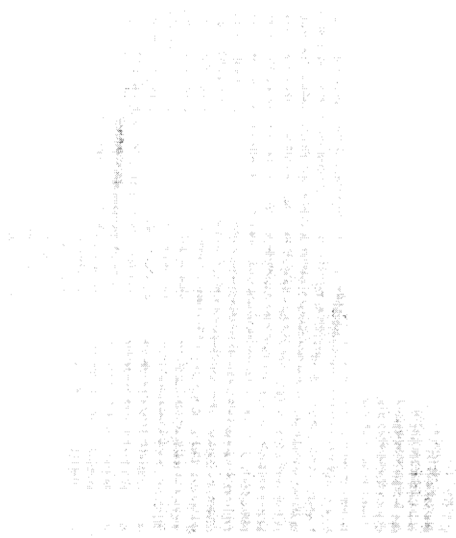
Chapter 5
Safety



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INTRODUCTION

One of the most serious concerns with the Library of Congress' program and the DEZ process has been safety. Because of the attention given to the accident during tests at NASA Goddard in 1986, many critics focused on the question of whether DEZ could be handled safely in the future. This chapter discusses the hazards that are present and the effort the Library has made and must continue to make to manage those hazards to ensure the safe operation of a full-scale plant.

HAZARDS

DEZ is considered a hazardous material. It is very reactive with certain compounds and is capable of releasing large amounts of energy. Fire is the principal hazard and, under certain specific conditions, explosions could occur.

DEZ is pyrophoric, meaning it will spontaneously ignite if it comes in contact with air (or, more specifically, the oxygen in air). The reaction is very fast, and releases a great amount of heat. The intensity of the heat is itself a hazard. It could ignite flammable materials nearby, cause damage to nearby structures or property, or cause injury directly. The byproducts of the reaction, carbon dioxide, water, and zinc oxide, are stable. Large leaks or spills of DEZ could pose a significant fire hazard. The product of DEZ reactions (ethane gas) can reach an explosive mixture with air. Under certain conditions, in unvented containers, DEZ reactions can also cause a pressure buildup which could cause an explosive rupture of the container.

DEZ is also very reactive with water. The byproducts are ethane gas and zinc oxide. If liquid DEZ and liquid water come into contact, the react ion that takes place can be very vigorous, releasing large amounts of ethane gas very quickly. The reaction between DEZ vapors and water vapor is not as vigorous, especially the reaction between DEZ vapor and absorbed water that takes place within books during deacidification.

The reaction between DEZ and water also releases heat. Although the amount of heat that is released is about 10 times less than the amount released during a reaction between DEZ and air, it is enough to require careful monitoring during deacidification. During normal book treatment conditions, within a processing chamber, the DEZ vapor is circulated at very low pressures and any reactions with air has been shown to result in only small temperature increases and no flames or pressure increases. Tests to confirm this have been done by the Library.

DEZ will begin to decompose at 120° C, into hydrogen, ethane or other hydrocarbons, and zinc. Heat is again released. At 1500 C, decomposition becomes autocatalytic. This means that the heat released will cause decomposition to proceed on its own and prevent it from being stopped. Autocatalytic decomposition of liquid DEZ would result in a very rapid and uncontrollable release of gases. Monitoring and controlling DEZ gas temperature in the process becomes critical to prevent the decomposition of DEZ. Early tests with the Houston pilot plant show adequate DEZ temperature control is possible within safe ranges to prevent autocatalytic decomposition.

The rapid release of gases associated with the decomposition of DEZ and with reactions between DEZ and water pose a significant hazard. If they occur in a contained environment, the resulting overpressure situation could cause rupture and subsequent fire. Storage vessels in a processing plant must therefore be designed with pressure relief systems. Explosion is a potential hazard because under certain conditions both ethane and hydrogen gas mixtures with air are explosive.

Photo credit: Library of Congress

Hooking up DEZ for NASA 5,000-book test

The amount of DEZ that will be used at the deacidification plant (up to 3,900 pounds in storage, and approximately 50 pounds per treatment) limits the scope of these hazards. Large numbers of people will not be at risk. However, they do pose significant risks for plant operators, safety personnel, and the immediate surrounding property. Such risks can be managed with proper attention to design and safe operating practices. As an example, the Library intends to locate DEZ storage containers at a distance away from the chemical plant and provide barriers to contain a potential fire.

SAFETY—A CRITICAL ISSUE

The potential for fire and explosion associated with the use of DEZ makes safety a critical issue for the DEZ process. The basic goal of safety management is to eliminate or reduce to an acceptable level the risk of injury or damage to personnel, material, or property associated with a given hazard.

There is a generally accepted priority to reducing the risk to personnel and property:

1. eliminate or reduce the hazard through design and operations,
2. isolate the hazard,
3. train personnel to operate around the hazard, and
4. provide protective and emergency systems and procedures.

The use of DEZ precludes eliminating the hazards associated with it. However, the relatively safe manufacture of DEZ by Texas Alkyls, Inc., and its use in a number of applications over the last 20 years suggests that the risks can be kept at acceptable levels. This requires a good understanding of the chemical and physical properties of the materials and processes involved, good design, detailed and safe operating procedures (including inspection and maintenance procedures), experienced operators who receive continuous training in operational and emergency procedures, and a good safety review program.

The importance of these issues as they relate to the DEZ process can be seen by reviewing the events leading to the failure of the first pilot plant. The following discussion is based on the NASA Accident Investigation Board's Report and discussion with NASA and Northrup personnel.

Importance of Safety—The Goddard Accidents

Construction of the first DEZ pilot plant at NASA's Goddard Space Flight Center was completed in October of 1985. System checks were initiated in October. The first full-scale test, a complete cycle but without the books, was initiated on December 5. Immediately upon initiating the dehydration phase of that operation, by introducing liquid water into the chamber, the pressure rose forcing the door open and a fire broke out in the chamber. There were two people in the processing area at the time, but there were no injuries. The fire burned itself out quickly, but not before causing extensive damage to the chamber and surrounding instrumentation and hardware.

The system was secured and the power turned off. Cleanup and repairs proceeded through January. In February, procedures were drafted for deactivating the system and to resume testing.

When the system was turned on, a pressure build-up in the line between a condenser and the brine seal tank was detected (see figure 18). The pressure buildup exceeded the range of the pressure gauge for that line. The deactivation procedures were then revised to include relieving the pressure in the line by first testing the valves for operability, and then to progressively pump the system to vacuum.

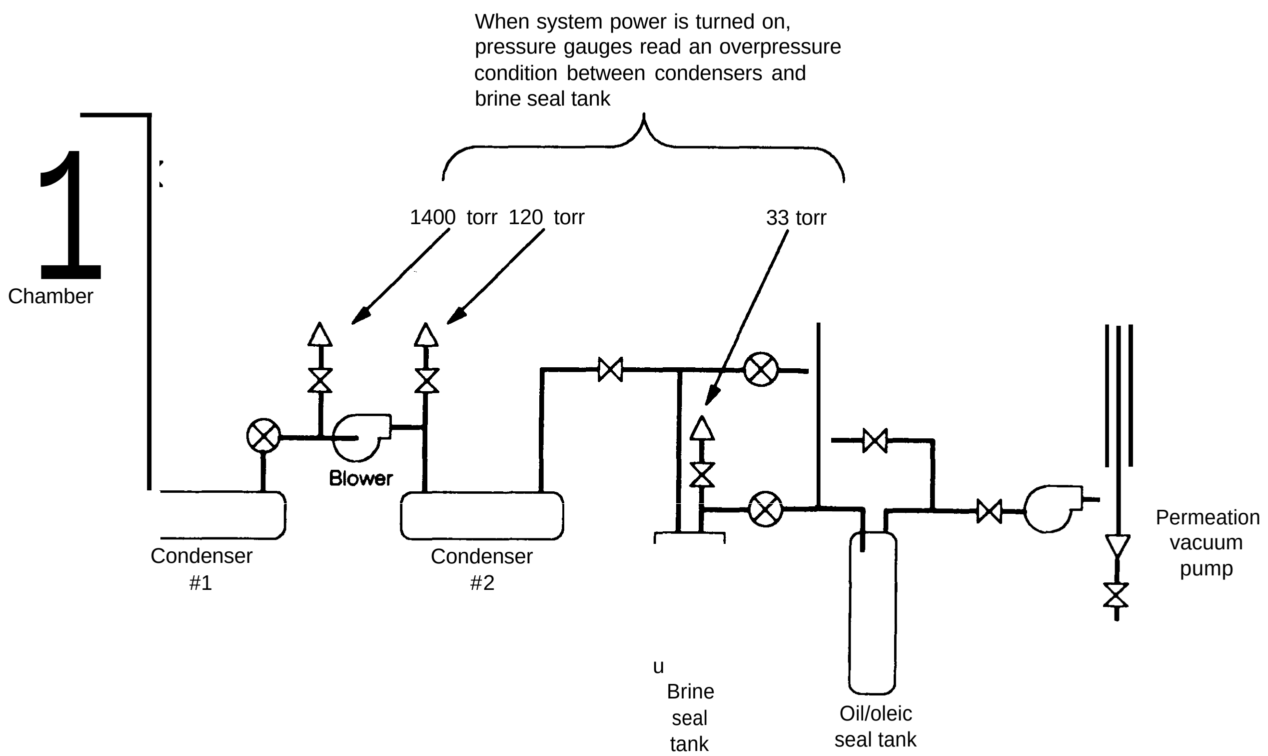
Valves were tested, beginning at the vacuum pump, and leading back toward the condenser. When the valve between the condenser and the brine seal tank was cycled, contents from the brine seal tank squirted out from a defective seal in the tank (see figure 19). The seal tank was replaced, and the valve tests completed. The system was then progressively pumped to vacuum. When a valve in a section of line upstream from the condenser was opened, an explosion occurred in the line between the condenser and the brine seal tank, and a second fire broke out (see figure 20). The explosion was of sufficient force to blow out two doors in the processing area, The subsequent fire burned out quickly, but caused substantial damage to the plant and surrounding area. There was one person in the processing area at the time of the accident, but there were no injuries.

The system remained in an unstable condition. After careful consideration of how to proceed, an army demolition team was called in to dismantle the plant.

The apparent cause of the first fire was the presence of liquid DEZ in the chamber. When water was introduced, the reaction with the DEZ rapidly evolved ethane gas which blew the chamber door open. With the door open, air came into contact with the DEZ and the fire started.

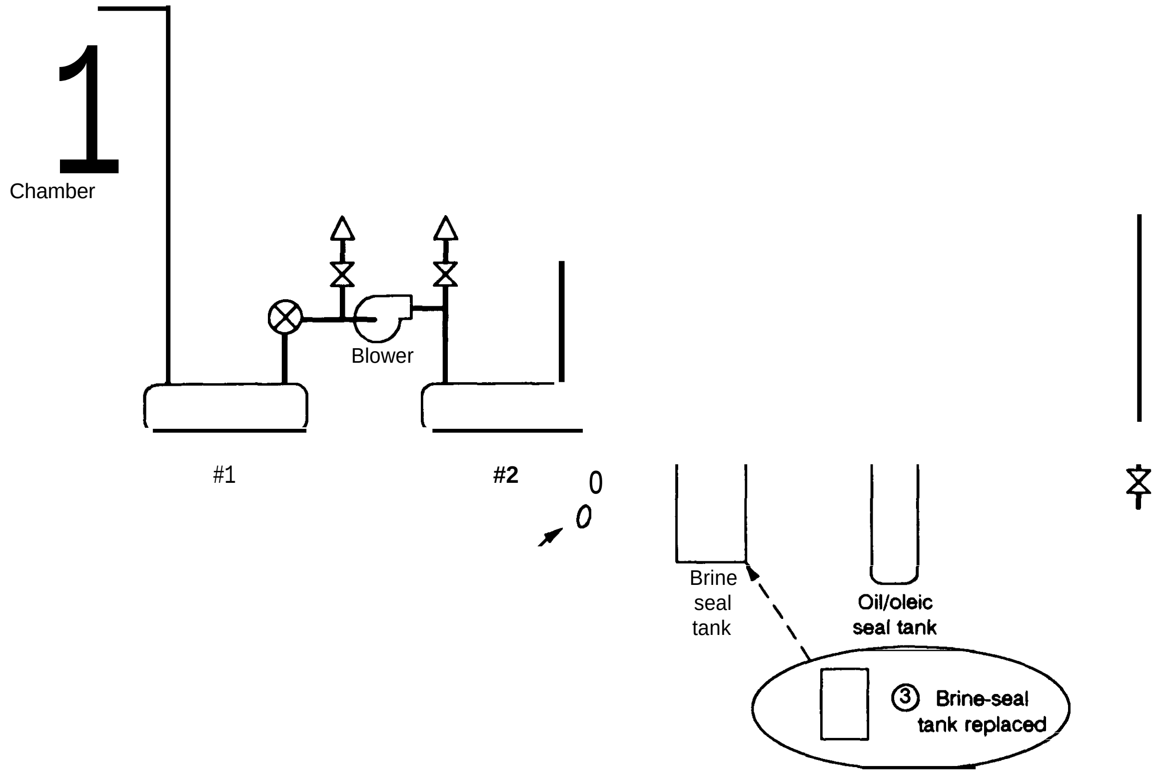
It is not known for certain how liquid DEZ came to be in the chamber. The apparent cause was condensation of DEZ in the vapor line leading into the chamber. The line heater for that section of the line

Figure 18.-Chronology of Second Goddard Incident



SOURCE: Office of Technology Assessment, 1988

Figure 19.-Chronology of Second Goddard Incident (continued)



SOURCE: Office of Technology Assessment, 1988

was working intermittently, and some of the insulation around the line was missing. Due to the configuration of the line as built, liquid DEZ ran into the chamber instead of away from the chamber.

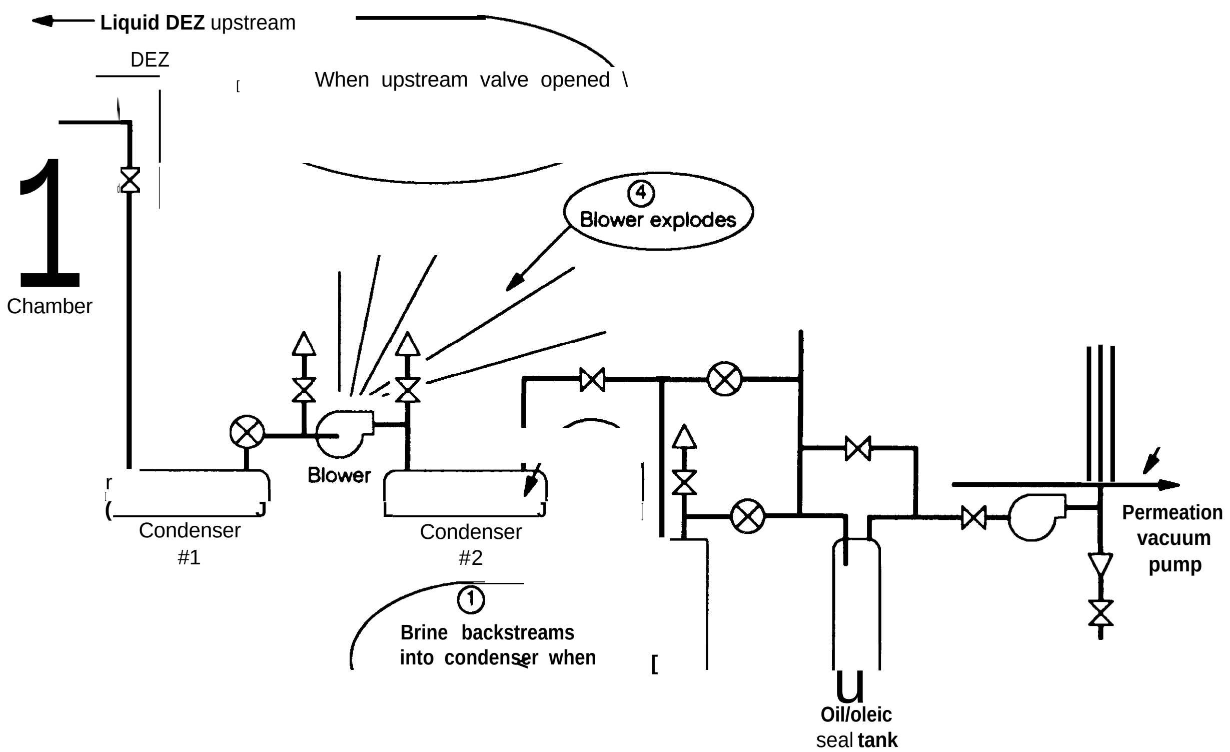
The explosion and second fire were apparently caused by brine and liquid DEZ reacting in the condenser. Evidence of brine was found in the condenser, and probably backstreamed into the condenser when the defective brine seal was replaced. Liquid DEZ must have been present upstream from the condenser. When the upstream valve was opened, the liquid DEZ traveled down the line and into the condenser, and reacted with the brine. The reaction rapidly produced a large amount of ethane which ruptured the line and caused the fire.

The presence of liquid DEZ in the line was supported by the fact that over 700 pounds of DEZ was pumped into the system, instead of the 30 pounds called for in the test. This was not immediately known, however, because the DEZ tanks were not on load cells as called for in the design. It wasn't until after the first accident that the tanks were weighed and the discovery was made. The presence of excess liquid DEZ in the system explains the pressure buildup that occurred while the system was being repaired.

The general conclusion of the NASA Accident Investigation Board[1] was that no one involved "fully appreciated the engineering challenges' associated with scaling up the continuous DEZ feed and recycling system. The care and diligence that went into the design and operation of the 5,000 -book test was not carried forward to the NASA pilot plant development.

[1]Accident Investigation Board Report on the Mishaps at the Deacitification Pilot Plant, Building 306, on Dec. 5, 1985 and Feb. 14, 1986; Sept. 4, 1986.

Figure 20.-Chronology of Second Goddard Incident (continued)



SOURCE: office of Technology Assessment, 198S

More specifically, the board came to the following conclusions:

(Excerpt from the NASA accident report)

There was a lack of appropriate instrumentation. In general, the system was under instrumented. Pressure gauges did not have a high enough range to monitor overpressure situations. There were no pressure relief valves in the lines, and most notably none in the chamber. Venting of the chamber was through the door. The use of semi-automatic valves required that personnel be present in the processing area during an operation. Also, real time monitoring of the system would be more appropriate. The presence of liquid DEZ in the chamber was actually picked up by a thermocouple reading at the bottom of the chamber. It was recorded on a strip chart but not monitored by the controller.

There was a failure to install the instrumentation called for by the plant design. The failure to place the DEZ tanks on load cells was a serious oversight. With a substance as hazardous as DEZ, an accurate inventory must be kept.

There was a failure to develop and follow procedures. The contract between Northrup and NASA requires the development of at least five procedures; a facility operating procedure that gives detailed operating instructions for both normal and emergency situations, an operations test procedure that gives special instructions pertinent to the test at hand, a pre-start check list, an operations log which records all significant events during operation, and an engineering log that also records all significant events and all activities and calculations pertaining to the test. The systems tests begun in October and the full- scale test in December were run without test procedures. No operations or engineering logs were kept. Furthermore, deactivating of the system began before the clean-up procedures were approved, and they were revised without review. Also, the poor condition of the insulation on the vapor line leading into the chamber indicated that there was inadequate routine inspection of the system.

There was one significant design deficiency, the piping configuration allowed liquid DEZ to flow into the chamber rather than away from the chamber. The use of a brine seal tank is questionable.

In the 5000 book test, brine seal tanks were advised against, because of the violent reaction that occurs between DEZ and brine. Finally, normal safety procedures were compromised. A Failure Mode and Effects Analysis 'was carried out and presented to a NASA review board. The analysis was accepted and operation approved. However, there was no documentation of who received and approved the report.

Only the results of the analysis were presented to the board with little or no documentation or explanation. Approval was granted although necessary procedures were not available. The analysis was not submitted for outside review. And there was no verification or inspection of the final construction and installation.

The accident investigation board made the following recommendations:

- The plant should be more fully instrumented, especially in regards to monitoring the inventory of DEZ. It should also allow remote operation of the system.
- The process should be controlled by an automated process controller to provide real time monitoring and display and to operate safety interlocks.
- The design, construction, and operations of the plant should be subjected to a third party review.

Importance of Safety—Accident at Ethyl Corp.

Another example of the potential hazards associated with metal alkyls is an accident that occurred at an Ethyl Corp. facility in 1986. Ethyl is also a major producer of metal alkyls and the only other domestic supplier of DEZ (although they have not produced DEZ in recent years). During the manufacture of a metal alkyl product, a large explosion occurred. Although details of the accident are not publicly available, there were some injuries, the damage was extensive, and the plant had to be rebuilt.

SAFETY AT THE TEXAS ALKYLS PILOT PLANT

This section discusses the safety of the Texas Alkyls pilot plant by examining the actions taken by the Library and its contractors in the following areas: understanding of the physical and chemical properties of all reactants and products; design-for-safety; operation~ safety; safety management and review. The deficiencies noted in the first pilot plant effort have been addressed and the margin of safety improved. However, whether the actions have been sufficient can only be demonstrated by repeated testing of the system.

Understanding the Physical and Chemical Properties of Products and Reactants

It is important to know as much as possible about the physical and chemical properties of all the materials involved in a process and to understand the thermodynamic and thermochemical properties of all possible reactions. Of particular importance is the amount of energy released during various reactions and the stability of the reactants and products in the presence of that energy. The physical and chemical properties of DEZ, and its reactions with other compounds have been studied for many years. Texas Alkyls' sales brochure for DEZ lists some of these properties and reactions. Critical safety information is available in the Product Safety Information Data Sheet (see figure 21).

As mentioned DEZ is pyrophoric. The heat of combustion is high. DEZ is also very reactive with free hydrogen ions, hence its reactivity with acids and water. These reactions are fairly well-understood. Stauffers (one of Texas Alkyls' parent companies) has done some additional experiments with liquid DEZ and liquid water reactions, measuring the amount of ethane that is evolved.

According to tests performed by the Library, DEZ does not react with most book materials. In particular, the Library has concluded that DEZ

Figure 21 .—Product Safety Information Sheet for Diethylzinc

DIETHYLZINC (DEZ)

This Product Safety Information Sheet is principally directed to managerial, safety, hygiene and medical personnel. The description of physical, chemical and toxicological properties and handling advice is based on past experience. It is intended as a starting point for the development of safety and health procedures.

This sheet gives information only for the pure form of the chemical. Because the product is frequently sold in solution, the physical properties and toxicology of the particular solvent involved should also be considered in developing safety and health procedures.

This product should not be used until personnel handling it have been thoroughly trained. Contact Texas Alkyls, Inc., c/o Stauffer Chemical Company, Specialty Chemical Division, Westport, Connecticut 06880.

1. PHYSICAL AND CHEMICAL PROPERTIES

Chemical Formula: $(C_2H_5)_2Zn$
Molecular Weight 123.50
Physical State: Clear, colorless liquid
Melting Point: –30°C
Boiling Point: 117.6°C/760 mm Hg
Vapor Pressure: 15 mm Hg @ 20° C
Density: 1.198 g/ml @ 30° C
Viscosity: 0.7 centipoise @ 20” C
Flash Point: Pyrophoric — ignites spontaneously in air

II. CHEMICAL REACTIVITY

Reacts violently with water, air and compounds containing active hydrogen. Ignites spontaneously on contact with air. Compounds containing oxygen or organic halide may react vigorously with the material.

III. STABILITY

Diethylzinc is stable when stored under an inert atmosphere and away from heat. Dry nitrogen is a suitable inert gas. **Diethylzinc decomposes evolving hydrogen,** hydrocarbons and elemental zinc when heated to temperatures greater than 120° C, *Caution—decom-***position** may be **violent when temperatures exceed 150°C.**

IV. FIRE HAZARD

Product is spontaneously flammable in air. Pyrophoric by the paper char test* **used to gauge pyrophoricity for transportation.**

V. FIREFIGHTING TECHNIQUE

Protecting against fire by strict adherence to safe operating procedures and proper equipment design is the best way to minimize the possibility of fire damage. Immediate action should be taken to confine the fire. All lines and equipment which could contribute to the **fire should be shut off. The most effective fire extinguishing agent is dry chemical powder pressurized with nitrogen. Sand, vermiculite or CO_2 may be used.** *Caution* — **reignition may occur.**

DO NOT USE WATER, FOAM, CARBON TETRACHLORIDE OR CHLOROBROMOMETHANE **extinguishing agents as product reacts violently or liberates toxic fumes on contact with these agents.**

A **standard aluminized firefighting suit** is **recommended for fighting large zinc alkyl fires.**

Human exposure must be prevented and nonessential personnel evacuated from the immediate area. Breathing vapors from zinc alkyl fires should be avoided by using proper respiratory equipment. NIOSH-MESA approved air-supplied full face respirator should be used.

VI. TOXICOLOGY

1. Hazardous Combustion Products

In the presence of air, the compound will combust violently to form zinc oxide, CO_2, and water. Toxic irritants may result from incomplete combustion

In case of suspected DEZ exposure, refer to the procedure in Section VII —FIRST AID. Immediately call, day and night, one of the following emergency contacts:

—Local Physician (Veterinarian, if animal exposure is suspected)
—Nearest Hospital or Poison Control Center
—Texas Alkyls, Inc. (Call Collect) (713) 479-8411
–Stauffer Chemical Company (Call Collect) (203) 226-6602

In case of spillage or contamination of other materials with the product, refer to Section IX — HANDLING SPILLS and call:

–Texas Alkyls, Inc. (Call Collect) (713) 479-8411
–Stauffer Chemical Company (Call Collect) (203) 226-6602
–Chemtrec (800) 424-9300

*Reference W L Mudry, D C Burleson, D B Malpass, S C Watson, *J. Fire and Flammability,* 6, 478 (1975)

EXCLUSIVE SALES AGENT:
STAUFFER CHEMICAL COMPANY
Specialty Chemical Division
Westport, Connecticut 06880
(203)222-3000

SOURCE Texas Alkyls, Inc

2. Ingestion
Because of the highly motive nature of this compound with #r, ingestion is highly unlikely (See Skin Contact).

3. Inhalation
Because of the highly reactive nature of this compound with air, inhalation of this compound is highly unlikely.

4. Skin contact
Concentrated product will react immediately with moisture on the skin to produce severe thermal and chemical bum.

5. Eye Contact
Concentrated product will react immediately with moisture in the eye to produce severe chemical and thermal burns.

6. Threshold Limit Value (TLV)
There is no TLV for the product because the compound does not exist in air.

VII. FIRST AID

If a known exposure occurs, immediately initiate tha recommended procedures below. Simultaneously *Contact a Physician.* Describe the type *and* extant of exposure and symptoms.

1. Eye Contact
Immediately flush the eyes with large quantities of running water for • minimum of 15 minutes. Hold the eyelids apart 4&ring the irrigation to ensure flushing Of the entire surface Of the eye and lids with water. Do not attempt to neutralize with chemical agents. Obtain medical attention as soon as possible. Oils or ointmanta should be used only on the advice of a physician. Continue the irrigation for an additional 15 minutes if the physician is not immediately available.

2. Skin Contact
Immediately remove contaminated clothing tinder • safety shower. Flush all ● ffeoted areas with large amounts of water for at least 15 minutes. Do not attempt to neutralize with chemical agents. If ice is available, ● pply locally to the affected area. Obtain medical advice - - - & 4

3. Inhalation
Exposure to combustion products may cause respiratory symptoms. Remove from contaminated atmosphere. If breathing has ceased, clear the victim's airway and start mouth-to-mouth artificial respiration, which maybe supplemented by the use of a bag-mask respirator, or a manually-triggered oxygen supply capable of delivering 1 liter/second or more. If the victim is breathing, oxygen may be administered from a demand-type or continuous-flow inhalator. ● nd preferably with • physician's advice. Contact a physician immediately.

VIII. INDUSTRIAL HYGIENE PRACTICES

1. General Practices
Food should be kept in clean designated areas. Before eating or consuming beverages, face and hands should be thoroughly washed.

2. Inhalation
This compound should be handled in well-ventilated areas in order to minimize the potential exposure to combustion products. Control of those inhalation exposure can be achieved through the use of • cartridge-type NIOSH-MESA approved respirator.

3. Skin Contact
Dermal exposure must be avoided through the use of fire retardant clothing. During sampling, disconnecting lines or opening connections, additional protective outerwear including full face shield, impervious gloves. aluminized Nomex coat, a hard hat and chemical safety goggles should also be worn.

4. Eye contact
During sampling, disconnecting lines or opening connections, chemical safety goggles and a full face shield should be worn.

IX. HANDLING SPILLS

Block off source of spill, extinguish fire with extinguishing agent—see Section V. *Caution*—Reignition may occur. If fire cannot be controlled with extinguishing agent, keep a safe distance, protect adjacent property and allow product to bum until consumed.

X. CORROSIVITY TO MATERIALS OF CONSTRUCTION

The product is not corrosive under inert conditions to metals commonly used in construction. some plastics ● nd elastomers may be attacked Texas Alkyls, {no. (713) 4?94411 or Stauffer Chemical company, Specialty Chemical Division (203) 222-3000 should be contacted for specific recommendations.

XI. STORAGE REQUIREMENTS

Exercise due caution to prevent damage or leakage of container. The product should be stored under an inert atmosphere and away from heat. See Sections III and X.

XII. DISPOSAL OF UNUSED MATERIAL

Combustion of the material by controlling feed of air and product is a suitable disposal procedure. The products from complete combustion are carbon #oxide, water ● nd zinc oxide. Alternately, disposal can be achieved by diluting the product with hydrocarbon (heptane, etc.) to less than 3 weight percent metal alkyl concentration and treating the hydrocarbon solution with water under • nitrogen atmosphere in a vented and agitated container. Allow for the generation of heat and flammable gas when treating with water. The products from hydrolysis are ethane and zinc oxide (hydrated). Conduct water treatment in the absence of oxygen to avoid possible ignition of flammable material.

XIII. DISPOSAL OF CONTAINERS

Zinc ● lky{ shipping containers • re returnable to Texas Alkyls, Inc., Deer Park, Texas. Return shipments of containers are to be made under DOT regulations.

does not significantly react with cellulose under process conditions. Although cellulose has compounds with loosely held hydrogen ions attached to it, some have hypothesized that the oxidation of these compounds in air binds the hydrogen ions. If there is any reaction with the DEZ, however, it is very slow.

Most common metals used in equipment and construction do not react with DEZ. In general, metal alkyls are not corrosive and the original plants at Texas Alkyls are still in operation. DEZ does, however, degrade many elastomers used in gaskets and seals. Texas Alkyls has developed over the years numerous specifications for gaskets, seals, piping, valves, etc. Other materials being used in the plant that have not been specifed by Texas Alkyls have been tested for compatibility by soaking samples in DEZ at ambient conditions.

There are two critical physical properties of DEZ which are not known that impact the design of the hardware. One of these is the specific heat of DEZ. The specific heat of a material determines the temperature changes that occur when the material is expanded or compressed. DEZ vapor is expanded and compressed a number of times during permeation. To ensure that DEZ does not get too hot during compression, pumping rates and pipe sizes must be specified according to the specific heat of the material. Since this has not yet been determined, the most conservative values, those for nitrogen gas, have been used for design purposes. Early pilot plant tests indicate that DEZ vapor temperatures can be satisfactorily controlled.

Heat transfer properties of DEZ are also not known. These properties are needed for designing the condensers and vaporizer. Heat transfer values for a typical hydrocarbon believed to behave similarly to DEZ were used for design. The actual values for both heat transfer and for specific heat will be determined during testing and incorporated in the full-scale design.

Although the exothermic reactions are well-established, it is difficult to predict what changes in temperature will occur in the books and the chamber during permeation. Heat will be generated in the books from the reactions taking place, and other possible causes. Attempts have been made to model the amount of heat retained by the books, the amount exchanged with the gases, and the amount dissipated by the chamber, however, the results have not agreed with the experimental data from the previous NASA tests.

Design and operating conditions have been developed based on the maximum temperature increase observed in previous tests. Extensive instrumentation, a conservative temperature limit for the system, and the ability to quickly introduce cool nitrogen gas into the chamber should allow an acceptable level of control of temperatures.

Also important is an understanding of the compatibility of various fire-fighting agents and techniques. Obviously, water as an extinguishing agent would not be appropriate for fighting a DEZ fire. DEZ fires are difficult to extinguish, however, reasonably effective techniques for controlling a DEZ fire have been established. Fire associated with small spills can be controlled by spreading dry chemicals, sand, or vermiculite over the spill. This prevents DEZ vapors from coming into contact with the air. However, if the spill is disturbed, the trapped vapors could escape and reignite. If the spill is large, the fire is normally allowed to burn itself out. If a large fire is in an area that threatens other equipment, a fine water mist can be used to dissipate the heat of the fire, thus protecting nearby equipment, storage tanks, etc.

Design for Safety

The Library has put together a competent design team for the second pilot plant. They have retained the full-time service of a chemical engineer (consultant) who is responsible for overseeing the design, construction, and operation of the plant on a day-to-day basis.

The Library has contracted with Texas Alkyls to design, construct, and operate the plant. Texas Alkyls has been manufacturing metal alkyls since 1959, and DEZ for nearly as long. They have developed well-established specifications for materials for construction, hardware, etc.

The actual design and construction of the plant has been subcontracted to S&B Engineering. S&B

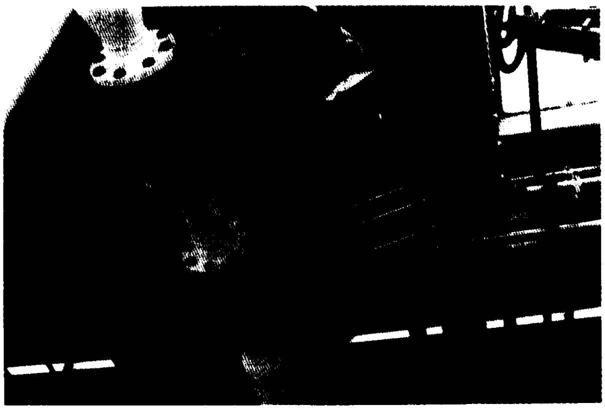


Photo credit: Library of Congress

This double-block valve at Texas Alkyls pilot plant is a key element in the safety system. It is controlled by the computerized distributive control system (DCS).

has designed and constructed two other metal alkyl plants for Texas Alkyls.

The principal safety-related design criteria for the second pilot plant, and those which will probably be used for the full-scale plant as well, are:

- use a minimum amount of DEZ, and keep a strict inventory;
- keep DEZ in the system and air out of the system;
- prohibit liquid DEZ or liquid water from getting into the chamber, or from coming into contact with each other anywhere else in the system;
- keep the temperature throughout the system below 80° C;
- use a computerized distributive control system (DCS) to operate a series of safety interlocks; and
- design all lines and containment vessels for both high and low pressure and provide proper pressure relief mechanisms.

A minimum amount of DEZ will be in the sys- tern at any one time. Only the amount needed to complete one batch treatment plus some reserve to allow for variations in DEZ requirements will be transferred from the liquid DEZ storage tank, located 15 feet from the plant, to a DEZ holding tank inside the plant. The holding tank is separated from all other plant systems by a fire wall. The DEZ is vaporized and recycled continuously during permeation.

To reduce the risk of component or line failures and the subsequent release of DEZ to the atmosphere, well-established specifications developed over the years by Texas Alkyls are used for materials and construction. Wherever possible, reliable (and tested) off-the-shelf pumps, valves, heat exchangers, etc. are used. In cases where hardware may use materials not specified by Texas Alkyls, materials compatibility tests have been run, by exposing the materials to liquid DEZ for a few days and analyzing for deleterious reactions.

The design deficiencies cited in the first pilot plant accident report have been eliminated. Redundancies have been designed into the system to prevent either liquid DEZ or liquid water from getting into the chamber and to prevent water and liquid DEZ from coming into contact with each other anywhere in the system. The design of the chamber was evaluated against a worst case scenario where liquid DEZ comes in contact with liquid water in the chamber. The design was reviewed by two independent consultants to ensure that the chamber could contain the resulting overpressure and safely vent it to the atmosphere.

To ensure temperatures stay below 800 C, more instrumentation has been added to monitor temperatures and pressures. The capability to circulate heated or cooled nitrogen gas through the chamber has been added to better regulate book temperatures during processing.

Operation of the pilot plant will be aided by a computerized distributive control system (DC S). The DCS will continuously monitor the entire system and manage a series of interlocks to ensure that all operations are performed in the proper sequence and under accepted conditions. If operations have been performed out of sequence or if conditions in the system are not acceptable, the DCS will not allow the process to proceed. The operator cannot override the DCS without action from the shift supervisor. In an emergency situation, the DCS will safely shut the system down. A backup electrical supply will allow the DCS to safely shut the system down in the event of a power failure. Texas Alkyls has gone as far as requiring a check for thunderstorms which may affect power supplies before initiating the permeation stage of the process.

Should a spill, leak, or over pressure situation arise, measures have been taken to isolate the hazard from personnel and from as much of the plant as possible. Liquid DEZ is kept in one corner of the processing area, behind a fire wall. The floor is sloped to route any spills and fire away from the processing area and other liquid DEZ vessels. Remote handling of the system will keep the operator isolated in a control room behind a fire wall and away from any flares due to DEZ leaks. All lines and containment vessels are equipped with pressure relief valves that will safely vent gases to the outside environment. All pressure relief systems are designed to National Fire Protection Association codes.

Hazard alarms have been placed around the plant to alert the operator to heat, fire, or explosion. Hand-held extinguishers are placed around the plant for both electrical fires and DEZ-related fires. Manually initiated sprinkler systems capable of applying a fine mist of water have been installed throughout the plant to help dissipate the heat from any fire and protect personnel and surrounding equipment. The sprinkler system is not activated automatically, since it may not be the appropriate response. The appropriate fire control action is left to the judgment of the operator. The alarm systems, sprinkler system, and hand-held fire extinguishers have been designed in accordance with accepted National Fire Protection Association codes.

It has also been suggested by the Library's outside safety specialists that (for the full-scale plant) the building and the fire wall separating the chamber room from the control room be designed to withstand an overpressure of 80 to 100 pounds per square foot, in case of explosion.

Operational Safety

The safe operation of the system demands skilled and experienced operators. These operators must be thoroughly trained not only in the operation and logic of the entire system, but also trained in the hazards of DEZ, in general, safety and emergency operations (including fire fighting and first aid), housekeeping, and maintenance. The consequences of a breakdown in operational safety are evident in the first pilot plant accident.

The use of a computerized distributive control system demands that the interaction between man and computer is firmly established. This requires a detailed operating manual that clearly spells out the respective responsibilities of the operator and the computer and extensive hands-on training.

Texas Alkyls brings over 20 years of expertise to the operation of the pilot plant. Texas Alkyls has developed safe and effective operating, inspection, maintenance, housekeeping, and emergency procedures. They have reported only five loss time accidents since 1959. Furthermore, they have reassigned eight of their top operators to work on the deacidification program. These operators have received 12 hours of training on the distributive control system as well as 11/2 months of training on the total system during the commissioning of the plant.

Safe operation of the DEZ system also requires detailed operating procedures. The pilot plant operating manual was reviewed by OTA, as well as the Library's outside consultants. In general, the degree of detail was judged to be satisfactory, although it was not yet complete at the time of the review. The manual divides the 3 major steps of the process into 17 smaller, more detailed steps. Each step contained a general description, a detailed set of operations, which included the reason for each operation and appropriate precautions, a list of the permissive that must be met before initiating the step, and a list of the various interlocking conditions governing the step. The manual also contained the startup and shutdown procedures and a general description of emergency procedures. There was some concern that the manual may be vague in certain areas, relying too much on the expertise already existing with the Texas Alkyls operators. If this manual serves as the basis for the manual used at the full-scale facility, it must be modified to apply to operation by personnel with less plant experience.

Safety Management and Review

Safety management and review is so important that it must be considered at every stage of process development— design, construction, and operation.

It is advisable, at the beginning of a development program, to setup a distinct safety function within the management of the program. This management would be responsible and accountable for designing and implementing a safety plan. The plan should establish what kind of safety analyses and outside reviews are appropriate; schedule and conduct these analyses at the appropriate times; document the safety needs and requirements that come out of the analyses; ensure that these needs and requirements are included in the design and specifications of the plant, hardware, and operation manuals; and document the implementation of these needs and requirements in the final construction and installation of equipment.

Analysis is a key element to a successful safety program. There are a variety of safety analyses that have been developed. They all incorporate the same basic principles—identify the hazards associated with the process or plant, determine the various ways these hazards may come about and the consequences of them occuring, and determine the best way to eliminate or reduce the chance or the consequences of them occurring.

The analyses, however, are of no practical use if the results are not carried out. Documentation and verification are critical.

The Library has made safety a distinct function within the management of their program. The consulting project engineer has coordinated both in-house and outside reviews, and has received reports on the results.

The Library, Texas Alkyls, and S&B Engineering conducted an in-house "HAZOP' review. "HAZOP" was developed by DuPont Management Consulting Services to assist in identifying and eliminating or minimizing the risks associated with chemical processes. The review used piping and instrumentation diagrams and examined them line by line. For each line the following questions were asked:

- What happens to the process as a whole if the following deviations occur in this line?
  —Flow—too high, too low, reversed?
  —Pressure— too high, too low?
  —Temperature—too high, too low?
  —Concentration—too high, too low, Contaminant?
  —Batch timing—too soon, too late, too short, too long?
  —Utilities—failure?
  —Others—commissioning, maintenance?

Besides examining each line, each major piece of hardware is also reviewed.

If any credible consequences were identified, the process was examined for possible causes (including multiple failures), in the absence of protection. If possible causes were identified, then the effectiveness of the existing protections were reviewed. If the existing protections were considered inadequate, assignments were made to study the problem further and take appropriate action. This was done before specifications, layouts, and procedures are finalized to allow flexibility in solving problems.

The results of this review have been tabulated, but the documentation could be improved. A number of possible events (or causes) are identified. Associated with each event is a general description of the existing protection, the necessary actions to be taken and those responsible for taking the action. The actions to be taken were written in very general terms, for example:

- action—DC logic (the distributive control system), or
- action—define operating procedures.

Before testing began, some of those who participated in the HAZOP exercise reviewed the various action items to ensure they were accomplished satisfactorily y.

Outside Reviews

The Library has hired six outside consultants to perform independent reviews in the following areas: plant operability, pressure vessel design; vacuum design; fire safety; and a worst case scenario. The consultants reviewed the designs for the pilot plant and those that exist for the commercial plant, before any hardware orders were placed. Written reports were presented to the Library. Any differences in opinion were discussed and resolved by consensus, although there is no documentation of this. However, the Library did perform a second outside safety review after the final construction of the pilot plant to verify that the various safety requirements and recommendations were implemented. The review was conducted by the same six outside consultants. Those with comments were invited back a second time to review the implementation of their recommendations.

SAFETY OF FULL-SCALE PLANT

Although a successful pilot plant program can demonstrate the safety of the DEZ system, it cannot assure it. The safety of a full-scale plant will depend on carrying forward all of the efforts and expertise that have gone into the pilot plant program. In addition, the full-scale plant will introduce public safety concerns.

Transportation Issues

The transportation of liquid DEZ to the full-scale plant will present a new set of risks to public safety. The principal hazard is fire. Leaky valves, a common event in the transport and handling of tanks, could cause DEZ vapors or liquid to be released and ignited. There is also the threat of explosion or rupture if the DEZ inside the tank disassociates. A firey truck accident, also not uncommon, could damage the relief valve and expose the tank to very high temperatures. If gases evolved as a result of rapid disassociation cannot be vented safely or quickly enough, an explosion could occur.

During the course of a year, Texas Alkyls will be trucking 15 to 20, 430-gallon tanks of neat liquid DEZ from their facility in Houston to the full-scale plant site. These will be individual shipments, since the storage of DEZ at the plant site will be kept to a minimum.

The 430-gallon tank will actually contain a nominal 390 gallons of DEZ, or 3,900 pounds. The tanks are standard portable steel tanks, constructed in accordance with DOT regulations (DOT CFR 178.245). They are designed to contain pressures up to 200 psig. The DEZ will be shipped under low pressure. The tank is fitted with a 45-psig relief valve. The tank has a frame around it to facilitate handling,

Texas Alkyls normally ships its DEZ diluted in hexane. Although it is still pyrophoric, the hexane acts as a heat sink, keeping the DEZ below its disassociation temperature. However, because it will be shipping neat DEZ, Texas Alkyls has taken the added precaution of insulating the tank with 4 inches of calcium silicate, and wrapping it in a stainless steel shield.

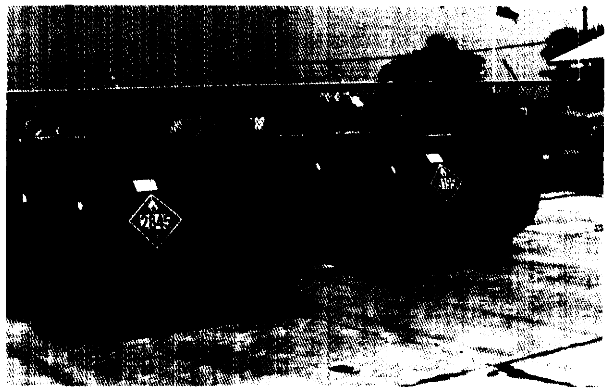


Photo credit: Library of Congress

430-gallon DEZ storage tanks at Texas Alkyls

The insulated tank was designed with the help of Stauffer Chemicals Research. The design criteria was to limit the temperature rise of the DEZ in the tank to less than 40 C when exposed to a standard DOT bonfire test. The standard DOT bonfire test exposes objects to a temperature of 870°C for 1/2 hour. A small test cylinder insulated with calcium silicate was subjected to the bonfire test. The cylinder survived the test, the DEZ temperature inside the tank remained virtually unchanged and the paint underneath the insulation showed no signs of being affected by the heat. A similar uninsulated cylinder of propane was tested along side the DEZ cylinder and exploded. Calculations indicated that the 430-gallon tank would require 2 inches of insulation, 4 inches were added as an additional safety factor.

Incidents Involving the Transportation of DEZ

All incidents associated with the transportation of hazardous materials must be reported to DOT. Since 1979, no incidents involving DEZ have been reported. There have been five incidents involving metal alkyls. All involved relatively small volumes. All were fire-related, resulting from faulty valves or valve connections. No injuries were reported; losses totaling about $11,000 were attributed to the incidents.

These incidents apparently involve secondary shipments of metal alkyls. There are no reports that Texas Alkyls has had any incident involving the transportation of its products. They ship their products in sizes ranging from one-liter vessels to railroad tank cars that can hold about 30,000 gallons.

Shipping Plans

The details concerning who and how DEZ will be shipped to the full-scale plant have not been developed. Texas Alkyls contracts a commercial carrier to ship their products. Shipments are normally made in in enclosed van. Normally, Texas Alkyls only provides training to tank truck drivers. They are given a demonstration of what a pyrophoric fire is like, shown a film on the safe handling of DEZ, and instructions on how to deal with local officials in the case of an accident, If considered useful, this training could also be made available to those enclosed van drivers shipping DEZ to the full-scale plant.

During the testing at NASA-Goddard, the Library made preliminary contact with the fire marshalls at Fort Detrick and Frederick because of the plans to locate the full-scale plant at the Fort. Discussions on a safe route from the interstate to the site and fire control techniques were discussed. No formal plans were developed. The Library also approached the Frederick City Council, where the safety of the proposed shipments was debated. These contacts were suspended after the NASA-Goddard accident. If the Library locates the plant at Fort Detrick, the Library intends to revive these discussions sometime in 1989, possibly through the Army Corps of Engineers.

Other Safety Issues Related to the Full-Scale Operation

The decisions as to who will finally be responsible for designing, constructing, managing, and operating the full-scale plant must still be made. From a safety point of view it is imperative that the effort that went into the Texas Alkyls' pilot plant be carried forward completely to the full-scale plant.

It is important that the contractor for the construction of the full-scale plant establish, as early as possible, effective communication with Texas Alkyls and S&B Engineering, who will have acquired the most experience with the process. It is critical that the expertise of Texas Alkyls is transferred completely to the full-scale operation. It is possible that the contract will go to Texas Alkyls.

RISKS

The transportation and use of DEZ poses risks to workers, the public, the plant, and books. These are discussed briefly in the following section.

Risk to Workers

Leaks or spills during operation pose a minimal risk to the worker if safe operations are followed. Operation is remote and the operator sits behind a fire wall. Liquid DEZ is located in the far corner of the plant. The fire control panel used to operate the automatic sprinkler system would be located some distance away from the plant.

During a fire the risk is higher. The operator must decide whether to use the sprinkler system or not. There is an opportunity for an error in judgment. The fire or the intensity of heat can cause injury if the choice has been made to control the fire manually. Proper clothing and breathing devices as well as fire-fighting devices are needed.

The greatest risk to workers occurs during maintenance. Detailed maintenance procedures and tests are needed to reduce the chance of burns. Proper clothing and breathing devices (for enclosed spaces) are needed, and work should be done in teams. The only injury recorded during the development of the DEZ process was a worker at the G.E. test facility that burned his arm when some DEZ mixture dripped on his skin from piping that he was cleaning. The injury was minor, however, and did not require hospitalization.

There is some risk of injury or asphyxiation if a person enters the chamber when the door to the chamber is opened, since this is also a manual operation.

Proper strengthening of walls, etc. should reduce the risks associated with explosion for any enclosed spaces.

Risk to Public

For the full-scale plant, the public is at some risk due to the transportation of DEZ from Houston, Truck accidents are the most frequent incident involving the release of hazardous materials. [2] Furthermore, the tipping or loss of portable tanks during transit are a common mode of accident. Nevertheless, fire during transit would be localized and would not expose a large number of people to the hazard. A more complete transportation risk assessment could be included in the environmental assessment yet to be completed for the full-scale plant.

2 U.S. Congress, Office of Technology Assessment, *Transportation of Hazardous Materials,* OTA-SET-304 (Washington, DC: U.S. Government Printing Office, July 1986).

Risk to Plant

The plant is at greatest risk. Fire due to leaks or spills are inevitable, even if the chances are kept low by proper inspection and maintenance. The types of fire that can be expected will be short in duration but very hot and could cause extensive damage. Damage can be controlled by keeping the fire isolated and cool with an appropriately designed sprinkler system, The chance of explosion is more remote than fire, but the consequences could be much greater.

Risk to Books

The books remain relatively safe. Fire in the chamber is a very remote possibility, given the redundancy in design, Excess zinc oxide deposition, although not necessarily harmful, may create visual problems. Wear and tear from book handling may also cause damage.

DISCUSSION

DEZ is a hazardous substance. Any system using DEZ is susceptible to fire and explosion. However, with proper design and operation, these hazards can be managed.

The second pilot plant has been built to good chemical process engineering standards with careful attention to safety. OTA finds these efforts adequate, but the pilot plant tests during 1988 are needed to demonstrate all safety aspects. As of February 1988, four initial commissioning runs of the pilot plant have been completed in a safe manner and without incident.

The full-scale plant will need equal or greater engineering attention. Scale-up design will need to consider some additional engineering problems. Safety practices will need to consider problems related to a new site, new plant management, new operators, and a new community setting.

OTA has qualitatively assessed the risks and feels the greatest risk is damage to the plant itself. The greatest human risk is to plant workers during initial hookup of the DEZ storage tank, maintenance, or fire-fighting.

There is a marginal risk to the public as a result of shipping DEZ. The Library must take extra precaution to analyze that risk and work with the local community in minimizing those risks.