. They said they would prefer not to do that and they put in sniffers, and in six months, the plant had a major leak, and they had the explosion, and the sniffer did not function quickly enough to actuate the deluge system or the fans.

MR. KNOX: Let me say that, first of all, we did go to our insurers at length and discussed it; we went to the client's insurers and at length discussed what percentage of the lower explosion limit they thought it should be set at. After a lot of doing and frowing, 60 percent was decided on. The reason for the five seconds -- there is the disadvantage that a man finding himself in the middle of the deluge may have a difficulty finding his way out, and more damage might be done under those circumstances, certainly if it was a false signal. The second thing, if it will help to put your former friend's mind at ease, there has been a system such as this installed at Calvert City, and was shut down. It is still there in some kind of condition if you would like to see it.

MR. D. G. IRWIN: I am concerned about the amount of polymer that might carry over into the line in the scrubber system as a result of venting a reactor under emergency conditions. To your knowledge has this type of system been tried in industrial practice before?

MR. KNOX: I don't know that. Perhaps John Barr can answer the question. It was certainly considered, and it was not intended to vent the reactor suddently.

MR. JEREMIAH LYNCH: Mr. Schroy, where would we go with the methodology now; is it more fruitful to try to perfect the emission rate data; what do you think?

MR. JERRY M. SCHROY: Validating the model, since it is a gaussian model that has been worked up on a myriad of people, would not be fruitful. I think it would be better to define good emission rate data. That is the reason I mentioned the EPA study and their intent to define emission rate in basic terms, such that the data would apply from location to location and one chemical to another. We are trying to provide a validation of as much as we can and get it into literature. The question of validating the area pools and area sources, we feel has been validated enough. The accuracy of the gaussian model is at best a factor of two.

If you're extremely lucky, you might be able to predict levels which are within a factor of and a half and the worst might be a factor of three. But since you're trying to protect people, there's nothing wrong with using the model even considering potential errors of this magnitude.

MR. BILL THOMAS: I was wondering if any of these predictive design techniques are promulgated in standards?

MR. JERRY M. SCHROY: I think they would be helpful in understanding the impact. The idea of a standard being set from a method like this goes against the use of a method. The idea of being able to understand the impact of a seal in an acrylonitrile design situation versus the same seal in a vinyl chloride plant in valuable. I think it has merit in defining the situation for the person writing the regulation but not as part of the regulation. I agree with Nick Wheeler on the performed standards requirement.

MR. RALPH BARLEY: Relative to Arthur's comments a couple of minutes ago, I would like to offer an opinion. First of all, I don't think the deluge system is intended to relate to any compliance with EPA; another is I don't think it is intended, at least directly, to prevent explosions. The next point is that if it relates to an OSHA requirement, I think it is more or less incidental if it just happens to. I believe the main purpose of the deluge system is to reduce insurance premiums relative to equipment losses. In other words, to prevent fire; to keep the equipment from damage in an ensuing fire.

MR. SPIEGELMAN: First of all, you're wrong in just two counts. First, it is intended to quench the explosion that may take place. I don't think it works too well myself, but you know that certain insurance organizations have been sold on the idea that you can quench an explosion by flooding the area with little drops of water. It sometimes works the other way because the water droplets may turn to steam and add to the explosion force. But there are opinions which honest people can have and still not agree. It does not affect the insurance rates, as far as I know. As far as I know, it wasn't intended to be a means of reducing insurance rates.

MR. SCHROY: A deluge system, as we use it, whether or not it is the system he is talking about, is meant to disperse the material that is generating the vapors; not to quench a fire or quench an explosion.

MR. JOHN T. BARR: I was present at the conversation with the insurance people when the design was established, and to my knowledge no one else in this room was. The reason the insurance company insisted that we have this was to protect the equipment after the inevitable fire occurred. It has nothing to do with stopping explosions. It has to do with keeping the steel cool so the building doesn't fall down.

MR. JOHN T. TALTY: Our next speaker is William Wier, an attorney. He received his bachelor of arts Degree in Philosophy from Colgate University, and his law degree from Yale Law School in 1960.

He has been a member of the Legal Department with DuPont out of Wilmington for two years. He is a member of the American, Delaware State, and Federal Bar Association, and he's presently a member of the firm of Bader, Dorsey & Kresshtool in Wilmington, Delaware, where he has been involved in many cases throughout his career involving anti-trust and patent infringement cases. The topic of his presentation is Methods of Dealing with Proprietary Information in the Transfer of Technology.

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Control Technology in the Plastics and Resins Industry

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