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**REVIEW OF CONTROL OPTIONS
FOR METHYL BROMIDE
IN COMMODITY TREATMENT**

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16. ABSTRACT: The report describes recent developments in the control of methyl bromide (MeBr) and discusses technical considerations and requirements for and economic feasibility of recovery. (NOTE: MeBr, a fumigant for agricultural commodities, is an ozone depleting chemical. The U.S. EPA has banned its use beginning in 2001. In some applications, a suitable substitute for MeBr has not been found, so the report discusses an exempted use of MeBr with capture and recovery or recycle for some applications.) The primary focus of the report is on quarantine applications using MeBr. Two of the most promising approaches to recovery, recycle, and reuse continue to be physical adsorption on a solid sorbent and cryogenic condensation. In addition to discussing these technologies, the report identifies some of the critical considerations for process economics and remaining information gaps. The review concludes that recovery, recycle, and reuse appear to be feasible, have not been unequivocally proven to be so, and there is little current incentive to pursue such technologies unless there is hope of exemptions to or rescission of the MeBr ban.		
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FOREWORD

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ABSTRACT

Methyl bromide (MeBr), a significant fumigant for agricultural commodities, is listed by the Montreal Protocol as an ozone depleting chemical. The U.S. Environmental Protection Agency has banned methyl bromide use beginning in 2001. In some applications, a suitable substitute for methyl bromide has not been found. Therefore, in 1994, a brief study was undertaken to characterize fumigation processes for one important type of commodity fumigation, space fumigation, and to identify potential methods for control, recovery, and recycle. EPA issued a report in 1994. Since that time, there have been additional developments in finding appropriate technologies for this purpose. Continuing interest in the subject has been reflected in two prominent forums for disseminating information related to methyl bromide. The first was a conference held in Orlando, Florida in November, 1994. The second was in the contents of a report issued by the United Nations Methyl Bromide Technical Options Committee, in 1995. Also an important development was the installation and testing of methyl bromide treatment and reuse system at the Port of San Diego in 1995. Because of these advances, and additional study, the present report was prepared to communicate information on these developments and to discuss further technical considerations and requirements for technical and economic feasibility of recovery. The primary focus of the present report is on methyl bromide treatment in quarantine applications.

At this time, two of the most promising approaches to recovery, recycle, and reuse continue to be physical adsorption on a solid sorbent and cryogenic condensation.

A new adsorption system was installed and tested at the Port of San Diego. Based on zeolite adsorption technology, the system achieved over 95% removal efficiency of methyl bromide from the post-fumigation vent stream. This is consistent with expectations based on other tests that have been reported in the past. In addition to zeolite adsorption, condensation at cryogenic temperatures still appears to be a potentially feasible candidate for some applications. However, like activated carbon, another candidate technology, little if any new activity in these areas appears to have occurred recently. In addition to discussions on each of these technologies

and their costs, this report identifies some of the critical considerations for process economics and identifies remaining information gaps and further needs. The overall conclusion of this review is that recovery, recycle, and reuse appears to be feasible, has not been unequivocally proven to be so, and that there is little current incentive to pursue such technologies unless there is hope of exemptions to or a rescission of the methyl bromide ban.

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CONVERSION FACTORS

Certain nonmetric units are used in this report for the reader's convenience.

Readers more familiar with metric units may use the following factors to convert to that system.

<u>Nonmetric</u>	<u>Multiplied by</u>	<u>Yields metric</u>
atm	98.1	kPa
Btu/hr	0.293	W
cal	4.18	J
cfm	0.000472	m ³ /s
°F	5/9 (°F-32)	°C
ft	0.305	m
ft ²	0.0929	m ²
ft ³	0.0283	m ³
gal.	0.00379	m ³
hp	0.746	kW
in	0.0254	m
in. WC	0.249	kPa
lb	0.454	kg
mil	0.0000254	m
psi	6.89	kPa
ton	907	kg

SECTION 1.0

INTRODUCTION

Methyl bromide (methyl bromide), with the chemical formula CH_3Br , also called bromomethane, is listed by the 1991 Montreal Protocol as an ozone depleting chemical similar to the other halogenated hydrocarbons such as the chlorofluorocarbons (CFCs). The U.S. Environmental Protection Agency's (EPA's) regulations authorized by the Clean Air Act (CAA) call for a phaseout of methyl bromide as of January 1, 2001. This means an end to commodity fumigation uses that emit methyl bromide to the atmosphere. In some applications, there is no apparent, ready substitute for methyl bromide.

In 1994, a brief study was undertaken to identify potential methods for emissions control, recovery, and reuse. A report was issued by EPA in July 1994 (1). The study discussed possible means for methyl bromide recovery for reuse as well as for destruction to prevent atmospheric emissions of any residual methyl bromide in vent streams. Since that time, there have been additional developments on the subject. While developments have not radically altered the findings and conclusions of the earlier report, some additional information is included here.

Continuing interest in methyl bromide emission control has been reflected in two forums for disseminating information on methyl bromide. The first was a conference, the 1994 International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, held in Orlando, Florida in November, 1994 (2). The second was in the contents of a report on the 1994 International Research Conference on Methyl Bromide Alternatives and Emissions Reduction, issued in 1995, by the United Nations Technical Options Committee for Methyl Bromide (3).

Also a new methyl bromide recovery and recycle system, offered by Halozone Recycling, Inc., was installed and tested at the Port of San Diego in 1995. Additional activities

by this firm also include a test on shiphold and structural fumigations, and a commercial unit in Chile. Because of these developments and additional study, the present report was prepared to discuss these developments and further technical considerations on the technical and economic feasibility requirements of recovery and recycle. The primary focus of the present report is on methyl bromide treatment in quarantine applications.

This report was prepared as a brief update on recent activities and is not intended as a complete compendium or research review. The study did not attempt to identify all possible technologies that might be applied or programs underway. It does discuss key developments and insights that have occurred since the earlier report was issued.

The remainder of the report discusses quarantine applications (Section 2), technologies for recovery and recycle (Section 3), and information gaps and future needs (Section 4).

SECTION 2.0

QUARANTINE APPLICATIONS OF METHYL BROMIDE

2.1 Overview

Treatment processes for commodities using methyl bromide can be classified according to the commodities being treated and the reasons for the treatment. Regardless of these classifications, however, there are many similarities with the overall procedure for the fumigation. The primary differences between the various applications is in the way in which the commodities are contained during fumigation and the dosages and duration of treatment. However, these differences do not fundamentally alter the applicability of possible emissions control technologies that might be applied for recovery and recycle; only the volumes involved and, therefore, the potential economics of treatment.

Some classifications of treatment are as follows:

- Durables fumigation;
- Perishables fumigation;
- Structural fumigation;
- Soil fumigation;
- Long-term storage fumigation; and
- Quarantine fumigation.

Of the various applications, quarantine treatment has been singled out for closer examination in this study. Such treatment typically occurs in relatively small volumes at port facilities where fumigation must accommodate irregular schedules, short durations, and minimal technical resources. In this application, other pest control methods, as alternatives to methyl bromide fumigations, might be more difficult to implement than in non-quarantine applications.

2.2 Definition of Quarantine Treatment

Quarantine treatment is the treatment of commodities just prior to shipment to another jurisdiction or upon receipt from another jurisdiction, whether it be a state or another country. In some cases quarantine treatment is a standing requirement for certain commodities and certain jurisdictions; for others it is left to the discretion of a commodities inspector or other authority that may call for its use in a given situation.

Most commonly, quarantine treatment takes place with tarpaulin covered commodities in the open or in warehouses; in special buildings or rooms called fumigation chambers; or in trucks or ships.

For those ports that have a specific building for commodity quarantine treatment, a recovery and recycle system could be a permanent installation. For cases where the location might vary or where the fumigation would take place in a truck or ship, a portable unit, perhaps on a flat-bed truck would be appropriate.

In either case, the basic technology would be the same. The process system would be designed to accommodate the flow rate, temperature, pressure, and composition of the fumigation vent stream being treated. The characteristics of that vent stream depend on the manner in which the fumigation process is carried out.

At this time, it does not appear that there is a single, comprehensive listing of all quarantine application sites in the country. In general, quarantine fumigation will take place at major shipping ports, both seaports and overland shipping locations, such as between the United States and Mexico.

2.3 Characteristics of the Fumigation Process

The details of fumigation are discussed in more detail elsewhere (1). Briefly, the enclosed commodity, in bulk or in containers (boxes or bags) that are permeable to methyl bromide gas, is exposed for a specified period of time to a specified concentration of methyl bromide injected into the air space surrounding the commodity. The methyl bromide is introduced for a specified time and rate into the enclosed fumigation space and the supply shut off. After a specified holding time period, the space is then vented to remove the residual methyl bromide. For enclosed spaces, the venting is accomplished by sweeping fresh air through the space. The vent stream has been traditionally exhausted directly to the atmosphere. In the traditional tarp configuration, the tarp was often merely removed from covering the commodity and the methyl bromide allowed to escape to the atmosphere.

If methyl bromide recovery and recycle is to be practiced, there will have to be a single location from under the tarp from which the venting would take place through a hose or ducting, or the commodities would have to be fumigated within a building or room that would then provide controlled venting through ducting to an emission control device and recovery system. However, for the most effective control, it is advantageous to avoid any more dilution of the vent stream than is absolutely necessary.

As an example of a typical treatment, methyl bromide might be fed into a fumigation chamber at a dosage of 200 pounds or more and the commodity held in the methyl bromide atmosphere for 1.5 to 2 hours. The feed to achieve this concentration would take place over a period of 30 minutes. After fumigation, the venting period would be about 2 hours.

An obvious characteristic of the fumigation process that affects design of a recovery and recycle system is that it is intermittent and yields a varying concentration of methyl bromide in the vent stream. The process itself is applied irregularly according to shipping schedules of specific commodities and it is applied seasonally according to the harvests. Therefore, the economics of such a process suggests that portability, not only at a given port facility, but perhaps between port facilities might be desirable.

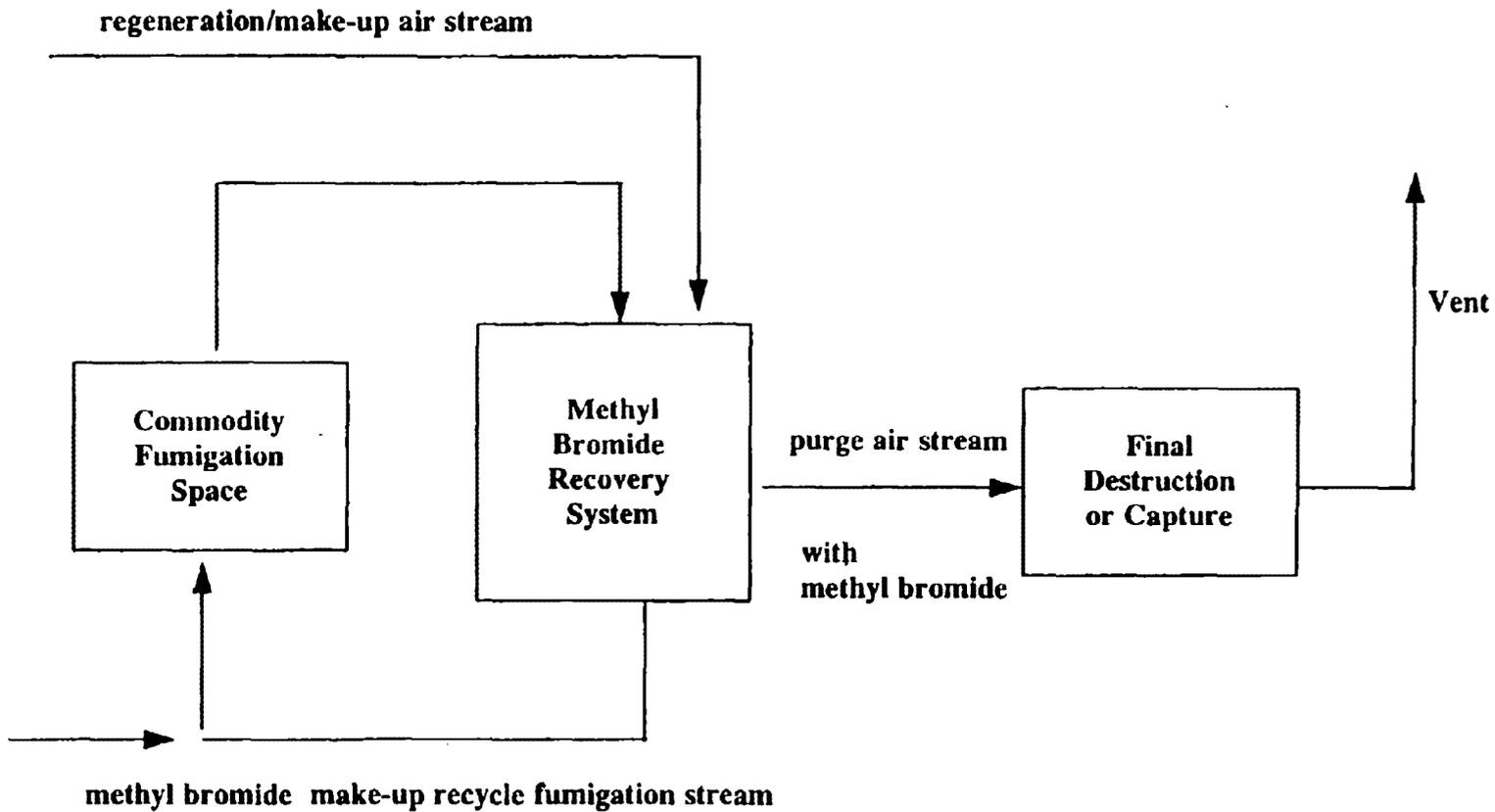
SECTION 3.0

TECHNOLOGIES FOR RECOVERY AND RECYCLE

3.1 Overview

In a 1994 report (1), various technology options were identified and discussed. Since that time, it is apparent that the main thrust of this new work has focused on adsorption processes, but the application of condensation processes should not be ignored. The overall level of development activity for any technology appears to remain fairly low because the major focus of responding to the stated ban on methyl bromide has been toward finding methyl bromide substitutes and alternative methods of pest control, rather than methods for methyl bromide recovery and recycle. This is logical considering that there is little economic incentive for researching recovery and recycle if the use of methyl bromide is going to be banned. Should this policy change, more interest in recovery and recycle could be expected to arise.

There are several features of the recovery and recycle concept that will be common, regardless of the technology to be used. Figure 3-1 illustrates the overall concept of a methyl bromide recovery and recycle process applied to commodity fumigation. The commodity to be treated is held in an enclosed fumigation space. The fumigation stream consisting of air and methyl bromide enters the fumigation space and is held for a specified period as in the conventional process. The difference is that the fumigation stream contains recycled methyl bromide in air from intermediate storage after recovery from the vent removal process, or directly from the regeneration of an adsorption removal process run in a recovery or regeneration mode. Some methyl bromide makeup would also be added to the fumigation stream to compensate for losses. A makeup or regeneration air stream would also enter the overall process loop. Some purge air and minor amounts of methyl bromide



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Figure 3-1. Overall Concept of Methyl Bromide Emission Control, Reuse, and Recycle from Commodity Space Fumigations

would also be vented to form the basic treatment and recovery process. This stream would either vent to the atmosphere or through a final destruction or capture device as shown in the figure.

The discussions that follow describe key features of the various technologies that could be applied in the methyl bromide recovery system and the final destruction or capture system of the process. This follows from earlier reporting on the general characteristics of these technologies and their potential applicability to this problem. The technologies discussed include:

- 1) Adsorption;
- 2) Condensation; and
- 3) Other technologies, some of which would apply to final destruction of methyl bromide residuals in the vent stream rather than recovery, recycle, and reuse.

3.2 Adsorption Processes

Recovery of methyl bromide by adsorption was described in EPA's July 1994 report (1). In a typical adsorption process, the exhaust air from a fumigation chamber is passed through a vessel containing a fixed bed of a solid sorbent material that has an affinity for methyl bromide. The methyl bromide vapor is transferred to the sorbent and the cleaned exhaust air is either discharged or recirculated to the chamber. The sorbent containing the adsorbed methyl bromide is then either regenerated or disposed of. If the sorbent is regenerated, the methyl bromide may either be recycled directly to the chamber for reuse, recovered for intermediate storage, or fed to a destruction process. For a methyl bromide adsorption system, the most practical method of regeneration appears to be by heating the bed in hot air. This causes the methyl bromide to desorb from the sorbent into the hot air stream.

The extent of methyl bromide recovery in an adsorption process depends on the following factors:

- The equilibrium relationship between the vapor-phase and adsorbed-phase concentrations of the methyl bromide. The equilibrium relationship is also referred to as the adsorption isotherm because it is a function of temperature.
- The rate of adsorption or transfer of the methyl bromide from the exhaust air to the sorbent. This rate is a complex function of the rates of several individual steps that occur in series in the overall adsorption process.
- The arrangement and operating conditions of the adsorption process equipment. This includes such factors as the dimensions of the sorbent bed and the volumetric flow rate of exhaust air through the sorbent bed as well as the conditions of the regeneration step, if employed.

Recently published information regarding the use and performance of two different adsorption processes for recovery of methyl bromide is discussed below. One process uses a synthetic solid adsorbent. The other process uses activated carbon.

3.2.1 The Bromosorb™ Process (Zeolite Adsorption)

The Bromosorb™ Process is an adsorption process that uses a proprietary synthetic zeolite, or "molecular sieve", as the sorbent. The process is offered by Halozone Technologies, Inc. of Mississauga, Ontario, Canada. The synthetic zeolite sorbent is reported to selectively adsorb methyl bromide from humid air without adsorbing a significant amount of moisture.

Results of demonstration tests using the Bromosorb process were reported by Halozone at the 1994 International Research Conference on Methyl Bromide Alternatives and Emissions Reduction in Orlando, Florida (4). The process was tested on a 1,640-m³ (cubic meters) fumigation chamber at Stemilt Growers in Wenatchee, Washington during July 1994.

Figure 3-2 shows the process configuration for these tests. The process equipment consists of two fixed-bed adsorbers operated in parallel. In the adsorption part of the operation, during the post fumigation venting, exhaust air containing nominally 55-60 g/m³ (grams/cubic meter)(1.4-1.5% vol) methyl bromide is evacuated from the chamber by a circulation fan and passes through each of the two beds containing the zeolite. Effluent air from the adsorbers containing a reduced concentration of methyl bromide is recirculated to the chamber. After three to four air changes have been processed (about 1.5 to 2 hours), the concentration of methyl bromide in the chamber exhaust air is reduced to that of the effluent air from the adsorption beds, and the adsorption part of the recovery cycle is completed. The unit is then isolated from the chamber. Residual methyl bromide in the chamber air is then vented to the atmosphere. However, the quantity of vented methyl bromide has been reduced to about 5% of what would have been vented without the treatment device. The chamber is then shut down and the fumigated commodity removed.

Following the adsorption step and chamber venting, when the chamber is ready for the next fumigation cycle, the regeneration and reuse part of the process is initiated. Exhaust air from the chamber is again recirculated through the adsorbers, but only after the air is heated to about 121 °C by a gas-fired indirect heat exchanger. This increase in temperature is sufficient to desorb the methyl bromide, circulating it back into the fumigation chamber for reuse. The desorption part of the process requires less time: about 30 to 45 minutes.

Reported performance results for the Bromosorb demonstration at Stemilt Growers showed that an average of slightly more than 95% of the available methyl bromide following fumigation could be captured by the process, and more than 99% of the captured methyl bromide could be recovered for reuse in the chamber. A sample of the recovered methyl bromide was collected by condensation for subsequent chemical analyses. Independent analytical results by the U.S. Department of Agriculture (U.S.D.A.) showed no significant difference in composition between the recovered methyl bromide and virgin methyl bromide supplied by Great Lakes Chemical Company.

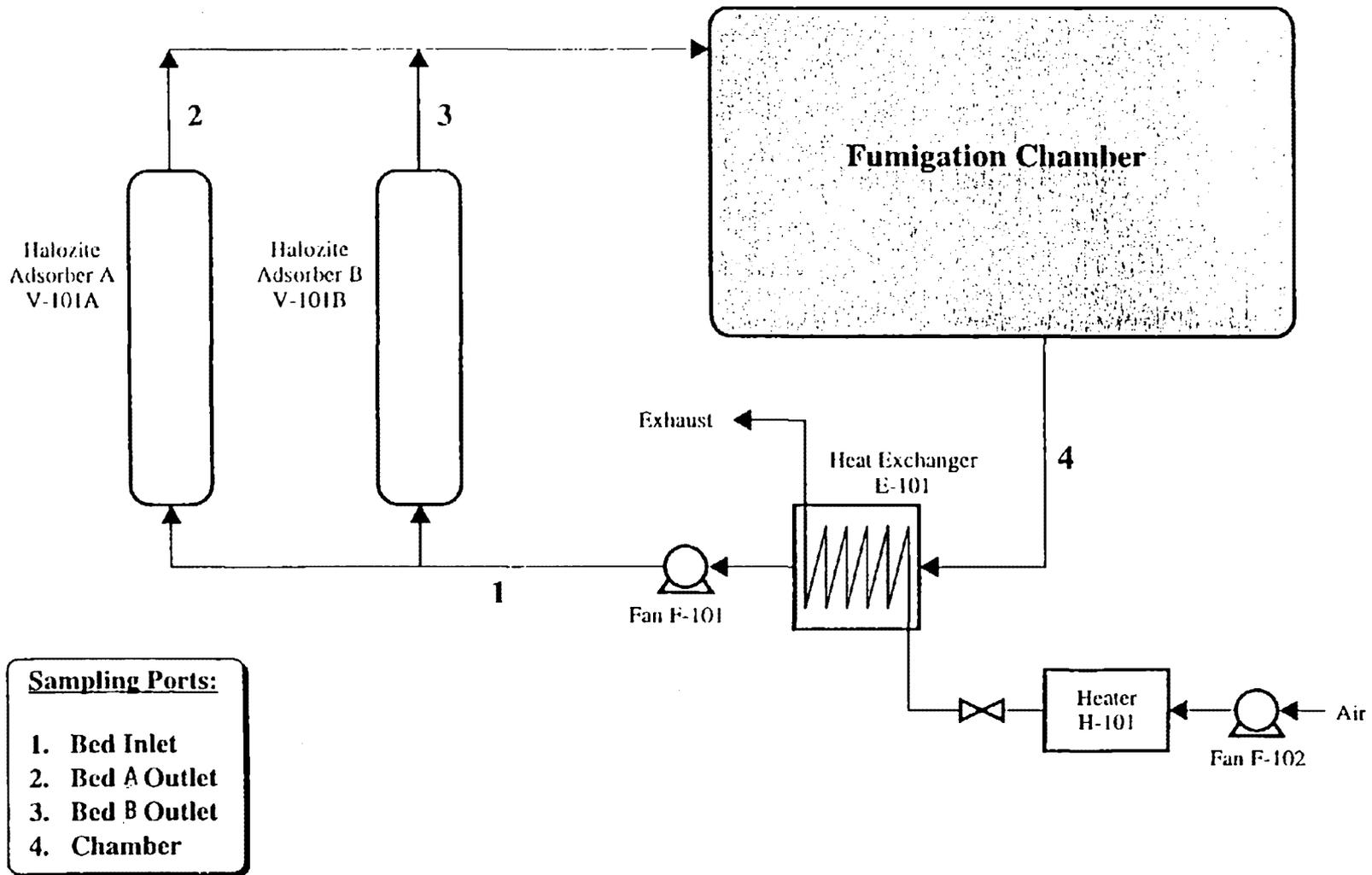


Figure 3-2. Bromosorb™ Test Unit for Methyl Bromide Recovery and Reuse

Following the successful results of the above demonstration program, a commercial installation of the Bromosorb process was designed and constructed for a 2,000-m³ fumigation chamber operated by the San Diego Unified Port District of San Diego, California. Test results obtained during February of 1995 for this unit have also been recently reported (5).

The process configuration of the San Diego unit is similar to that shown in Figure 3-2, except that a cooling heat exchanger is also supplied on the effluent side of the adsorbers. This enables more rapid desorption without overheating the recirculated air in the chamber. Test results for this unit showed an average capture of 95.4% of the methyl bromide from chamber air containing nominally 50-60 g/m³ methyl bromide. Again, no residual impurities were detected in the recovered methyl bromide after a number of adsorption/regeneration cycles. Cycle times for this unit were less than 30 minutes for adsorption and 15 minutes for regeneration and recycle. The residual methyl bromide concentration in the exhaust air vented to the atmosphere was about 670 ppmv.

The capital cost for the San Diego Bromosorb unit is reported to be about \$960,000, including the cost of performance tests (1,6). Assuming that the equipment capital cost is about \$900,000, after deducting for the performance tests, the annualized capital charge for this process is about \$150,000 (amortized over 10 years at 10.6% interest). The primary operating costs include heat for the desorption cycle and power for the recirculation fans. Assuming that two chamber volumes of air are heated in the desorption step and that an equivalent amount of heat is needed to heat the process equipment and sorbent, then the total heat energy consumed per cycle is about 1 million kJ (kilojoules). If natural gas is burned to supply this heat at a cost of \$3/10⁶ kJ, the fuel costs amount to about \$3.00 per cycle. The circulating fan sizes are not reported, but assuming that two 20-hp fans are used (one for circulating; one for heating or cooling), the total fan power per 45-minute cycle is about \$0.50. The cost for sorbent replacement has not been reported, but sorbent life is estimated at 10 years.

For each fumigation cycle, about 100 kg (kilograms) of methyl bromide that would otherwise have been vented is recovered and reused. The facility at San Diego is used only part of the year. Assuming 40 fumigation days per year, and 4 cycles per day, the number of cycles per year is 160. Then the total annualized cost per cycle is about \$938 (exclusive of sorbent replacement), nearly all of which is capital charges. Assuming that nominally 100 kg of methyl bromide is recovered per cycle, the recovery cost is about \$9.38/kg, which is considerably more than the reported cost for makeup methyl bromide of \$1.70/kg (7). Obviously, as the on-stream time or number of cycles per year increases, the cost of recovered methyl bromide will decrease.

The design recovery-efficiency of an adsorption process such as Bromosorb can be increased (with a constant cycle time) by increasing the depth and/or cross-sectional area of the adsorber bed. For example, Nagji and Veljovic estimate that a system could be designed for 99% capture at a cost of two to three times that of the 95%-system (4). For the same cost and on-stream time assumptions used above, the marginal cost per unit of additional methyl bromide captured in going from a 95%-efficient to a 99%-efficient system would be \$35 to \$70/kg, and the overall average recovery cost would increase to \$3 to \$6/kg methyl bromide. Thus, the economics also depends highly on the level of any allowable emissions from recovery and reuse process venting.

Additional work with this type of unit in 1995 includes testing on shiphold and large structural fumigations (200,000 ft³ and more) and sale of a commercial unit in Chile. The latter application is for a 10,000 ft³ chamber quarantine fumigation. The capital cost of the system has been reported as \$ 250,000 (8). Further details were not available for this report.

3.2.2 Carbon Adsorption

Another adsorption process for methyl bromide is carbon adsorption. Progress in the use of carbon adsorption for methyl bromide recovery and recycle has also been

reported since EPA's previous report. In that report, bench-scale and pilot-scale tests completed by Australian investigators during the late 1970's were described. More recently, the UN Methyl Bromide Technical Options Committee reports several applications of activated carbon for methyl bromide capture (3).

Five small (30 m³) chambers in the Netherlands are using once-through activated carbon beds for capturing methyl bromide from chamber exhaust air. Each adsorber has a 70-kg carbon bed that is reported to recover 40 to 50% of the methyl bromide following fumigation at an inlet loading of 30 g/m³. This particular installation is only for emissions reduction, however. Recovery and recycle is not practiced. After about 40 fumigation cycles, the spent carbon is incinerated in a regulated facility. Based on the above operational description, the average methyl bromide loading on the spent carbon would be about 16 to 20%, assuming that 80% of the 30 g/m³ initial charge is available for capture. This loading agrees approximately with the bench-scale data in Radian's previous report (1).

For this type of once-through application, equipment costs should be relatively low and the cost of the carbon sorbent replacement and spent carbon disposal will be the major costs. For example, if carbon can be loaded to an average of 16% by weight before disposal, then the carbon consumption will be 6.25 kg carbon/kg methyl bromide. Small quantities of activated carbon cost about \$6/kg, so that the equivalent carbon cost will be about \$37/kg methyl bromide. Disposal of small volumes of the spent carbon as a hazardous waste in the U.S. is expected to cost as much as \$2/kg based on Radian's in-house experience. This brings the total cost for 40 to 50% methyl bromide capture by a once-through carbon system to about \$50/kg methyl bromide.

The above example (40 to 50% capture) results in a relatively high concentration of methyl bromide in the exhaust air from the chamber to the atmosphere. As with the synthetic zeolite, lower concentrations of methyl bromide can be adsorbed with carbon, but at reduced loading. For example, at a residual methyl bromide concentration of 100 ppmv (99%+ capture for a typical chamber concentration of 1.5%), the equilibrium

loading on the carbon will be only 0.4% at 30°C. For this case with 99% capture, the average loading on the carbon might be only one-fourth that in the above example at 40 to 50% capture, increasing the average cost to about \$100/kg methyl bromide captured.

Processes for methyl bromide capture and recycle with activated carbon are also being developed. A mill in Germany reportedly has been equipped with a full-scale activated carbon system for methyl bromide capture and recycle (3). This process is said to include a concentration and condensation step as part of the desorption cycle. Details of the total process design are not available, but pilot-scale test results for the desorption method (direct electrical heating under vacuum) have been published (9). In these tests, the total energy used for desorption was about 14,000 kJ/kg, which is equivalent to an energy cost of only \$0.20/kg at \$0.05/kWhr. The investigators pointed out that the desorption temperature must be limited to less than about 120°C to avoid decomposition of the methyl bromide and production of hydrogen bromide due to the reaction of methyl bromide with water on the carbon surface.

Costs for an integrated recovery, recycle, and reuse system using activated carbon have not been reported, but are expected to be the same order of magnitude as those for the Halozone system described above, because of similarities in the types of equipment for adsorption systems in general.

3.3 Condensation Processes

Methyl Bromide is a relatively volatile gas and therefore is difficult to condense. Figure 3-3 is a vapor pressure curve for methyl bromide, based on technical literature information(10), plotted as $\ln P$ (atm) versus $1/T$ (K) to yield a straight line. For convenience, a few points for temperatures in °C and vapor pressures in atmospheres are also shown. For example, at the normal chamber concentration of 1.5% methyl bromide in air, condensation of methyl bromide (at atmospheric pressure) would begin at a temperature of -71°C, which is well below temperatures that can be produced by normal mechanical

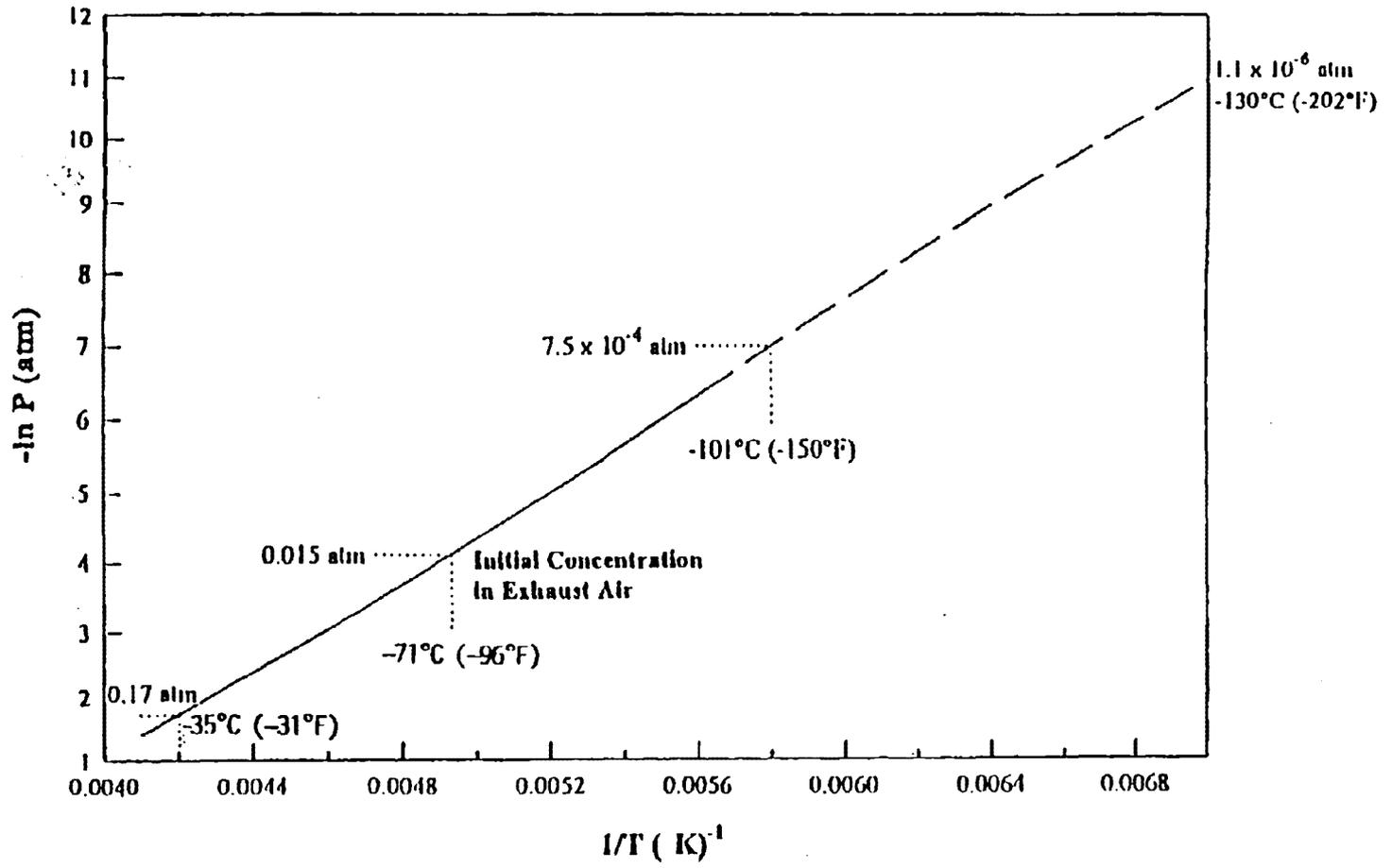


Figure 3-3. Methyl Bromide Vapor Pressure

cooling systems. Recovery of 95% of the methyl bromide from the exhaust air (as with the adsorption processes), leaving a residual concentration of 750 ppmv, would require cooling to about -101 °C.

A condensation process using liquid nitrogen was reported as recovering 98% of the available methyl bromide from two vacuum fumigation chambers at Pacific Coast Fumigation, Inc., Terminal Island, CA (3,11). This process condenses methyl bromide from a single volume of chamber air, and the residual methyl bromide is then captured by activated carbon. No details of the process design or equipment costs are available. Because liquid nitrogen boils at -196 °C, there is ample temperature difference for cooling the air stream. The facility is no longer in use due to high electricity costs.

The heats of vaporization of nitrogen and methyl bromide are 19.9 and 30.7 kJ/kg, respectively. Therefore, about 1.5 kg N₂/kg methyl bromide will be required at a minimum to remove the latent heat of condensation. Assuming that one chamber volume of air is cooled to -101 °C, and the initial air/methyl bromide weight ratio is 20:1 (for 1.5% methyl bromide by volume), then the heat duty for air cooling (from 25 °C to -101 °C) will be about 2,500 kJ/kg methyl bromide, and the liquid nitrogen demand for air cooling will be about 125 kg/kg methyl bromide. Allowing for heat losses, the actual quantity might be as high as 150 kg N₂/kg methyl bromide. Liquid nitrogen is available at a cost of about \$0.05/kg. At this cost, the operating cost for a condensation process using liquid nitrogen to cool one chamber volume of air plus methyl bromide would be a minimum of \$7.50/kg methyl bromide (not including annualized equipment costs). This cost compares favorably with the once-through carbon system described above for the 30-m³ chambers, even if the annualized equipment charges are significant for the condensation system.

Methyl bromide condensation can be conducted at higher temperatures if the concentration and/or total pressure can be increased. Therefore, condensation can be applied downstream of an adsorption process to condense the methyl bromide following the desorption cycle. If the desorption is conducted under partial vacuum and by direct heating,

high concentrations of methyl bromide can be obtained. Suppose, for example, that a stream of 25% methyl bromide in air can be obtained from the desorption cycle. A brine cooler can obtain a temperature of about -35°C , at which the partial pressure of methyl bromide is about 0.17 atm. At atmospheric pressure, only about 30% of the methyl bromide could be condensed at this temperature, but if the total pressure in the condenser were raised to 5 atm, the recovery would increase to about 86%. Similarly, at 10 atm, about 93% condensation could be obtained.

A two-stage high-pressure condensation system with intercooling was one of the designs proposed for the San Diego Port District (1). This system was to be operated at 70 atm. No details of this process design are available. However, at this pressure, good methyl bromide condensation can be obtained even with low inlet concentrations without an intermediate adsorption/desorption step. For example, assuming that the methyl bromide concentration in the chamber exhaust air is 1.5%, then the partial pressure of methyl bromide after compression to 70 atm is about 1 atm. With a condenser temperature of -35°C at 70 atm, a recovery of about 80% would be obtained.

Figure 3-4 summarizes the above discussion. The percentage of inlet methyl bromide that can be condensed at -35°C is plotted versus the condenser operating pressure. Two curves are shown. The lower curve represents direct condensation, with no intermediate adsorption/desorption cycle, assuming that the condenser inlet methyl bromide concentration is 1.5% in air. The upper curve represents condensation of 25% methyl bromide in air, produced during a desorption cycle. These results are only approximate, especially at high pressure, because ideal gas behavior was assumed.

To reuse the methyl bromide, condensation processes will require that water vapor be separated from the air before methyl bromide is condensed. Technically this should not be difficult, because the vapor pressure of water is much lower than that of methyl bromide at equivalent temperature, but it would require a two-stage process with intermediate removal of condensed water. The condensed water, which might contain methyl bromide

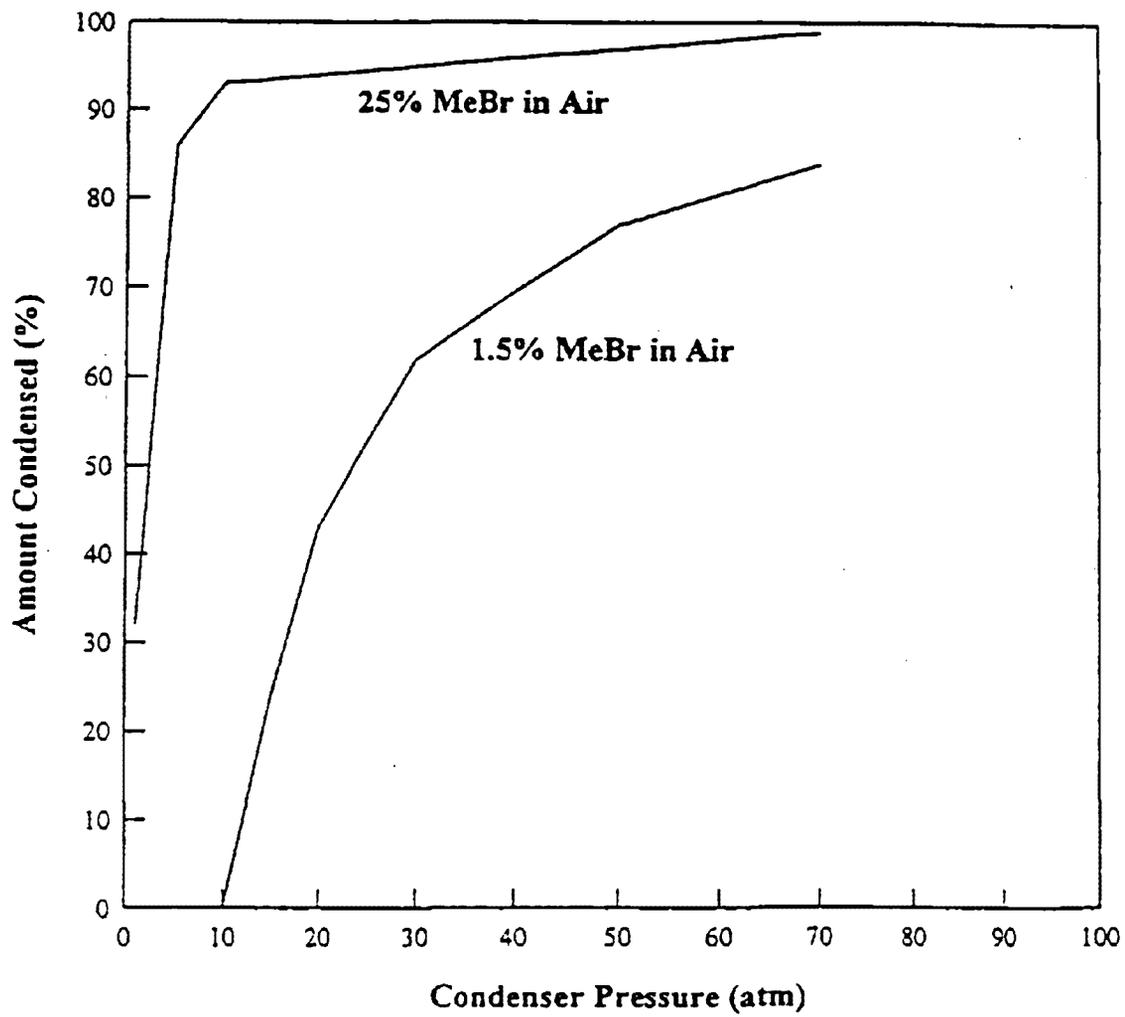


Figure 3-4. Methyl Bromide Condensation at -35°C Condenser Temperature

and other contaminants, would require proper disposal methods to be for the process to be commercially viable.

3.4 Additional Considerations for Adsorption and Condensation

Based on the information presented above, technology for capture and recycle of methyl bromide is advancing at the demonstration level. For large and/or frequently used chambers where high capital investment is justified, an adsorption/desorption process with direct recovery, recycle, and reuse may be the most cost-effective method if purity of the recycled methyl bromide is not a significant issue. The cost of recycled methyl bromide for reuse depends heavily on the number of fumigation cycles per year for a given facility. These systems appear to have the capability of capturing and recycling/ reusing methyl bromide at a cost that is roughly equivalent to purchasing virgin methyl bromide. However, more long-term performance data will be needed to completely characterize the suitability of these processes for direct reuse of methyl bromide in the fumigation chamber.

The issue of methyl bromide purity may become more important as operating experience is gained with adsorption processes. If captured methyl bromide is not suitable for direct reuse, a condensation step must be added to the process to produce liquid methyl bromide for reclaiming by the manufacturer or other party. This will add to equipment costs, and may also eliminate the economic credit for avoided purchase of virgin methyl bromide. Facilities that use this recovery method may be required to become US EPA regulated pesticide facilities.

The cost trade-offs between different approaches depends primarily on the chamber size and frequency of use, which fix the total amount of methyl bromide that must be captured.

Activated carbon may also be used to capture residual methyl bromide that cannot be economically recovered by an adsorption/desorption process. Very low

concentrations of methyl bromide may be captured, but at correspondingly low carbon loading and therefore high cost. Again, the cost trade-off between adsorption/desorption recovery efficiency and residual methyl bromide capture on once-through carbon will be site-specific.

The most significant economic factor is the annual quantity of commodities treated. The greater the quantity the lower the unit cost of the system applied to each batch of commodities treated. Approximate values of treatment cost with and without recycle/reuse and recovery related to total volume treated can easily be estimated.

For a given capital investment and the operating and maintenance costs for the emission control, recovery/reuse, and treatment system, the economics of treatment will depend on the following variables:

- 1) Total treatment volume per batch of commodity;
- 2) Methyl bromide requirement per treatment;
- 3) Methyl bromide recovery efficiency for recycle/reuse; and
- 4) Number of fumigations per year.

3.5 Effect of Impurities on Direct Recycle/Reuse of Methyl Bromide

In adsorption systems where capture and direct recycle/reuse of methyl bromide is intended, the potential effect of impurities in the methyl bromide must be considered. For example, natural odorant compounds from agricultural products or other compounds such as wood preservatives from pallets or off-gases from synthetic packaging materials might contaminate the recovered methyl bromide, making direct reuse impractical. In this case, the captured methyl bromide must be condensed and recovered as a liquid to be purified before reuse.

3.6 Other Technologies

So far we have discussed adsorption and condensation which appear to be the most promising technological approaches, to date, for recovery and recycle of methyl bromide for on-site reuse. One other technology that has shown promise in other applications for separations of organic substances from air streams is membrane separation (12). This technique compresses a gas stream to a suitable pressure, typically in the range of 45 to 200 psig, passes it through a condenser, and then a separation element containing a porous semipermeable membrane of a composite material. The organic compound passes through, while the air is retained on the high pressure side. The recovered organic, now much more concentrated than it was before, is more readily condensed for recovery. It is not known whether any attempt has been made to use this for methyl bromide or not. The suitability of this technology for methyl bromide recovery would have to be tried before data were available to make a realistic comparison between it and the other techniques already discussed. One reference states that membranes can be used with methyl bromide (13).

For final destruction of residual methyl bromide in any final vent stream, several methods were previously discussed (1). Methods include incineration, either direct or of spent activated carbon, chemical reagent scrubbing, and ultraviolet irradiation. We have not delved into the details of the latter method for this report, however, this technology has seen increasing application in recent years and might offer potential for methyl bromide destruction.

Our overall conclusion at this time is that adsorption techniques show genuine promise for methyl bromide recovery and reuse. However, the economics are very dependent on the total on-stream time in a year. Further, there still are some questions regarding sustained long term effects of reuse because of the possibility over time for the build up of contaminants, either from the commodities or from decomposition or reaction product with the methyl bromide. The incentive for more work in developing and testing recovery, recycle, and reuse techniques depends very much on the prospect for a change in the statutory ban on methyl bromide for 2001.

SECTION 4.0

INFORMATION GAPS AND FUTURE NEEDS

Research efforts at control appear to have been very limited. Although there have been many conferences on methyl bromide phase-out, they have all centered on finding an alternative replacement for methyl bromide, rather than on recovery and emissions control. Examples of these technical meetings are:

- UNEP Methyl Bromide Technical Options Committee meetings (held around the world);
- Methyl Bromide Alternatives Conference, Sponsored by Alliance for Responsible CFC Policy, and the U.S. Environmental Protection Agency, March 8-9, 1993, Fresno, CA.
- USDA Workshop on Alternatives for Methyl Bromide, June 29 - July 1, 1993, Crystal City, VA; and
- 1994 International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, Orlando, FL., November 1994.

Progress has been made and continues to be made concerning possible emissions control and recycle, recovery, and reuse technologies. There are still some remaining questions that must be answered and more experience is required before it can be stated unequivocally that the recycle, recovery, and reuse of methyl bromide is generally feasible. The future application of the required technologies appears to depend on expectations regarding the likelihood that regulatory exemptions on methyl bromide use could occur as the deadline of 2001 for the methyl bromide ban approaches. Only with the realistic prospect of such exemptions, or rescinding the ban entirely, would one expect there to be a strong incentive for extensive further research, development, and application of technology.

In the July 1994 report (1), some key issues that were identified as significantly influencing the progress of methyl bromide recovery, recycle, and reuse were the following:

- 1) Regulatory issues;
- 2) Stream characteristics;
- 3) Fumigation commodity containment options;
- 4) Achievable recovery from fumigation;
- 5) Technology performance characteristics;
- 6) Economic issues; and
- 7) Availability of substitutes.

Since 1994, the regulatory issues remain the same, with the future ban on methyl bromide still in effect. In spite of the most recent testing at the Port of San Diego, stream characteristics are still not defined. The testing there was based solely on methyl bromide removal and the quality of recycled methyl bromide, but did not examine other contents of the vent stream.

Achievable recovery information has advanced based on the most recent testing, and technology characteristics have been further clarified based on the recent tests. The operation of this system has contributed to a further understanding of the technical information needed for an economic evaluation, but such an evaluation still has not been performed. The availability of substitutes both in terms of substitute chemicals and new processes for pest control has received extensive investigation and continues to do so.

The fundamental performance characteristics for each potential recovery technology have not been established. Removal efficiency from the aeration stream has not been established. This information has not been obtained for:

- Specific commodities and commodity classes;
- Different containment options and fumigation applications; and

- Different control technologies.

The most critical needs appear to be for adsorption systems, especially with regard to contaminant effects from organic substances picked up from the commodities themselves and with regard to partial decomposition of the methyl bromide on the adsorbent. In addition to activated carbon, data are not available for zeolites and other adsorbents that might be candidates for adsorption applications.

Research on combustion and condensation would appear to be less critical, although the destruction efficiency at different flame temperatures and other combustion conditions is not available.

Additional considerations include:

- Performing tests on different commodities would be advisable to determine if differences between commodities might result in different levels and types of contamination in recycled/reused methyl bromide.
- Testing long-term operation through repeated removal and recovery cycles would be needed to prove that no breakdown products such as hydrogen bromide and other compounds nor accumulation of detrimental trace chemical materials would occur, especially as the recycle/reuse ratio of methyl bromide to makeup increased.
- Performing a detailed economic analysis between molecular sieve (zeolite) adsorption, activated carbon adsorption, and condensation (and other applicable technologies) should be made to determine the relative advantages and disadvantages across a full range of applications.
- Evaluating the implications of and costs of achieving different total emission limits for methyl bromide would have to be evaluated if methyl bromide were permitted in limited applications. The relative effectiveness and costs of greater removal efficiencies from the vent stream compared with requirements for final destruction of methyl bromide residuals from a recycle/reuse system would have to be compared.
- Establishing chemical purity specifications and standard analytical

protocols for recycled/reused methyl bromide to ensure its suitability for reuse.

Future needs in the development of methods for methyl bromide recovery, recycle, and reuse basically would be to expand the applications and performance data to establish the conditions under which the practice is feasible.

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