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PLANNING AN ENVIRONMENTALLY BENIGN FUMIGATOR/FREEZE DRYER FOR THE PROVINCIAL ARCHIVES OF MANITOBA

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A Fumigator/Freeze-Dryer which eliminates exposure of personnel to ethylene oxide is described. Novel features include double O-ring seals, unlimited water removal capacity per load, dew point control, multiple vacuum-cycle fumigant removal with adjustable dwell time and complete oxidative destruction of waste ethylene oxide.

Of the ten Provincial Government Archives and two Territorial Archives in Canada only three possess fumigation chambers. It is not that Provincial Archivists fail to see the need for fumigating acquisitions, nor that they fail to see the need for in-house conservation facilities -- but the cost of such equipment and facilities may well be prohibitive.

When the Provincial Archives of Manitoba decided in 1980 -- with approval of the Provincial Government -- to proceed with the designing and installation of a new and completely modern, fully equipped conservation laboratory and to hire a conservator to assist in the realization of this project ... from the beginning along with the planning of proper environmental controls for the storage areas, the installation of a fumigation chamber was seen as an integral part of the overall conservation planning and thrust.

We were assisted in our planning by several conservation scientists whose knowledge of and experience in the field of fumigation is considerable. We had several major concerns that guided us in directing our engineers, designers and architects in the realization of the completed chamber.

Of primary concern was the selection of a fumigant that would be most effective as a fungicide, bactericide and insecticide without causing damage to paper materials, and at the same time present the least health hazard to the operator. Dr. John Dawson, conservation scientist of the Canadian Conservation Institute both through his publications (1) and through personal contacts by telephone was of great help. Phillips (1957) reported that the following materials have been undamaged by sterilization with ethylene oxide: leather, wool, cotton, rayon, silk, felt, nylon, paper, plastic, wood, straw, linoleum, cellophane, metallic textiles, rubber, bedding, medical instruments, plaster bandages. (2) Ethylene oxide is flammable in its pure form, also explosive and toxic. When it is used as a mixture -- 10% ethylene oxide and 90% carbon dioxide -- its toxicity, explosiveness and flammability are very much reduced.

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Of paramount concern was the health risk to the operator of the chamber and the amount of residual fumigation gas remaining in the documents. Dr. Organ (1957) reported finding ethylene oxide levels of 260 ppm. upon opening the Smithsonian's fumigation chamber following three evacuations of the chamber. (3) Dr. Dawson reports that "At present, the TLV (the Threshold Limit Value represents the average safe toxicant concentration that can be tolerated on a repetitive basis, usually an eight hour day, 5 day week) is 50 ppm. In the near future the American and Canadian governments are expected to lower the TLV to 10 ppm. or even lower. The reason for this proposed change is that ethylene oxide is considered to be more toxic; it is now a recognized mutagen and is suspected to be a carcinogen." (4) In 1981 Dr. Organ demonstrated his fumigation chamber to me at the Smithsonian Institute. He was concerned that chambers like his own were passing off the spent fumigation gases into the atmosphere after the fumigation cycle. This concern led us to request of our designer-engineers that some mechanism be incorporated in the chamber or near the chamber that would destruct these gases and so prevent contamination of the atmosphere. And to give added health protection to the operator we requested that all controls for the chamber and destruction unit be housed in a separately sealed off room so that the complete fumigation cycle could be operated remotely.

Through a series of telephone conversations and also through personal conversation with Dr. Robert McComb of the Library of Congress we were given additional guidance in the overall design of our chamber. Dr. McComb pointed out the importance of real humidity control during the entire fumigation cycle for the effective killing efficiency of the fumigant, particularly for spores. Since commercial available fumigation chambers appear to have a major shortcoming in humidity control this led us to insist that there be controlled humidity throughout the fumigation cycle.

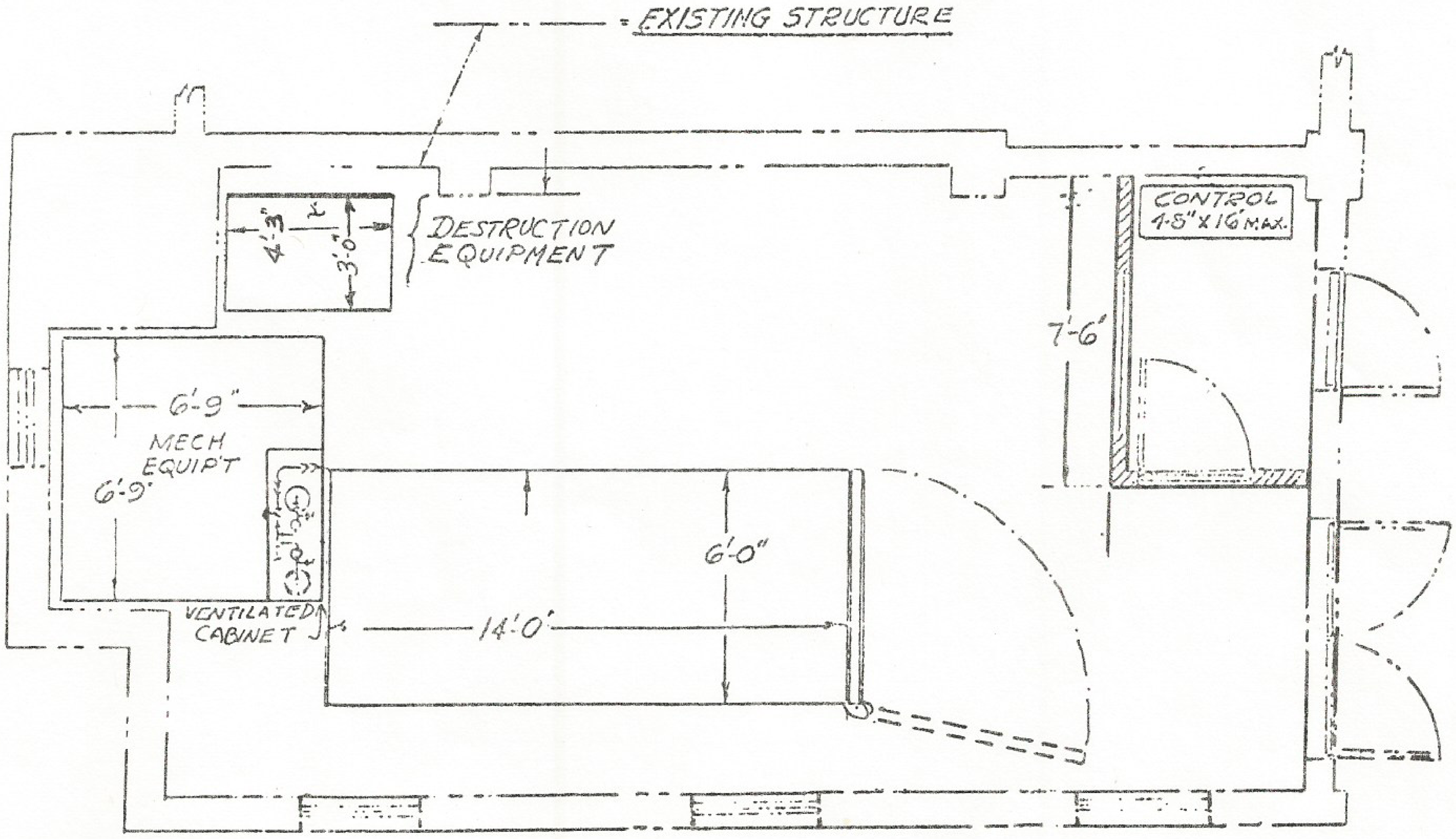
Our final stipulation in the design of the chamber was that the chamber serve in addition as a vacuum freeze-drying chamber for drying frozen documents that had suffered fire or water damage. This need was brought home to us when in January, 1981, the conservation and archive staff of the Provincial Archives of Manitoba was called upon to rescue and recover documents belonging to the Provincial Government and private enterprize as well that had suffered fire and water damage. (5) Use was made of the hypobaric chamber of the Canadian Forces Base, Winnipeg. Although the drying treatment proved successful, a need was felt for a chamber that would in addition vacuum-freeze dry frozen documents to prevent bleeding of inks (6) and especially since the Canadian Forces Base Chamber was being moved to another part of Canada.

With these concerns in mind the design and construction of the chamber went out for tender. The successful competitor was Slack Associates, Inc., 540 S. Longwood Street, Baltimore, Maryland, a designer and builder of custom equipment, specializing in high vacuum and cryogenic processing equipment. Mr. Clair Milton of that firm is the designer-engineer.

Disposition of Waste Fumigant

In the past ethylene oxide was either discharged to the atmosphere or washed down the sewer. Dilution and discharge to the out-of-doors frequently resulted in vapors reentering the ventilation system of the building, while discharge to the sewer resulted in vapors coming up out of floor drains, even into other rooms in the same building. Disposal by acid hydrolysis has been suggested, but the slow rate of the reaction, the great difficulty with which even 95% of the ETO vapor can be absorbed and the necessities of handling corrosive chemicals and keeping the concentrations proper make this method unattractive.

Rather than discharging ETO to the sewer or the atmosphere, the Provincial Archives of Manitoba's system destroys waste ethylene oxide by oxidizing it catalytically. The oxidation system functions automatically and is interlocked in such a way that (a) the chamber cannot be opened until it has been evacuated and backfilled a predetermined number of times, and (b) it cannot be evacuated except when the catalytic oxidation unit is in operation and at a sufficiently high temperature to effectively destroy all of the ethylene oxide.



FREEZER DRYER/FUMIGATOR EQUIPMENT LAYOUT

SCALE: NONE DATE: 10 SEPT. 81 DRG. NO. P-576-A-002

SLACK ASSOCIATES, INC., BALTIMORE, MARYLAND

Exposure of Personnel

In conventional fumigation installations the most serious exposure of operating personnel to the vapors of ethylene oxide has occurred when the sterilized material was being moved from the fumigation chamber to some other location for "air sweeping", or upon removal of material from a chamber which employed internal air sweeping. Due to the nature of the diffusion process, ethylene oxide is not removed quantitatively by merely storing books for a few days in a stream of moving air. It can be removed much more effectively by the process of pulling it out with a vacuum, allowing some time under vacuum for it to desorb, refilling with air, and repeating this sequence a number of times. In the Winnipeg equipment the pressure is reduced to 0.76 Torr (101 Pa or .001 atm.) so that the concentration is reduced by a factor of 1000 on each cycle. On each evacuation the air entrains fumigant which might otherwise have remained in the interstices of a porous material and removes it effectively. No trace of residual ethylene oxide can be found using either color-indicating gas detector tubes or flame ionization detectors with sensitivities down to 1 ppm.

Hospitals and manufacturers of medical equipment have a problem which conservators seldom encounter. To retain sterility after treatment, items must be enclosed by a membrane which is impermeable to microorganisms. The process must not rupture this membrane, be it paper or plastic. Archives normally process porous materials, which unlike medical items are not harmed by even quite rapid evacuation. Essentially all of the free ETO can be removed by four deep evacuations. This may be compared with a load of medical items sterilized in a 2 x 3 x 4 foot sterilizer. Barron, Gunther, Durnick and Young (7) reported that such a load produced a concentration of 2 ppm. at the breathing zone of the operator in a 6400 cubic foot room when, after a double evacuation and "dynamic air flushing", the door was opened 6 inches, and produced a concentration of 5 ppm. when the load was moved out into the room.

The Manitoba sterilizer operates slightly below atmospheric pressure. This slight vacuum pulls the door tightly against its O-ring seals. There are two such rings, and the evacuated space between them is swept constantly by a slow stream of air which serves as gas ballast for the vacuum pump. The tiny amount of ETO which diffuses through the inner O-ring, under the differential pressure of ETO existing between inside and outside, is thus captured and pumped out through the destructor. No special local exhaust is required to keep the ETO concentration vanishingly small outside of the chamber.

Humidification and Humidity Control

Robert R. Ernst published an excellent review of ETO sterilization in Industrial Sterilization in 1972. (8) While covering most topics of interest to prospective users he emphasized that the most important step in the process is prehumidification -- adjustment of the humidity of the load prior to introduction of the sterilant. If the load is too dry (moisture content below that in equilibrium with 35% R.H.) killing efficiency drops. If moisture content is too high, too much of the ethylene oxide will react with water, leaving an undesirable residue of ethylene glycol in the treated material. Typical loads vary in mass and moisture content, and since ordinarily the latter is not known, the optimum quantity of moisture to be added cannot be calculated. The Manitoba installation solves this problem by controlling the dew point in the chamber, not only initially, but throughout the entire period of exposure. Dew point was chosen because the more common methods of measuring humidity are unreliable in the chamber atmosphere of ethylene oxide and diluent.

ETO Concentration and Diluent Options

Pure ethylene oxide boils at 10.7 C. (51.3 F.). Its upper and lower limits of flammability are 3% and 100% . These may be compared with those of methane (5% and only 15%), acetylene (2.5% and 80%), and hydrogen (4% and 74.2%). Any concentration in air greater than 3% can explode. As a consequence most sterilizers employ it in the form of a mixture with a diluent to render it non-flammable or to reduce its flammability. In the interest of rapid sterilization, one commercial system does employ pure ETO. Because the concentration employed (1.164 KG/m), is nearly six times the lower explosive limit in air, maintenance of safety depends upon exhausting the ETO to below this limit before backfilling the chamber, and also upon diluting the ETO in the exhaust stream to below this limit. Some 10 separate safety systems monitor for operator error and mechanical malfunction. Our engineers chose a completely non-flammable mixture.

The two diluents employed commercially are dichlorodifluoromethane and carbon dioxide. If the mixtures with the highest concentrations of ETO which are not flammable are compared, that with the halocarbon has a higher concentration of ETO at any total pressure, and hence a somewhat more rapid sterilizing action. Unfortunately discharge of fluorocarbons to the atmosphere is now thought to be deleterious to the ozone layer, while destruction of these chemicals involves highly corrosive and toxic products whose management is not simple. Mixtures of carbon dioxide and ETO, on the other hand, are readily oxidized to water and carbon dioxide. On this basis carbon dioxide was chosen as diluent.

Sterilizing efficiency is usually evaluated by determining the survival rates of dried spores of Bacillus subtilis var niger. Ernst and Shull (9) found that above about 110 F. the killing rate was hardly a function of concentration, but at 80 F. a concentration of 440 mg/l took about 160 minutes to kill these spores to the degree to which 1500 mg/l required 70 minutes. All of the death time-temperature curves are logarithmic in time. If it is undesirable to expose documentary materials to 120 to 130 F., at least at relatively high humidity levels, then archival facilities are faced with the choice of either using relatively high concentrations of ETO or of fumigating for many hours. High concentrations cannot be reached with completely non-flammable mixtures with carbon dioxide, so in the interest of safety our engineers have chosen to install a relatively large chamber, in which extended exposure times are practical.

Some molds are more resistant than B subtilis. R. Wade, of the USDA recently reported that cotton which had been sterilized with ETO was rendered essentially free from bacteria, but still contaminated with unidentified growing mold. Furthermore, deactivation of spores depends upon their being suitably hydrated and penetrated. There is a great deal of evidence that clean spores are inactivated much more readily than those which are surrounded by organic debris, and that spores occluded in crystals will not be killed at all unless the crystals dissolve. While we do not anticipate encountering spores protected by crystals, we routinely process unclean material, and consider it essential to allow extra exposure time for penetration of spores protected by dirt. Exposures demonstrably effective in deactivating spores on clean test strips are not necessarily adequate for everything which an archival facility processes.

Stratification is eliminated and uniformity of humidity assured by the provision of circulating blowers within the chamber. They operate only when the chamber is full of sterilant.

Catalytic Destruction of Ethylene Oxide

If a 90/10 mixture of ethylene oxide and carbon dioxide were mixed with just the quantity of air required for its complete combustion and then oxidized, a very high temperature would result. At this temperature the catalyst would be destroyed. Therefore, the mixture is diluted with just the particular excess of air which will hold the exhaust temperature to a value which the catalyst can tolerate. In order to get the reaction started, the stream is preheated to at least 316° C. The exhaust temperature is controlled automatically. Oxidation is nearly quantitative, and the exhaust is further mixed with ambient air to reduce its temperature to 150° C. so that it can be handled by standard ductwork.

Freeze Drying

Soaked documents are best reclaimed by quick-freezing them, then removing the water in the vapor state under a vacuum which prevents the water from passing through a liquid state during the process. Since water vapor occupies enormous volumes at low pressures, in installations of substantial size it is most economical to pump the water vapor with cooled surfaces, and use mechanical pumps to remove the permanent gases. The Manitoba equipment can pump any quantity of water from a load, since there are two chilled surfaces, each in its own compartment. One can be pumping water vapor while the ice on the other is being melted and removed. The pumping capacity of each for water vapor is estimated as exceeding 50,000 cfm. Freezing surfaces are maintained at -20° to -40° C.

The rate at which water is removed is determined by the rate at which heat can reach the interface between ice and vacuum, for about 1200 BTU is absorbed at this interface for each pound of water which evaporates. Documents are rather good insulators, and since we are unwilling to subject the edges of the documents to temperatures much above 80° F., evaporation is quite slow after the first few hours.

Heat is supplied in our unit by radiation from panels which cover both side walls and from a panel which extends the length of the chamber down its center. The panels are heated by circulating warm water, so there is no possibility of overheating.

Trucks of books are rolled into the spaces between the panels. The chamber will accommodate six trucks. Each truck is loaded five shelves high, with two rows of books, spine down, on each shelf. The trucks are aluminum, the bottoms of the shelves being black to promote radiative heat transfer.

Interior dimensions of the working portion of the chamber are 11'6" x 5'3" x 5'6" high.

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