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INTEROFFICE / LAKE CHARLES

TO O. L. Cromeans

DATE June 25, 1976

FROM R. E. Sanders

SUBJECT Loss Prevention Review of
Liquefaction's Gunk Tank
Neutralization Project
LD-1616

R E Sanders

A Loss Prevention Review was made of the subject project. The work of the review team is attached. There is one unresolved question which must be focused upon before this scheme should be placed in operation.

The contents of this report are considered confidential.

RES:fd

Attachment

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LOSS PREVENTION REVIEW

LIQUEFACTION GUNK TANK NEUTRALIZATION

PROJECT LD-1616

INTRODUCTION

The Liquefaction scrubber system removes trace organics from chlorine produced in the Diaphragm Cell area. These organic impurities, called "gunk", are periodically discarded to the sewer. In order to meet the NPDES permit level of organics in the plant effluent, this gunk must be disposed of in another manner.

A formal Loss Prevention Review was deemed necessary owing to the problems which have occurred in the Lake Charles and Natrium works in gunk tanks and gunk tank neutralization operations in the past ten years. Other significant reasons for a formal review are that chloroform (the major ingredient in gunk) is being investigated as a carcinogen, the handling of chlorinated hydrocarbons not saturated with free chlorine is new to Plant A operations, interarea activity is required for the disposal of the organics phase and some previously established gunk tank operating guides may be changed.

DISCUSSION

Two batches of gunk per week will be treated with dilute cell liquor to neutralize the residual free chlorine and destroy the Nitrogen Trichloride. There will be less than two tons of organics in each batch of this manually controlled operation. The organics phase contains over fourteen chlorinated hydrocarbons. Chloroform (52 - 66%), Carbon Tetrachloride (8 - 9%), Perchloroethylene (12 - 18%) and Hexachloroethane (10 - 16%) are the major compounds in these organics.*

The initial plans were to transport the neutralized organics in a tote tank to the Per-Tri acid pit. However, ACT LC-1229 was disapproved on the basis that the final disposal of the organics should be re-evaluated. This Loss Prevention Review was nearly complete at the time word was received that the ACT was disapproved and only a minor portion of the report pertains to the Per-Tri area, so this review was completed and the report distributed.

This review and review report are a joint effort. The Hazards Review Manual was used as a backbone for techniques and questions. About 25 man hours were devoted strictly to probing questions related to Loss Prevention. Significant questions and their responses are listed below. The nucleus of the review team consisted of Lew Hazlewood, Doc Pair, Fred Pugh and Roy Sanders. Supportive help in selective meetings came from Garnett Bedenbaugh and Charles Dorsett.

The scope of this review encompassed the gunk tanks, the neutralizing tank, the recirculating pump and cooler, the portable tank and the acid pit at Per-Tri.

* "Neutralization of Gunk Tank Bottoms", LD-1438, Charles Dorsett, March 1974

There was only ONE unresolved question. It appears at the conclusion of this report, but certain other questions require more consideration, study and action. They were noted by a triple asterisk (***) prefix. These questions were so designated so that others may focus on the group's comments and offer suggestions if required.

RESOLVED QUESTIONS ON OPERATING PROCEDURES

1. Has a detailed operating procedure been written up for this operation?

Ans. No. It is too premature at this time. Process Engineering is assigned this task.

*** 2. Will this material be used to update the Liquefaction Operating Manual and be incorporated in it?

Ans. Yes. However, we should also update the entire manual since the last revision was eight years ago in July, 1968.

RESOLVED QUESTIONS ON EQUIPMENT DESIGN - VESSELS

1. Are the outlet pipes on all safety relief devices located so as not to present a hazard to personnel if a safety device opens?

Ans. No. The safety relief valves on the gunk tanks discharge in a semi-confined area. The tail piping should be rerouted. Operations will initiate a work order to alter this situation.

2. Is the transport tank equipped with a rupture disc?

Ans. It should be and Process Engineering will see to it that it is.

*** 3. Is the temperature in the gunk tank properly monitored with redundant temperature sensing elements?

Ans. It is questionable since there are two thermocouples in the gunk tank, but they are both in the same thermowell and conduit and hence subject to common mode failures as a leaking thermowell, broken conduit, etc.

Operations will request engineering help on this.

4. Can the Operations team monitor the reaction temperature in the neutralization tank from the control room?

Ans. The initial plans called for a locally mounted temperature indicator. A board mounted temperature indicator will be discussed.

5. Is the level in the gunk tank system well monitored?

Ans. The frost line is used as the general level detector which is certainly slow to detect changes. Operations has generated an engineering work order to study other methods.

6. Can the interfacial level between the organics and aqueous phase in the neutralizing tank be clearly identified within the sight glass for densimetric separation?

Ans. Initial tests indicated a sharp separation.

*** 7. Will the addition of gunk into the neutralization tank have to proceed so slowly that the gunk tank contents heat up while this is in progress?

Ans. The speed of gunk addition into the neutralizing tank will partially depend on the temperature that the gunk is warmed up to in the tank before dumping (free chlorine content), and also on the rate of reaction between chlorine and the dilute cell liquor.

Process Engineering attempted to define the heat gain. Using available methods with controlling assumptions, it was determined if all 350 gallons of gunk were warmed to 55°F (3% free chlorine), and instantly transferred to the neutralization tank, the neutralizing tank would reach a final temperature of 109°F.

If a 350 gallon batch of 55°F gunk was transferred to the neutralizing tank at 3 GPM, the transfer would require about two hours and the gunk tank would reach 72°F.

If a 350 gallon batch of 55°F gunk was transferred to the neutralizing tank at 1 GPM, the transfer would require about six hours and the gunk tank would reach about 84°F.

Unfortunately, this will require operating experience to verify.

8. The neutralizing vessel will see concentrations of caustic, sodium chloride, hypochlorite, organics and possibly wet chlorine. Are the materials of construction durable for the service?

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Ans. A steel tank with phenolic coating will be used initially. Our Corrosion Engineer believes it to be a good economic balance between cost and durability.

- *** 9. What will prevent an overzealous operator from trying to quickly dump the gunk tank and having a chlorine release on a well travelled roadway?

Ans. Procedures will be spelled out, experienced individuals will perform the work and the neutralization phases will probably be carried out on shifts other than days.

- *** 10. How can we be assured that a leaking valve will not allow the neutralizing liquid to be sucked into a gunk tank under a vacuum setting up a place for rapid corrosion?

Ans. Continuing study is required. Our information says this occurred at the Natrium works.

11. Two of the three gunk tanks are overdue for an internal inspection according to Industrial Engineering records. What are the plans?

Ans. Operations will review.

RESOLVED QUESTIONS - MISCELLANEOUS EQUIPMENT

- *** 1. Will critical spare parts be on hand for this fragile high silicon iron recirculating pump?

Ans. Too premature for this review, but it will be looked into.

- *** 2. Will there be sufficient lighting around the neutralization equipment?

Ans. Operations and Process Engineering will review and correct if needed.

3. Should there be any special facilities at the Per-Tri acid pit for unloading?

Ans. A dip tube should be installed so that the tote tank can empty below the aqueous level in the acid pit to prevent rapid flashing of chloroform. Unloading facilities should include a method to wash the hose prior to disconnecting it.

RESOLVED QUESTIONS - CHEMISTRY AND CHEMICAL PROCESS

- *** 1. The dilute caustic treatment of this is aimed at neutralizing the free chlorine and destroying the nitrogen trichloride. Are there any possible undesirable side reactions?

Ans. Yes. There are several possible undesirable side reactions, including:

Carbon monoxide (a toxic gas with wide flammable limits) can be formed by chemically cracking chloroform with caustic. However, the formation of CO can be minimized by using dilute cell liquor and keeping the reaction temperature no higher than 90°F.

Caustic cracking of 1,1,2-Trichloroethane and Trichloroethylene can form Vinylidene Chloride and Dichloroacetylene respectively. Exposure to moderate quantities of either of these chemicals could be detrimental. But, under the conditions of operations, these compounds are not anticipated. Laboratory support tests indicated negligible caustic cracking.

Excessive rates of introduction of the chlorine saturated gunk or insufficiently distilled gunk could lead to evolution of irritating free chlorine.

Insufficient cooling could allow a temperature rise and excessive chloroform vaporization, but heat balance calculations do not support this excessive vaporization possibility.

2. The gunk is treated with caustic to destroy the nitrogen trichloride. If the neutralized gunk is acidified in an acid media like the Per-Tri acid pit, will the nitrogen trichloride reform?

Ans. The nitrogen trichloride is decomposed to ammonium chloride and dissolved in the aqueous phase and will not reform nitrogen trichloride.

3. Is it possible to carry a tote tank of the caustic bearing material and/or the aqueous phase to the Per-Tri acid pit? And, what are the possible results?

Ans. Yes. It is conceivable to carry the aqueous phase from the Liquefaction area to the Per-Tri pit. But, procedures will be spelled out, experienced individuals should be trained on both the sending and receiving end to observe for possible interfacial levels.

A dilute caustic stream entering a moderately acid stream could form a noticeably active reaction. Also, the aqueous phase contains dilute sodium hypochlorite which could convert to a dilute strong oxidant (sodium chlorate), and some free chlorine.

4. What are some of the most important criteria for operating the neutralization tank?

Ans. The temperature must be kept cool to stop the chloroform from vaporizing. The aqueous phase must be kept alkaline to prevent sodium chlorate formation and to decompose the nitrogen trichloride. However, on the basis of typical gunk analyses

and reaction stoichiometries, the neutralization vessel has been sized to accommodate 350 gallons of gunk and sufficient dilute cell liquor (3 wt.% NaOH), to supply a 10% excess of NaOH.

*** 5. If the aqueous phase is depleted of caustic, is there any harm in a rapid correction?

Ans. Yes. The pH should be slowly raised. Rapid addition of cell liquor, caustic liquor or PELS could possibly shock the system and produce undesirable carbon monoxide or chloroacetylenes. With the system volumes involved and operator education, pH shock should not be a problem.

*** 6. Can the chloroform in the gunk travel through the aqueous layer and present a possible personnel hazard around the neutralizing tank?

Ans. Estimates of diffusion of chloroform through the aqueous layer have been made. It appears there should be no employee exposure problems. As an added precaution, an air mover (air horn) has been incorporated within the scheme. In addition, the neutralizing tank has been designed to accommodate a tank top if required.

Plans are to monitor the environment around the neutralizing tank to check for trace organics during the initial operations.

7. What level of nitrogen trichloride is acceptable to the Per-Tri plant?

Ans. Plans are to destroy the nitrogen trichloride below the detectable level.

UNRESOLVED QUESTION

1. Does the proposed raising of the maximum gunk tank dump temperature from the present day 35°F to 55°F jeopardize our guarded position. Will problems be encountered in allowing the gunk tank to warm up during neutralization?

Additional Information

- a. If the gunk tank has an initial dump temperature of 55°F at the start of the dumping cycle, it could ultimately reach 84°F before the tank is finally emptied. This assumes that the gunk can be neutralized at about 1 GPM and our temperature increase estimates are accurate. Current operating guidelines specify that in NO CASE SHOULD A GUNK TANK REACH 60°F, unless it is completely empty. (see question 7 in the Equipment Design - Vessels section, page 2)

- b. The Technical Report LD-868A "Explosion of Gunk Tank 10A-70-3", dated April 26, 1968, by Lewis Henslee recommends that the nitrogen trichloride content be held below 1% by weight and never allowed to exceed 60°F.
- c. The same report quotes the Thiokol Chemical Company studies which imply that gunk samples with less than 6% nitrogen trichloride will not become explosive, regardless of temperature increases.
- d. Technical Report LD-868A contains the Thiokol test reports on the "Initiation Temperature" for exothermic reactions. The lower limit curve was defined at 95°F for a 1.5% weight percent nitrogen trichloride solution. The lower limit initiation temperature is an estimate of the minimum temperature at which a nitrogen trichloride in simulated gunk would start self heating.
- e. "The Minutes of the Second Interplant Task Group Session on Nitrogen Trichloride and Chlorine" dated December 5, 1968, defined a tentative maximum specification of 15,000 PPM nitrogen trichloride in the reboilers. These minutes reflect the fact that the temperatures of reboiler operation at the other PPG chemical plant locations differ from the Lake Charles operations.

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