Chapter 2

The DEZ Process and Its Development

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INTRODUCTION

This chapter briefly describes the DEZ process and its evolution. OTA finds that the evolution has followed a reasonable path from laboratory to pilot plant demonstration. However, OTA is conducting its evaluation in the middle of ongoing development efforts and there are a number of engineering issues that remain to be solved, including how the Library will scale-up to a full-scale facility.

THE DEZ PROCESS

General Description

The mass deacidification process that the Library has been developing uses DEZ vapors to treat books. DEZ belongs to a class of compounds called metal alkyls or organo-metallics. Metal alkyls, in general, and DEZ in particular, will react very quickly with free hydrogen ions. Therefore, acids, being generous donors of free hydrogen ions, will react very quickly with DEZ. Deacidiflcation occurs as DEZ vapors permeate the books and react with all acids in the paper converting them to zinc salts.

DEZ vapors also react with water in the paper to form zinc oxide. The zinc oxide acts as an alkaline buffer that can neutralize any acids that may form after treatment. The amount of zinc oxide that gets deposited depends in a large part on the amount of water in the books. It also depends on the amount of the DEZ used, time or rate of exposure, and particular permeability of the paper.

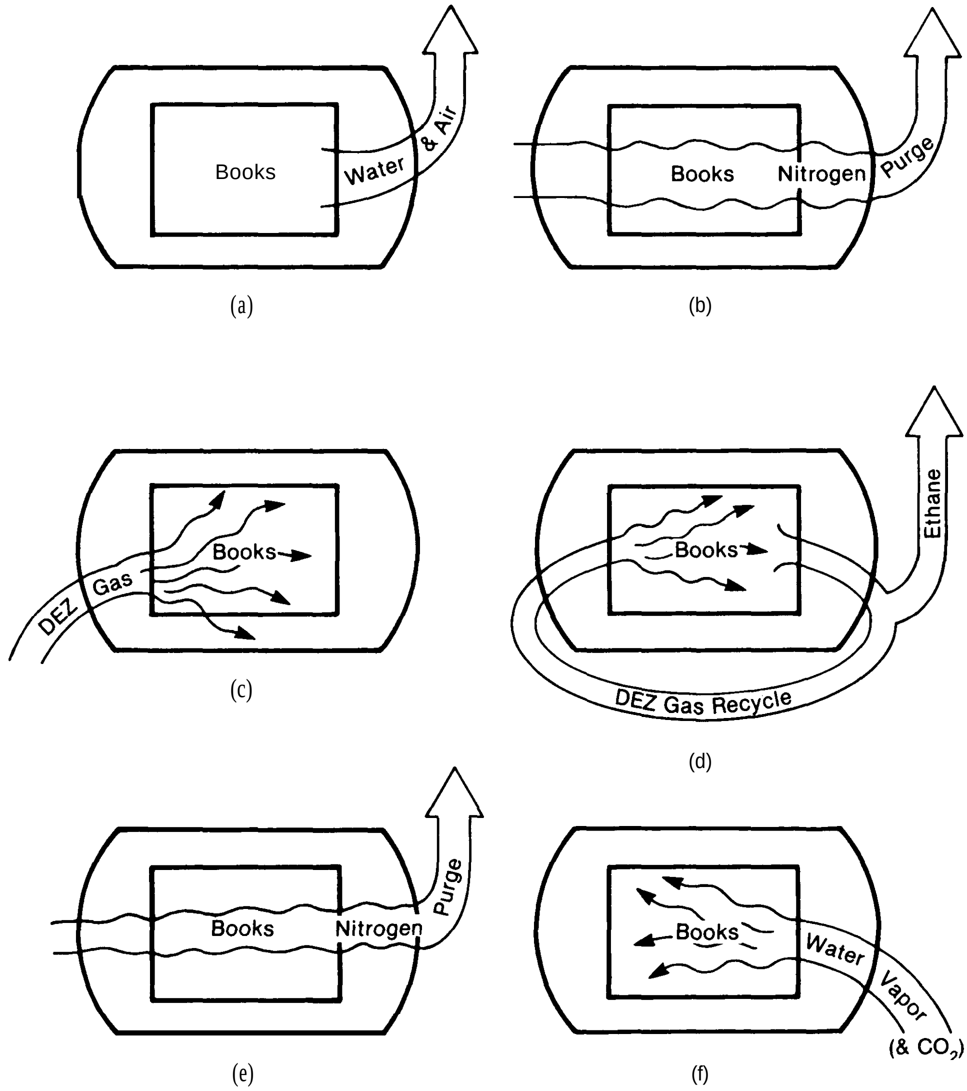
The process basically consists of three steps; dehydration, permeation, and dehydration. Dehydration reduces the amount of water in the books to some predetermined amount based on the amount of zinc oxide that is desired. Permeation exposes the books to the DEZ vapors. Dehydration soaks the books in water vapor to restore moisture to the books. An optional step during dehydration is to soak the books in moist carbon dioxide. This option will be discussed more fully later in this chapter.

Metal alkyls are pyrophoric, meaning they will spontaneously ignite if they come in contact with air. Therefore, the book treatment process must take place in an air-free environment within a vacuum chamber. The Library process uses DEZ as a gas only at very low pressure within the vacuum chamber.

The following is a general description of the process as it has evolved to date:

> Books are placed in a processing chamber. The air in the chamber is removed through a vacuum pump, lowering the pressure inside the chamber. The chamber is kept at a low pressure while the books are heated. Water migrates out of the books and evaporates. The evaporated water is removed through the vacuum pump. The amount of water removed is monitored indirectly by measuring book temperatures (see figure 5a).
>
> Once the desired amount of water has been removed, the chamber is purged with nitrogen gas to ensure that no air remains in the chamber (see figure 5b).
>
> After the chamber is purged, DEZ vapors are introduced into the chamber. DEZ vapors react with the acids and water in the books generating both heat and ethane gas. Exposure to the DEZ vapors continues until no more heat or ethane are evolved or until the desired amount of zinc oxide has been deposited. The amount of zinc oxide that has been deposited can be monitored indirectly by measuring book temperatures (see figure 5c).
>
> Ethane gas and unreacted DEZ vapors are removed from the chamber. The unreacted DEZ is condensed and recycled. The ethane is vented to the atmosphere (see figure 5d).
>
> When the permeation step has been completed, the chamber is again purged with nitrogen gas to ensure that all of the ethane and unreacted DEZ is removed (see figure 5e).
>
> After the chamber is purged, water vapor (or moist carbon dioxide) is introduced into the cham-

Figure 5.—Key Steps in the DEZ Treatment Process



SOURCE: Office of Technology Assessment, 1988.

ber. The books are allowed to soak in the water vapor until much of their original moisture content is restored. The amount of moisture taken in by the books is estimated by monitoring water introduced (see figure 5f.

When the desired amount of moisture has been restored, the chamber is vented to the atmosphere and opened and the books removed.

Process Control

Physical and chemical events during processing with DEZ occur over a relatively wide range of temperatures and pressures. Therefore, fine control of these parameters is not needed except to optimize the process. However, there are a few critical temperatures and pressures that do impose limits on the process. Thus the temperatures and pressures must be accurately monitored and measures must be incorporated to control them.

During dehydration, the books will lose heat. The book temperature must be controlled to prevent them from freezing and to keep cycle time short. Also during dehydration, it is undesirable for the water vapor in the chamber to condense, therefore, the interior surfaces in the chamber must be kept above the dew point temperature of water.

If the water does condense and remains in the chamber as a liquid it will react with the DEZ vapors during permeation and will foul the chamber with excess zinc oxide and will waste DEZ, If liquid DEZ should somehow enter the chamber during permeation and there is liquid water present, there will be a vigorous reaction, generating excess ethane and heat which will quickly raise the pressure and temperature inside the chamber. A pressure relief valve is fitted in case maximum pressure limits are exceeded.

During permeation, the DEZ reactions with the acids and water will generate heat. The book temperature will rise. Paper begins to degrade at 1000 C, and other book materials may be damaged. At 1500 C, the degradation can be very rapid. Therefore, temperatures inside the chamber are kept well below 1000 C. At the same time, however, it is undesirable for either the DEZ vapors or the ethane gas to condense inside the chamber. Therefore, the temperature of the internal surfaces within the chamber must be kept above both dew points.

The most critical constraint in the process is the stability of DEZ. DEZ begins to decompose at 1200 C. At 1500 C the decomposition will become self-sustaining and uncontrollable. Therefore, temperatures throughout the system, including the chamber, are kept below 800 C. The present system design goal is to keep book temperatures at 600 C or below. Ongoing pilot plant tests will confirm whether this goal is feasible.

Dehydration also generates heat, about as much and as rapidly as does permeation.

Temperature control in various pieces of hardware is maintained by circulating heated or cooled oil. The book temperature is controlled by introducing heated or cooled inert gas.

Besides monitoring and/or controlling temperature, pressure, and book weight, an accurate inventory of DEZ is maintained. The total amount of DEZ at the start of the cycle must be accounted for at the end of the cycle. All DEZ holding vessels are weighed. The difference in weight before and after treatment must be balanced by the amount of DEZ that was reacted in the books. The latter amount can be determined by the weight gain in the books during permeation. Pilot plant tests will confirm whether this measurement or some other means of monitoring is feasible. The importance of maintaining an accurate DEZ inventory will be evident in the discussion of the first pilot plant's accident, in chapter 5.

In general, the process is relatively straightforward, but it does involve a complex sequence of operations. It also requires extensive monitoring to ensure safe and efficient operation. A computerized distributive control system (DCS) has been incorporated to assist the operator in monitoring, managing, and controlling the system.

The computer continuously monitors pressures, temperatures, flow rates, etc. throughout the system. In addition, it continuously monitors the status of all valves (e. g., open/closed) and pieces of equipment (e. g,, on/off). Before the initiation of any action, the computer checks these parameters against a set of predetermined values, called "permissive, that are programmed for that stage of the process. Any action, whether initiated by the operator or the computer, cannot be performed if these permissive are not satisfied. If the permissive are breached during operation, or in the case of an emergency, the computer is programmed to safely halt or shut down the process. The interaction between the human operator and the computer is critical for the safe operation of the plant and will be discussed further in chapter 5.

Cycle Times

Current estimates of the cycle time for a full-scale operation range from 45 to 55 hours. The cycle time is limited mainly by the rate at which books can be dehydrated. Depending on how the books are stacked in the chamber, the larger the number of books being treated, the longer it takes for books in the interior of the stack to give up their water. Dehydration times can be affected by the rate the water vapor is pumped out of the chamber. Pumping too fast, however, will lower the book temperature too fast. As of this writing, estimated dehydration times for a full-scale operation would range from 25 to 30 hours. Permeation, in a full-scale operation, would take from 6 to 9 hours and dehydration 7 to 8 hours. Other steps as well as loading and unloading books would bring total cycle time to 45 to 55 hours.

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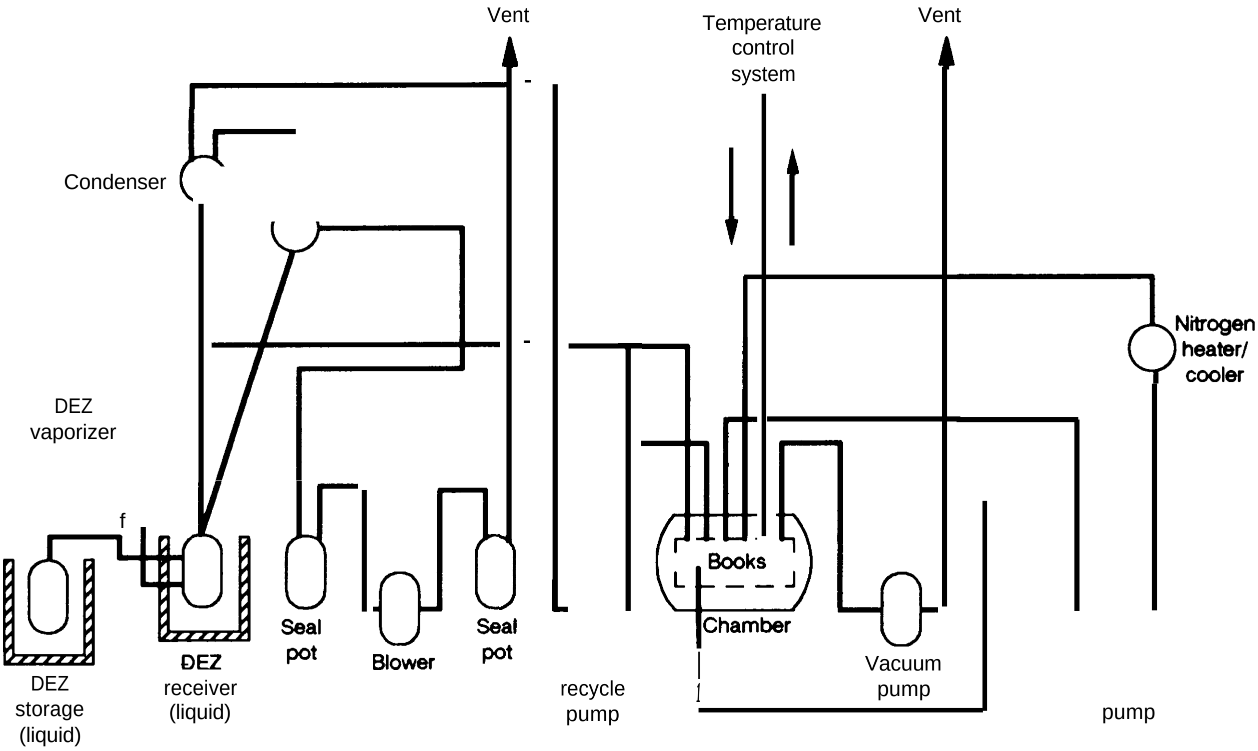
Figure 6.-Simpltfied DEZ Process Flow Diagram



SOURCE: Office of Technology Assessment, 19%0

Hardware

The hardware and capital investment required for the Library plant is large. Because of the hazardous nature of DEZ, the need to locate in an area zoned for chemical operations, and the lack of available space near the Library of Congress, a separate facility away from the Library would have to be built. A simplified flow diagram is shown in figure 6. The system would consist of the following subsystems:

- processing chamber or chambers;
- a vacuum system;
- a DEZ handling system that would nominally include liquid DEZ containers, a DEZ vaporizer, condenser(s), pump, and sealpots;
- a nitrogen gas system;
- a water vapor system; and
- a heat exchanger system used for temperature control.

As mentioned, the operation of the system will be managed by a computerized distributive control system.

Capital costs are discussed more fully in chapter 4, A detailed design of the full-scale plant has not yet been started but the general approach would be to scale-up from the pilot plant making any modifications that appear warranted after completing pilot plant tests. The book treatment capacity of the pilot plant is about l/25th the scale envisaged for the full-scale plant.

DEVELOPMENT HISTORY OF THE DEZ PROCESS

Objectives

Since its beginning in 1973 the objective of the mass deacidification development program has been to develop a process that would:

- process large numbers of books and other formats, capable of treating the entire book collection in 20 years;
- require no preelection (i. e., be compatible with all other book materials, inks, pigments, etc. and cause no visual or tangible differences in the treated material);
- prolong the life of the book as much as possible (i.e., permanently and completely neutralize all acids and deposit a sufficient permanent and uniform alkaline buffer);
- be cost-effective; and
- be safe.

Selection of DEZ

Based on the above goals, the Library decided to pursue the development of a vapor phase process as opposed to a liquid phase process. The Library's chemists felt that large numbers of books could be more quickly and uniformly treated by vapor reactants diffusing around and through the books. Also, the liquid phase processes in use required pretesting to ensure that the materials to be treated were compatible with the solvents used.

There were a few vapor phase deacidification processes that had already been developed. A morpholine process was developed at the Barrows Laboratory, and two amine-based processes, one using cyclohexylamine carbonate and one using ammonia, were developed in England and India, respectively.

The Library experimented with the morpholine process. The principal limitation of this process is its bad odors that cause headaches and nausea in process workers. Other problems include an insufficient buffer, and questionable health effects. The process had the potential of forming nitrosamines which could be inhaled by workers. Morpholine can also discolor paper.

The cyclohexylamine carbonate process was developed by Langwell in the early 1960s. The patents now reside with B.G. Robertson Laboratories, London. Interleaf, Inc. is the sole distributor of the product in the United States. This is basically a manual process, but is so simple that it could be used to treat a substantial number of books. Cyclohexylamine carbonate crystals are placed in a packet in a book every 100 pages. Cyclohexylamine is volatile and vapors containing the carbonate compound permeate through the book, reacting with and neutralizing the acids. This process does not leave an alkaline buffer, however, and the byproducts from the acid reactions are themselves volatile. Under certain conditions, these byproducts can revert back to the acid and give off an ammonia-like odor. Also, at the time the Library was investigating these various processes, the health effects of cyclamates were a concern, raising questions about the health effects of cyclohexylamines as well.

Kathpalia, also in the 1960s, developed an ammonia process. It suffers from many of the same problems as the cyclohexylamine process, except that the acid reaction byproducts are even more volatile.

Unable to justify developing any of the existing processes or chemicals, the Library began to search for its own chemical and process. Table 2 is a list of the compounds that were evaluated, To meet their objectives, the chemical had to have a high vapor pressure within the temperature limits of the process (i. e., between O and 800 C), it had to react with all acids present in books, without forming any deleterious reactions with any of the other book materials, the acid reaction byproducts had to be stable, and an alkaline buffer had to be created to neutralize any acids that could form after treatment.

Metal alkyls represented a class of compounds that met these various requirements. Metal alkyls are very reactive and will quickly neutralize all the types of acids found in paper. In addition, either directly or indirectly, the metal alkyls react with moisture in the paper to form stable alkaline com-

Table 2.—Compounds Tested by the Library's Laboratory for Deacidification of Paper, 1970.74

1. Triethyl aluminum
2. Diethylzinc
3. Ethylene imine cyclohexyl amine carbonate
4. Morpholine
   Hexamethylene diamine formaldehyde
: : Calcium hydroxide and calcium bicarbonate (Barrow two step)
7. Calcium chloride and ammonium carbonate (double decomposition)
8. Borax
9. Methyl zinc carbonate
10. Magnesium acetonyl acetonate
11. Magnesium hexafluoroacetyl acetonate
12. Barium acetyl acetonate
13. Cyclohexyl amine carbonate (Langwell VPD)[a]
14. Silane deacidification agent (Dow Corning Z-6020)
15. Sodium carbonate and magnesium chloride
16. Magnesium methoxide and methyl magnesium carbonate
17. Zinc ammonium carbonate
18. Ammonium zirconyl carbonate

[a]Compound used in the Interleaf process.
[b]Compound used in the Wei T'o Process.

SOURCE: Library of Congress.

pounds. The amount of stable alkaline compound deposited depends on the amount of moisture in the paper and can, therefore, be controlled.

The metal alkyls, however, were of concern regarding one major objective of the development program—safety. Metal alkyls are pyrophoric. If allowed to come in contact with air, they will spontaneously ignite. Furthermore, they react very vigorously with water. Both reactions give off ethane which is flammable and potentially explosive under certain conditions. The metal alkyl-water reaction that would deposit an alkaline buffer in a book involves very small volumes of these reactants and therefore is not a violent reaction. However, it will generate heat and must be controlled.

Metal alkyls have been used for many years in a variety of applications. Their major use today is as an intermediate in the manufacturing of polyethylene and polypropylene. Fully aware of the hazards associated with metal alkyls, the Library felt that these hazards were manageable and that the advantages of the compounds were worth the costs associated with developing a safe process.

Of the various metal alkyls tested, DEZ had the highest vapor pressure in the temperature range involved. Initial tests indicated that papers exposed to DEZ vapors were deacidified, had an alkaline zinc oxide buffer deposited, and appeared not to be adversely affected in any way. Based on these conclusions, the Library proceeded to develop a process around DEZ.

Process Chemistry

In the early stages of developing the DEZ process, the following reactions were thought to occur:

- DEZ vapors react with both weak and strong acids to form stable zinc salts and ethane gas.
- DEZ vapors react with hydroxyl groups on the cellulose molecule to form an unstable compound, ethylzincoxycellulose. During dehydration, this unstable compound would form zinc oxide and ethane and return the cellulose to its original form.
- DEZ vapors react with aldehyde groups on the cellulose molecule to form a stable alcohol and ethane gas.

Originally, processing was based on eliminating as much of the water as possible, and using the hydroxyl reaction to form the alkaline buffer. It was hypothesized that the amount of water in a book, nominally 6 percent of the book's weight, would impede the permeation of DEZ into the center of the book by immediately reacting with the DEZ on the book's outer edges. It was also thought that partial dehydration of the books during permeation would leave a moisture gradient within the books that would result in an undesirable gradient in the amount of zinc oxide that would get deposited. The hydroxyl group, however, could be expected to remain evenly distributed throughout the paper and the books and result in a uniform distribution of zinc oxide buffer.

Later experience indicated that this hydroxyl reaction must be slow and that most of the alkaline buffer that gets deposited is the result of the water reaction. A test that exposed very dry pure cellulose paper to DEZ vapors supports this observation. Therefore, the amount of alkaline buffer deposited in the books depends to a large extent on the amount of water left in the book. It also depends on the amount of DEZ the books are exposed to, possibly the rate and time of exposure, and the particular properties (e. g., permeability) of the paper being treated.

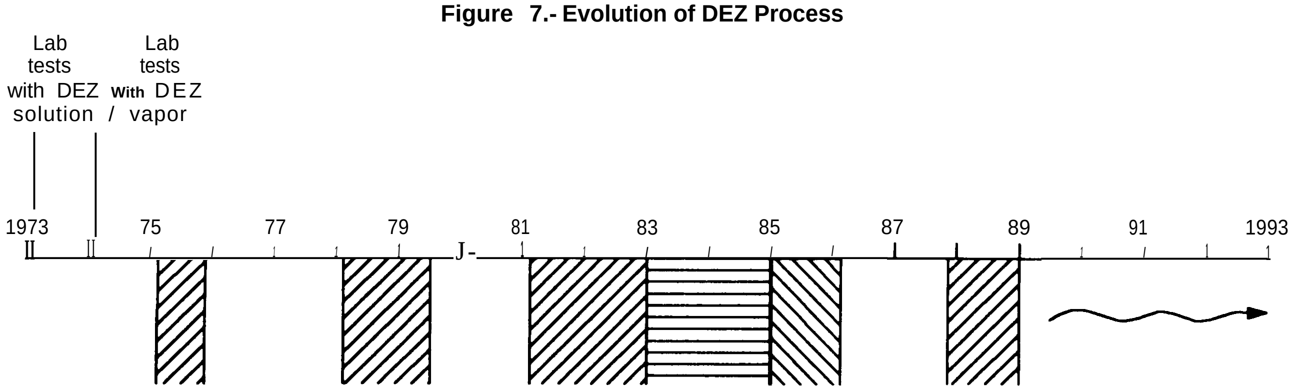
After development had proceeded, the Library chemists became aware of studies that indicated zinc oxide could promote photodegradation of paper. The Library conducted a few tests that showed treated papers were more sensitive to photodegradation.[1] Although photodegradation is not considered a serious problem at the Library, especially in relation to acid deterioration and other degradation mechanisms, a solution to the problem was sought. The solution sought by the Library was to convert zinc oxide to zinc carbonate, which does not promote photodegradation, by soaking the books in carbon dioxide after dehydration. However, subsequent tests have shown that little if any zinc carbonate forms after soaking the books in carbon dioxide. Whether the carbon dioxide soak is useful and will remain as part of the treatment will be determined in future tests.

[1] George B, Kelly and John C. Williams, "Inhibition of Light Sensitivity of Papers Treated With Diethylzinc, presented at the Annual Meeting of the American Chemical Society, Washington, DC, September 1979.

Development History

The evolution of the DEZ process is shown in figure 7. The Library began bench-scale development in 1974. During these bench-scale tests, a pressure cooker was used as a process chamber. Sheets of test paper (or segments of books) were placed in the cooker. Air was removed and the books dehydrated. Dehydration continued until the pressure in the cooker stabilized with the vacuum pump turned off, indicating maximum dehydration. DEZ mixed in various concentrations with hydrocarbons (e. g., octane) was injected into the cooker as a liquid. The liquid sat at the bottom of the chamber and evaporated. Vapors permeated up through the paper of books, deacidifying the paper. Unreacted vapors were condensed at the top of the cooker and the liquid recycled. Dehydration was typically accomplished with nitrogen gas or alcohol saturated with water vapor which also neutralized any unreacted DEZ liquid remaining at the bottom of the cooker.

Figure 7.- Evolution of DEZ Process



	Pressure cooker tests	G.E. tests	NASA large scale tests	NASA small scale tests	NASA pilot plant	Texas Alkyls pilot plant	Proposed Fort Detrick plant
Capacity	1 or 2 books or stack of papers	400 books	5,000 books	100 books	300 books	300 books	?
DEZ system	Liquid DEZ mixture with reflux	Liquid DEZ mixture incremental feed, no reflux	Vapor DEZ mixture incremental feed with recovery	Vapor DEZ heat continuous feed with recovery	Vapor DEZ heat continuous feed with recycle	Vapor DEZ heat continuous feed with recycle	Vapor DEZ heat continuous feed with *recycle*
Cycle times	10 hrs	24-72 hrs	244 hrs	45 hrs	?	Est. 5(-90 hrs	?

SOURCE: Office of Technology Assessment, 1988

Photo credit LIbrary of Congress

Original pressure cooker test of DEZ at Library of Congress

Typical dehydration times were about 5 hours. Permeation times were about 5 hours.

The treated papers were evaluated for pH, zinc oxide content, and brightness. Some of the papers' fold endurances were also measured after accelerated aging. Typically, the results were positive, and are discussed in more detail in the next chapter.

The goal of the program, to treat the entire book collection in 20 years, required that the system had to treat about 1 million books per year. If two single chambers were used, 7,500 books would have to be treated in a single chamber. To test the feasibility of the process at this scale, a series of larger scale tests were begun.

In 1979, the Library contracted with General Electric's (G. E.) Valley Forge Space Center to use one of their large thermal/vacuum chambers, normally used for simulating space environments. The tests treated 400 books at a time. The principal objective of these tests was to confirm the feasibility of the process at this moderate scale. In addition, a variety of processing conditions were evaluated, including different ways of stacking the books in the chamber.

The G.E. chamber that was used was 12 feet in diameter and 26 feet long. Various processing hardware was fitted onto the chamber. The system was essentially the same as that used in the Library. A vacuum pump removed the air from the chamber. Liquid DEZ mixed with a hydrocarbon, Isopar E, was introduced into the chamber and allowed to vaporize in the chamber (the last test used 100 percent DEZ, called neat DEZ). However, because of the larger volumes of DEZ required to treat 400 books, it was introduced incrementally, as a precaution, to ensure that the amount of heat generated would not raise the temperature above the limits mentioned earlier. A separate pump was used to remove the ethane and unreacted DEZ vapors. These were removed into sample bottles. Unreacted DEZ liquid at the bottom of the chamber was neutralized with alcohol.

A total of four tests were conducted. Complete deacidification was achieved in two of the tests. Zinc oxide contents ranged from 0.5 to 1.4 percent. It was concluded that the best operating conditions were long exposures at low pressures using 100 percent DEZ.

The best book-stacking configuration seemed to be closed with the spine down. However, in each of the tests, tide marks were observed on the covers. The tide marks were diffraction patterns caused by excess zinc oxide. It was hypothesized that the tide marks *were* caused by a thin film of DEZ trapped between the books. Book covers generally hold more water than the inside pages, providing excess moisture for the excess DEZ to react with. It was recommended that books be separated to allow good circulation of DEZ between the books.

Another observation was that moisture and small air leaks into the system seemed to produce unwanted zinc oxide throughout the system, presenting a potential maintenance problem. It is also possible that small air leaks lead to the visible zinc oxide surface deposition on books.

The test also demonstrated that relatively large amounts of DEZ could be handled safely during treatment. Further work would have to be done to optimize the treatment, to reduce the amount of cycle time, and to remove the tide marks from the covers.

Encouraged by these results, the Library continued scaling up the process. In 1981, the Library contracted with NASA's Goddard Space Flight Center to use one of their thermal/vacuum chambers to treat 5,000 books.

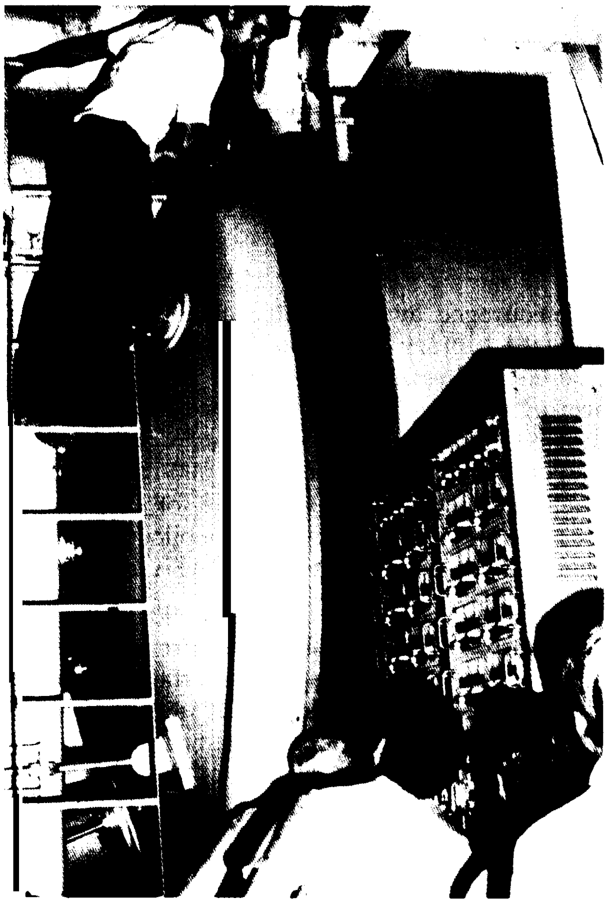


Photo credit: Library of Congress

Chamber used at NASA-Goddard for DEZ treatment

The size of the Goddard chamber was 10 feet in diameter and 15 feet long. The system was basically the same as the one used at G.E. with one major exception. DEZ, mixed with mineral oil, was first fed into a vaporizer and introduced into the chamber as a vapor. It was fed incrementally as a precaution and to control temperature rises in the books. The only temperature control for the books was radiant heat from the chamber walls. The unreacted DEZ was condensed and recovered. Alcohol was still available should any liquid DEZ be left in the chamber after permeation. Saturated carbon dioxide was introduced during dehydration to test the conversion of zinc oxide to zinc carbonate.

In addition to the system instrumentation, individual books were also monitored for weight and temperature to better track the process throughout the stack of 5,000 books.

Although this was basically a feasibility test, a substantial amount of engineering was done on the various pieces of hardware. A large number of safety reviews were conducted including a typical NASA fault tree analysis. Also, 15 *separate* subsystem operating procedures were detailed. This single test, including planning, design, and construction, took 1 year.

Books were loaded in crates, separated by spacers, and marked by their location within the chamber. Dehydration took 4 days (96 hours). The books were exposed to DEZ incrementally for 6 days (124 hours). The books were dehydrated for 24 hours.

The results of the test were mixed. There were three major problems.

First, treatment was not uniform throughout the stack of books. Books at the bottom half of the chamber were completely deacidified and had a average zinc oxide content of 2.2 percent. Books at the top levels of the chamber were hardly deacidified at all and had almost no zinc oxide deposited. Books in the middle of the stack were partially deacidified; the outer portion of pages were deacidified, but at the center of the book the pages were not deacidified. These middle books also had very little zinc oxide (about 0.2 percent). These results agreed with the data collected from the individual books that were monitored during the process.

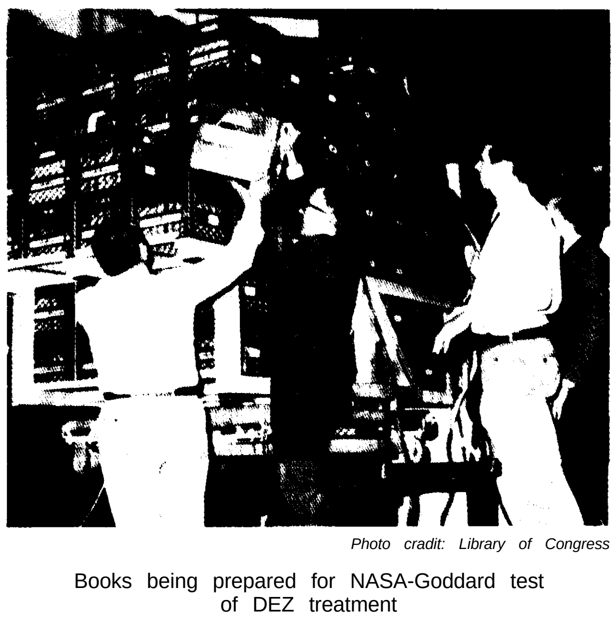


Photo cradit: Library of Congress

Books being prepared for NASA-Goddard test of DEZ treatment

Books at the top showed little temperature rise. The temperature of books in the middle rose near the end of the process, and the books at the bottom showed early increases in temperature. The evolution of ethane also indicated that most of the reactions occurred early in the process.

The cause of this first problem was judged to be stratification of the DEZ vapors and the evolved ethane. DEZ was introduced near the bottom of the chamber. Ethane, being lighter, naturally rose and sat at the top of the chamber. With only small amounts of DEZ being injected at any one time, the environment inside the chamber was basically static. Ethane impeded the flow of DEZ vapors to the upper books.

The second problem was that the zinc oxide was deposited in rings. The concentration of zinc oxide in these rings was high on the outside rings and diminished towards the center of the page. The rings were blamed on the incremental pulsing of the DEZ into the chamber. The hypothesis was that as the permeation step proceeded, water continued to migrate out to the edges of the books. With each new pulse, more zinc oxide would be deposited on the outside edges.

The third problem was that tide marks remained on the covers, duplicating the patterns of the spacers used to separate the books in the crates.

However, the tests were conducted safely at this scale.

To solve the treatment problems the Library continued with a series of smaller scale tests at Goddard. A large diffusion pump housing was used as the process chamber. Books were stacked in the test chamber in two 50-book stacks.

Thirteen tests were conducted. The first test duplicated the conditions and, thus, the problems of the 5,000-book run. The rest of the tests were aimed at solving the various problems. To correct the ring problem, a continuous DEZ vapor feed (1 pound per hour (lb/hr)) and collection system was developed. To correct for the stratification in the chamber, DEZ gas was fed through the system at a high rate to induce better mixing in the chamber. A variety of spacer designs and spacing dimensions were also tested.

Cycle times of these small-scale tests were reduced to about 45 hours. Complete deacidification throughout the stack of books was achieved in a number of these tests. Uniform zinc oxide was also achieved. None of the spacer designs totally eliminated the tide marks. However, by minimizing the contact between book and spacer the excess deposition of zinc oxide was reduced almost beyond detection.

Encouraged by the results of these small-scale tests, the Library decided to build a pilot plant at Goddard. This would be the first attempt at engineering a system for commercial feasibility. Northrup, NASA's engineering contractor at Goddard who designed and operated the 5,000-book and the small-scale tests, was responsible for the design, construction, and operation of the pilot plant. The plant was built in an existing NASA building.

The system was designed to treat 300 books. Two new continuous DEZ vaporizers were to be tested. One would feed DEZ vapors into the chamber at 60 lb/hr, the other would feed it in at 200 lb/hr. The DEZ vapors were to be condensed and recycled during the process.

Construction was completed in October 1985. In December, during the final check of the system, however, an accident occurred. A fire broke out in the chamber. There were no injuries; property damage to the building was minimal but somewhat more extensive to the processing equipment. While attempting to safely deactivate the system, an explosion occurred and another fire broke out. Again there were no injuries, however, the system was judged by NASA officials to be unsafe and an Army demolition team was brought in to safely decommission the plant with small explosives.

A more detailed account of the incident will be given in chapter 5. The information for this OTA study was taken from the NASA Accident Investigation Report of September 4, 1986, as well as OTA and NASA meetings and conversations during August-September 1987. However, the principal finding of the in-house accident review committee was that standard safety procedures and practices were not followed in both the design and operation of the the plant. The care and detailed analysis that went into the test facilities were not repeated in the pilot plant.

After the accident, the Library of Congress discontinued its working arrangement with NASA. However, using the experience gained in the failure of the first pilot plant, and implementing all of the recommendations made by the NASA accident review team, the Library has contracted for and built a second pilot plant at Texas Alkyls' site outside Houston, Texas. Texas Alkyls has been the Library's principal supplier of DEZ and has over 20 years of experience in manufacturing and handling DEZ and other metal alkyls.

The plant has been designed to treat about 300 books. The chamber is 6 feet in diameter and 6 feet long. The process uses 100 percent DEZ. The DEZ is continuously vaporized and introduced into the chamber at high flow rates. Unused DEZ gas and ethane is continuously pumped out of the chamber with the unused DEZ vapor condensed and recycled and the ethane vented.

DISCUSSION

A number of tests have been planned for the new pilot plant. In general these tests will provide engineering and operational information for the commercial plant, including maintenance needs, manpower requirements, reliability and safety of the design and operations, and optimal temperature/pressure parameters for the various steps in the process. Specifically, there are also four major development issues that still need to be resolved. These are optimizing the DEZ flow rate, optimizing book configuration, reducing cycle time, and collecting scale-up engineering data.

The flow rate of DEZ into the chamber is very critical for two reasons. First, it is important to simultaneously expose as many books as possible to the DEZ vapor. DEZ will start to react quickly with the first books that it comes in contact with. Therefore, if the DEZ is not uniformly distributed at a high enough rate, deacidification will not occur in a reasonable exposure time.

The flow rate is also critical in ensuring that the DEZ and the ethane that is evolved during permeation will be thoroughly mixed, prohibiting a stratification of gases within the chamber.

The small-scale tests run at NASA after the 5,000-book run showed that a high DEZ flow rate can eliminate the problem. A principal task during the pilot plant tests will be to duplicate these results. The pilot facility is capable of generating flow rates that would be equivalent to 10,000 lb/hr in the full-scale plant, but it is doubtful that a flow rate this high will be necessary.

Book configuration also plays a role in the circulation of vapors within the chamber. The principal issue involving book configuration, however, is the spacing between books. Spacing between books plays a critical role in preventing the excess zinc oxide coating from depositing on book covers. The problems of ring formation, chamber uniformity, and cover staining were resolved in the final small-scale tests at Goddard. The pilot facility will be used to duplicate these results.

The question of cycle times was discussed in the process description. A conservative estimate of the total treatment time ranges from 55 to 72 hours. A goal of the pilot plant studies is to reduce this, if possible, to 48 hours. This would greatly increase the number of books that could be processed and lower the costs.

The rate-limiting step appears to be the dehydration step. The time it takes for water to diffuse out of the books will depend on the rate at which the chamber can be pumped to a rough vacuum, and the rate at which the book's temperature can be controlled. The chamber vacuum pump is sized to bring the chamber down to a rough vacuum (about 2:5 torr[2]) in 12 hours. However, pumping too fast may lower the book temperature too much. A warm nitrogen gas step would then be required to raise the temperature of the books back to a higher temperature. Book configuration may also affect the time needed for this cycle. Book carts and spacers

[2] A measure of absolute pressure in millimeters of mercury—1 torr is equivalent to 1/760 of atmospheric pressure.

must be designed to allow books in the interior of a stack enough time to get to the desired moisture content.

The principal issue in scaling up to a commercial plant is whether to achieve the desired capacity with one larger chamber (up to 7,500 books per run) or to design multiple chambers of a size close to that of the pilot plant chamber. There are many reasons that favor the latter approach.

Multiple chambers would basically reduce the amount of down time in the system. If one chamber is shut down, the others can continue to operate. It also allows the various subsystems—i. e., the DEZ recycling pump, the chamber vacuum pump, etc. —to operate more continuously reducing the chance of failures associated with the startup and shutdown of those components.

Also, keeping the chamber not much larger than the pilot plant chamber will introduce less uncertainty in reproducing the flow characteristics achieved in the pilot plant. Although most of the scaling up associated with a (large) single-chamber design would be relatively straight forward, reproducing the flow characteristics in a greatly enlarged chamber would not.

The principal disadvantages in going to a multiple-chamber design would be some increase in the complexity of operations. Cost factors would also need to be evaluated. Depending on their design, several multiple chambers may cost more or less than a single large one. Also, the chemical plant section for multiple chambers could possibly be smaller and lower cost. Finally, with multiple chambers, the control of the process would require careful monitoring by the distributive control system and greater complexity in the interlock design and operations which may also affect cost.