

COMPILATION OF AVAILABLE DATA ON

Building Decontamination Alternatives

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COMPILATION OF AVAILABLE DATA ON BUILDING DECONTAMINATION ALTERNATIVES

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This report was prepared in an effort to promptly provide as much information as possible on technologies that could potentially be utilized in decontamination of a building that has been subjected to a chemical or biological attack. As a result, this report has compiled large amounts of data from a variety of sources, often including the vendors of the technologies being addressed. It has not been possible to independently evaluate the data that are presented. Accordingly, the appearance of data in this report should not be interpreted as implying EPA validation of these data, or of the experimental protocols or quality assurance measures used in generating the data.

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ABSTRACT

In September 2002, the U.S. Environmental Protection Agency (EPA) created the National Homeland Security Research Center (NHSRC) within the Agency's Office of Research and Development (ORD). As one of the elements within NHSRC, the Safe Buildings Team has, as a key part of its responsibilities, engineering and economic analysis of alternative technologies and approaches for decontaminating buildings following an attack using chemical and biological (CB) agents.

As an initial step in this Safe Buildings Team decontamination program, NHSRC commissioned this state-of-the-art report, to provide background information regarding potential building decontamination technologies. This review of decontamination technologies is intended to: 1) assist NHSRC in prioritizing the technologies to be evaluated under its decontamination program; and 2) serve as an educational tool for the various NHSRC clients interested in building decontamination.

This document presents an analysis of selected technologies that have been tested for their potential effectiveness in decontaminating a building that has been attacked using biological or chemical warfare agents, or using toxic industrial compounds. The technologies selected to be addressed here fall into three broad categories:

- Liquid-based topical agents, including hypochlorite (bleach), aqueous chlorine dioxide, aqueous hydrogen peroxide, and a proprietary product (TechXtract).
- Foams and gels, including Sandia Foam and Decon Green, CASCAD, and L-Gel.
- Gaseous and vapor technologies (fumigants), including chlorine dioxide gas, vapor-phase hydrogen peroxide, paraformaldehyde, and methyl bromide.

Each of these technologies is reviewed in terms of its principles of operation, technical maturity, available data, concerns for the user, commercial availability, and advantages and disadvantages. No single technology is applicable in all situations; some technologies are better selections than others. As a broad generality, liquids are effective cleaners of non-porous surfaces, but may cause corrosion or degradation of the surface. Foams and gels have shown some promising results against both biological and chemical contaminants, but present post-decontamination cleanup issues, and require further demonstration. Gases and vapors have been demonstrated to be effective in destroying biological contamination under controlled conditions (e.g., in sterilization chambers) and, in some cases, in field remediations, but have not been effective in removing chemical contamination, and warrant further demonstration under the less well controlled conditions that exist during fumigation of a large building.

This document has been peer and administratively reviewed by the U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation of their use.

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1. EXECUTIVE SUMMARY

1.1 Objective

In September 2002, the U.S. Environmental Protection Agency (EPA) created the National Homeland Security Research Center (NHSRC) within the Agency's Office of Research and Development (ORD). As one of the elements within NHSRC, the Safe Buildings Team has, as a key part of its responsibilities, engineering and economic analysis of alternative technologies and approaches for decontaminating buildings following an attack using chemical and biological (CB) agents. The ultimate objective of this decontamination program is to produce a rigorous guidance document that can assist a range of users – including governmental agencies, building owners and operators, and cleanup contractors – in most effectively selecting and implementing the decontamination approach for any particular building following a CB attack.

As an initial step in this Safe Buildings decontamination program, NHSRC commissioned this report, to provide background information regarding potential building decontamination technologies. This state-of-the-art review of decontamination technologies is intended to: 1) assist NHSRC in prioritizing the technologies to be evaluated under its decontamination program; and 2) serve as an educational tool for the various NHSRC clients interested in building decontamination.

1.2 Decontamination Technologies Addressed in this Document

This document presents an analysis of technologies that have been tested for their potential effectiveness in decontaminating a building that has been attacked using biological or chemical warfare agents, or using toxic industrial compounds. This document does not present an exhaustive evaluation of all potential technologies. Rather, the focus is on what are currently felt to be the most promising technologies, based upon commercial use in related applications (e.g., medical sterilization), and based upon their apparent potential for possible use in building decontamination. The technologies presented in this document include:

- Hypochlorite
- Aqueous chlorine dioxide
- Aqueous hydrogen peroxide
- TechXtract[®]
- Sandia Foam and Decon Green
- CASCAD[®]
- L-Gel
- Chlorine dioxide gas
- Hydrogen peroxide vapor
- Paraformaldehyde
- Methyl bromide

Before a chemical product intended for use in decontaminating biological agents may be sold or distributed in the United States, EPA must either register that product as a pesticide under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), or, in the absence of registration, must grant a crisis exemption allowing its use. Once registered or exempted for this use, the pesticide would be commercially and legally available for use in accordance with the terms of the registration or exemption. To date, EPA has not issued any registrations for decontamination of biological threat agents in buildings, but has issued crisis exemptions that have permitted the unregistered use of a number of liquid and gaseous and vapor products for the treatment of *Bacillus anthracis*. EPA performed a full review of available data for each product along with the remediation action plans for each site to ensure the product would be used safely and would likely be effective against *Bacillus anthracis*. A list of the crisis exemptions approved to date by EPA is found at www.epatechbit.org under "Crisis Exemptions."

There are additional technologies that are in the pipeline that could be effective for building remediation efforts. Because they are still under evaluation, these technologies are not addressed in this report. In addition, standard chemical spill technologies, such as the use of absorbents, can be considered as well. Prior to selecting the agent(s) judged to be most appropriate for remediating a contaminated building, the user should consider the type and layout of the contaminated building; the materials in the building; the nature and extent of the contamination; the toxicity, penetrability, and materials compatibility of the potential agent(s); the aeration of the agent and any other by-products produced during the clean-up; history of usage of the agent(s); the time required to complete the remediation; and the cost of the overall process.

1.3 Summary of Technology Status

The technologies evaluated fall into three broad categories – liquids, foams and gels, and gases and vapors. Each has advantages and disadvantages depending upon the type of contaminant, the type of materials to be decontaminated, and the size of the remediation area. No single technology is applicable in all situations; some technologies are better selections than others. As a broad generality, liquids are effective cleaners of non-porous surfaces, but may cause corrosion or degradation of the surface. Foams and gels have shown some promising results against both biological and chemical contaminants, but present post-decontamination cleanup issues, and require further demonstration. Gases and vapors have been demonstrated to be effective in destroying biological contamination under controlled conditions (e.g., in sterilization chambers), but have not been effective in removing chemical contamination. There have been several demonstrations of gaseous fumigants for the biological decontamination of portions (or the entirety) of buildings under the less well controlled conditions that exist in the field, but further field tests are required to demonstrate the practical engineering and economic applicability of some of the fumigants.

Table 1.3-1 presents a summary of the technologies evaluated in this report, their technical maturity (i.e., whether under development, demonstrated but not available, commercially available, and whether approved by EPA for use as a pesticide), the type(s) of contaminant to which they are applicable, the types of building applications in which they can be used, and a summary of their effectiveness. Within the context of this report, “commercially available” indicates that the technology is available for purchase; however, as discussed above, if the

technology is to be used to against biological agents, the technology would require EPA approval for use as a pesticide.

Table 1.3-2 summarizes treatment issues to consider in selecting a technology, including compatibility of the technology with typical building materials, a summary of the types of residuals that will be generated from treatment, and information on performance of or need for specialized hardware.

More detailed information on each technology can be found in Sections 3 through 5 of this report.

Table 1.3-1. Summary Table of Applicable Technologies

Technology	Technical Maturity	Applicable Agents	Scope of Building Applications	Effectiveness
Hypochlorite	Mature, commercially available.	Chemical agents: (nerve and blister) Biological agents (<i>Bacillus anthracis</i>)	Treatment of contaminated surfaces in sites of varying sizes.	Reports state the effectiveness on chemical agents, but no data are available. A 6 log kill of <i>Bacillus subtilis</i> was achieved on hard, non-porous surface treated with sodium hypochlorite at pH 7 with a 60-minute contact time.
Aqueous chlorine dioxide	Mature, commercially available.	Biological agents	Treatment of contaminated surfaces in sites of varying sizes.	EPA has data showing the efficacy of 500 ppm aqueous chlorine dioxide on hard, non-porous surfaces after 30 minute contact time. EPA issued a crisis exemption for building surfaces on this basis.
Aqueous hydrogen peroxide	Mature, commercially available.	Chemical agents: (nerve and blister) Biological agents	Treatment of contaminated surfaces in sites of varying sizes.	EPA reviewed data from companies showing the efficacy of one hydrogen peroxide product and four hydrogen peroxide & peracetic acid mixture products with contact times ranging from 10 to 30 minutes. On the basis of these data, EPA issued crisis exemptions for the use of these products on building surfaces.
TechXtract	Innovative, commercially available.	Toxic industrial materials	Removal of organics from porous materials (e.g., concrete floors) and from metal equipment.	Greater than 99.93% reduction in dioxin/furan concentrations; variable performance on removal of PCBs from concrete.
Sandia Foam and Decon Green	Sandia Foam: Commercially-available, full scale Decon Green: Not commercially available	Chemical agents: (nerve and blister) Biological agents (<i>Bacillus anthracis</i>)	Limited: wall and floor surfaces, small areas, non-sensitive equipment, personnel protective equipment, furnishings (non-fabric)	Potentially effective decontaminant for chemical agents in military and industrial applications; easy to apply. EPA issued a FIFRA crisis exemption for two foams derived from the Sandia formulation, but these were later withdrawn when one of the technologies failed to pass EPA's AOAC Sporocidal Activity Test. EPA has not received or reviewed data for Decon Green under FIFRA.

Technology	Technical Maturity	Applicable Agents	Scope of Building Applications	Effectiveness
CASCAD	Commercially available.	Chemical agents: (nerve and blister) Biological agents (<i>Bacillus anthracis</i>) Radiological containment	Product is not demonstrated in buildings but foam-based application to surfaces and walls is possible.	Vendor claims removal of nerve agents within five minutes of application. US test data show variability in treatment effectiveness that requires additional study. EPA has not received or reviewed data for CASCAD under FIFRA.
L-Gel	Innovative. Nearing commercialization.	Chemical agents: (nerve and blister) Biological agents (<i>Bacillus anthracis</i>)	Gel form will adhere to vertical and overhead surfaces. Penetrates paint and varnish.	Research shows more than 99 percent effective for all agents on all surfaces. EPA has not received or reviewed data for L-Gel under FIFRA.
Chlorine dioxide gas	Mature in a range of applications (medical sterilization, water treatment, oil well treatment). Commercially available.	Biological agents (<i>Bacillus anthracis</i>)	Used to fumigate three sites, ranging in volume from 90,000 to 14 million cubic feet, contaminated with <i>B. anthracis</i> . Need to achieve proper ranges of temperature, relative humidity, concentration and exposure duration to achieve effective kill rates. Must be able to seal area completely.	Data show six log kill in a reproducible fashion on specific surfaces under controlled conditions in test chambers or bio-medical sterilization units. Highly effective in reducing <i>B. anthracis</i> spore load in Hart Senate Office Building, though further surface treatment with liquid agent needed. In combination with other decon steps, successful in remediating the Brentwood (Washington, DC) postal facility, since all post-remediation environmental samples were negative. Along with other steps, also successful at the Trenton, NJ, postal facility.

Technology	Technical Maturity	Applicable Agents	Scope of Building Applications	Effectiveness
Hydrogen peroxide vapor	Mature in pharmaceutical applications. Commercially available.	Biological agents	Used in pharmaceutical industry to treat manufacturing clean rooms and laboratory animal toxicology rooms. Used to fumigate two federal mail facilities, with volumes of 1.4 to 1.7 million cubic feet, contaminated with <i>B. anthracis</i> spores. Both buildings were sub-divided into zones no greater than 250,000 cubic feet each. Zones were fumigated sequentially. Hydrogen peroxide vapor interacts with nylon and with porous surfaces, thereby losing effectiveness.	Documented effectiveness against viruses, bacteria, and spores under controlled conditions. Achieved log six kill on all <i>B. steartotherophilus</i> biological indicators in all zones fumigated at GSA Building 410 and at the Dept. of State mail annex SA-32. Special effort required to maintain H ₂ O ₂ concentration in SA-32 due to porous surfaces (e.g., unpainted concrete block) in the building.

Technology	Technical Maturity	Applicable Agents	Scope of Building Applications	Effectiveness
Paraformaldehyde	Mature in biomedical lab applications. Commercially available.	Biological agents	Used to decontaminate labs and biosafety hoods for range of bio agents, including <i>B. anthracis</i> . Following 2001 <i>B. anthracis</i> mail attack, was used successfully in Dept. of Justice mail facility to treat mail sorting equipment enclosed within a tented volume. Utilized by US Army Medical Research Institute of Infectious Diseases (USAMRIID) to decontaminate entire buildings with high levels of <i>B. anthracis</i> contamination. Has good penetrability of surfaces. The fumigant (which is a Hazardous Air Pollutant) – and the byproducts from reaction of the fumigant with organic compounds on surfaces – might de-gas from porous surfaces over a period of time.	Proven effectiveness in multiple settings, including labs, isolated volumes within buildings, and, in USAMRIID’s case, entire buildings. USAMRIID regulations for fumigations of articles and areas within buildings stipulates that spore strips containing 10 ⁵ spores of <i>B. stearothersophilus</i> and additional spore strips containing 10 ⁶ spores of <i>B. subtilis</i> var. <i>niger</i> all be negative for growth of the spores after fumigation; otherwise the fumigation is to be repeated.
Methyl bromide	Innovative in this application. Commercially available for residential, agricultural pest control applications.	Biological agents. (Has historically been applied for insects.)	Testing in a mobile home showed ability to kill spores in the Bacillus family in difficult-to-reach areas. A concern is that methyl bromide is an ozone depleter, and no effective system has yet been demonstrated for destroying the fumigant following fumigation.	In a test trailer, achieved 6-log kill of <i>B. anthracis</i> surrogates in hard-to-reach locations following a two-day fumigation.

Table 1.3-2. Summary of Technology Application Issues

Technology	Materials Compatibility	Residuals/ Degradation Products	Additional Hardware Requirements
Hypochlorite	Not compatible with dyes. Corrosive. Oxidant.	Corrosive nature of material means that waste products should be managed and disposed of as hazardous waste.	Not applicable.
Aqueous chlorine dioxide	Harmful to fabrics (oxidant)	Excess aqueous solution is an oxidant. If gas is generated on-site to produce the solution, byproducts of the generation process can include a brine solution, depending on the process.	Commercial aqueous ClO ₂ products can be imported from off-site, requiring no additional hardware on-site. Alternatively, aqueous ClO ₂ can be produced by solubilizing ClO ₂ gas manufactured on-site using on-site generators.
Aqueous hydrogen peroxide	Harmful to fabrics (oxidant)	None. Breaks down to water and oxygen after treatment.	Not applicable.
TechXtract	Abrades or dissolves away treated porous surface.	Fresh TechXtract solution is not hazardous, according to the vendor. Waste extract generated by the use of the product may contain hazardous chemicals.	No data.
Sandia Foam and Decon Green	Bare steel objects are susceptible to rust after application. Safe on all other surfaces, according to the vendor.	Foam requires removal and may be contaminated with removed chemicals.	Uses standard, commercially available paint sprayers.
CASCAD	No effect on paint, rubber, or aluminum, according to the vendor.	Foam requires removal and may be contaminated with removed chemicals.	Uses standard firehoses. A backpack version also can be purchased from the vendor.
L-Gel	No harm to carpet or paint, according to the developer.	Silica in gelling material considerably increases the amount of waste requiring management.	Uses standard, commercially available paint sprayers. Must use a metal nozzle due to corrosivity of L-Gel.
Chlorine dioxide gas	Bleaching of selected fabrics and photographic materials.	Wastes will include: a) wastes from generation of the ClO ₂ (e.g., a brine solution, depending upon the ClO ₂ vendor); and b) wastes from scrubbing the ClO ₂ from the fumigated area prior to aeration (e.g., a caustic sulfite/sulfate solution).	Gas is unstable and cannot be stored in canisters. A specialized, potentially sophisticated gas generation system is required, which will vary depending upon the ClO ₂ vendor. A system will also be required for scrubbing the residual ClO ₂ from the building air following fumigation.

Technology	Materials Compatibility	Residuals/ Degradation Products	Additional Hardware Requirements
Hydrogen peroxide vapor	Not corrosive, but will discolor dyes and have unfavorable interactions with nylon. Porous surfaces may degrade and inactivate hydrogen peroxide vapor.	None. Vapor introduced/withdrawn from site in closed system containing a catalyst on the return side which degrades hydrogen peroxide vapor to water and oxygen.	Hydrogen peroxide vapor is produced by heating a 35% solution of hydrogen peroxide.
Paraformaldehyde	No problems reported.	Following fumigation, the formaldehyde (a Hazardous Air Pollutant) is scrubbed from the treated area using, e.g., ammonium bicarbonate prior to aeration. Byproducts from this scrubbing process will be a waste.	<i>p</i> -Formaldehyde can be heated on hotplates using disposable pie tins or by using a generator system.
Methyl bromide	No damage to photographic, cellulosic, fabric, or electronic materials in two experiments in a trailer.	After treatment, the methyl bromide must be scrubbed from the treated area, and there will likely be wastes from this scrubbing process. Byproducts from this scrubbing process will be a waste. Currently, there is no treatment to destroy methyl bromide following fumigation; in the experiments performed to date, it has been released directly to the environment.	Liquid under pressure is heated on-site to create vapors that are pumped into the space to be fumigated.

1.4 Identification of Areas for Potential Research

Table 1.4-1 presents the areas of potential future research identified for each technology as well as those applicable to all.

Table 1.4-1. Potential Research Areas

Technology	Research Areas
Hypochlorite	<ul style="list-style-type: none"> • At what concentration, pH, contact time, or other parameters would hypochlorite be effective on porous surfaces.? • At what concentration, pH, contact time, or other parameters would hypochlorite be effective on biological agents other than anthrax spores?
Aqueous hydrogen peroxide	<ul style="list-style-type: none"> • Field testing is needed to determine treatment effectiveness and operational variables (e.g., contact time, concentration) towards both chemical and biological agents.
Aqueous chlorine dioxide	<ul style="list-style-type: none"> • Field testing is needed to determine treatment effectiveness and operational variables (e.g., contact time, concentration) towards both chemical and biological agents.
TechXtract	<ul style="list-style-type: none"> • Laboratory and field testing of the technology is needed, including destruction effectiveness, against chemical warfare agents such as VX and GB. • Testing is needed of treatment effectiveness on nonporous surfaces.
Sandia Foam/ Decon Green	<ul style="list-style-type: none"> • Field tests are needed to demonstrate the effectiveness of the technology and the stability of hydrogen peroxide in “dirty” environments.
CASCAD	<ul style="list-style-type: none"> • Independent verification of manufacturer’s claims is needed. • Validation is needed of use for initial isolation of contamination.
L-Gel	<ul style="list-style-type: none"> • Verification is required of pending improvements to increase penetration into porous surfaces and to aerosolize L-Gel for application to interior ventilation systems. • Mechanisms must be studied to minimize the mass of amorphous silica used. • Potential for stabilization of waste materials must be studied.
Chlorine dioxide gas	<ul style="list-style-type: none"> • Further research is needed to determine D-values for ClO₂ concentrations in range (750 - 2000 ppm) used for fumigations of three contaminated facilities • Reliable, rugged, and cost effective real-time monitors for ClO₂ concentration must be developed in the concentration range used for fumigations • Research is necessary on effectiveness against other biological agents. • Research is needed on effectiveness against chemical agents.
Hydrogen peroxide vapor	<ul style="list-style-type: none"> • Research is needed on materials in buildings which absorb and/or react with vapor, decreasing effective concentration in space being fumigated. • Research is needed to develop an improved system for vapor generation • Feasibility of scaling up technology to fumigate spaces larger than 200,000 cubic feet must be demonstrated.
Paraformaldehyde	<ul style="list-style-type: none"> • The optimal combination of vapor concentration, relative humidity, temperature, and contact time needed to achieve effective decontamination must be determined. • Quantification is needed of the effectiveness of treatment on porous surfaces and difficult to reach areas.
Methyl bromide	<ul style="list-style-type: none"> • More extensive research is needed on critical process parameters for effective spore kill; namely, temperature, relative humidity, vapor concentration, exposure time. • A practical system to destroy methyl bromide vapor following fumigation must be demonstrated, so as not to release it to the environment
Other	<ul style="list-style-type: none"> • A standardized method must be developed for preparation of bacterial and viral standards for remedial technology validation. • Effectiveness of using combinations of technologies (i.e., different gas phase technologies) as a treatment train should be studied.

1.5 The NHSRC Decontamination Program to Address these Issues

The NHSRC Safe Buildings decontamination program, designed to address the issues raised above, to the extent possible, is formulated as follows.

“Lessons Learned”. Extensive practical experience in building decontamination has been developed during the course of the building remediations that followed the 2001 anthrax mail attacks. Under the Safe Buildings program, NHSRC will interact with all of the principals involved in these remediations, compiling the data that were generated and documenting the practical field experience that was gained. This will enable NHSRC to provide decontamination guidance to future users that draws, as fully as possible, on the past experiences.

“Systematic Decon”. In a series of controlled experiments, NHSRC will determine how the performance of alternative decon technologies – liquids, foams and gels, and gases and vapors – vary as key parameters are varied. The parameters that will be varied include, e.g., the nature of the CB agent, the substrate on which the agent is deposited (wallboard, carpeting, etc.), the concentration of the decon agent, the exposure time, the temperature, and the relative humidity. Performance measures will include the efficacy of killing biological agents or neutralizing chemical agents, compatibility of the decon agent with the substrate, and residual degradation products left on the decontaminated surface. The results from these experiments will address many of the questions raised in Table 1.4-1, regarding the effectiveness of these decon agents under various conditions.

Decon Environmental Technology Verification (ETV). NHSRC has established a Decon ETV program, under which vendors of decontamination technologies can submit their technologies for independent testing by EPA under a standardized protocol. The results from this ETV testing will provide EPA and potential users with an increased, independent database on the performance of these technologies.

Engineering and Economic Analysis. Drawing from the above three projects, a parametric analysis will be conducted of the practical engineering issues that will have to be addressed, and the cost-effectiveness of the remediation, for alternative decontamination approaches. The parameters that will be addressed will include the nature of the CB attack, key variables defining the building, and key variables associated with each step of the overall remediation process. The results will be reviewed to determine whether preferred remediation approaches become apparent for particular building characteristics and attack scenarios.

Decon Technical Guidance Document. The results from all of the tasks above will be brought together in the development of a user-oriented technical guidance document for building decontamination. This document would assist building owners and operators, governmental agencies, remediation personnel, and others in the cost-effective selection and implementation of remedial action steps in the event of a CB attack on a large building. Once the user has defined the characteristics of the building and the extent and nature of the attack, the guidance document would suggest, for example: the extent, methods, and cost of sealing the “hot zone”; the extent (and costs) of removal of interior furnishings for disposal, prior to further building treatment; the nature and extent of interior decon (with HEPA vac and liquid agents) prior to fumigation, and the associated costs; fumigation methods, and cost-effective operating conditions; and the nature and amounts of wastes requiring disposal.

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2. INTRODUCTION

2.1 Scope, Purpose, and Summary

Following the events of September and October, 2001, there is increased concern regarding the possibility of the deliberate introduction of chemical or biological (CB) agents, toxic industrial chemicals (TICs), or toxic industrial materials (TIMs) into buildings by terrorists. Such an attack would require effective and prompt efforts to protect building occupants and to decontaminate the building for re-occupancy. Work on decontamination following CB attacks has been underway at the Department of Defense (DoD) and other agencies for many years, often focused on military applications.

On September 24, 2002, the EPA Administrator announced the formation of EPA's National Homeland Security Research Center, headquartered in Cincinnati, Ohio. The Center, as part of the Office of Research and Development (ORD), manages, coordinates, and supports a wide variety of homeland security research and technical assistance efforts. Research at the Center will focus on developing methods to: 1) protect building occupants during a CB attack, and to decontaminate contaminated buildings following the attack (including proper disposal of contaminated waste materials); 2) protect the nation's drinking water supply; and 3) improve risk assessment techniques. Research on homeland security will develop the scientific foundations to provide decision-makers with increased understanding and tools necessary to prevent or manage a range of potential treats.

This document is intended provide background information on potential post-attack building decontamination technologies, as an aid to EPA in planning their program and as an educational tool for other users. The document critically analyzes the general knowledge and primary references regarding commercial and near commercial technologies for decontamination of surfaces contaminated with CB agents, TICs, and TIMs. This document is intended for educational purposes. As such, it provides an overview of selected technologies, discusses the available data and efficacy, and highlights potential research needs.

2.2 Summary of Decontamination Technologies Selected for Evaluation

The starting point for identification of technologies was the *Review of Decontamination Technologies for Biological and Chemical Warfare Agents* (Mitretek, 2003) prepared by Mitretek for EPA, which provided an overview of potential remediation technologies and included a literature review. Other primary sources consulted were the DoD *Wide Area Decontamination Study* (Battelle, 1999), materials from the EPA Technology Innovation Office (TIO), and other readily available references. A list of potential technologies, shown below, was developed.

Surface-Applied Technologies

- Hypochlorite
- Aqueous hydrogen peroxide
- Aqueous chlorine dioxide
- HPO2[®] (enhanced aqueous H₂O₂)
- Decontaminating Solution 2 (DS2)
- TechXtract[®]
- Nanoemulsions
- Enzymes
- Sandia Foam and Decon Green
- CASCAD[®]
- L-Gel

Gas- and Vapor-Phase Technologies

- Ethylene oxide
- Chlorine dioxide gas
- Hydrogen peroxide vapor
- Paraformaldehyde
- Ozone
- Methyl bromide

Other Technologies

- Directed energy
- Photochemical
- Plasma

A brief synopsis of the potential for use of the technology in a building remediation application was drafted and formed the basis for determining the technologies to be included in this document. A summary of the determination on each technology is presented below.

2.2.1 Surface-Applied Technologies Considered

Surface applied technologies include liquids and foams or gels. Liquid technologies involve the application of liquid decontamination solutions directly on a surface contaminated with a biological or chemical agent. Eight technologies are evaluated in this category – hypochlorite (e.g., bleach), aqueous hydrogen peroxide, aqueous chlorine dioxide, HPO₂, DS2, a proprietary technology called TechXtract, and nanoemulsions. With these technologies, the solution is applied to the surface of the material to be decontaminated. The solution is removed by wiping or wet vacuuming.

Foam and gel technologies are designed to enhance surface removal of biological or chemical contaminants by delivering the decontamination formulation in a matrix that can be applied to vertical and horizontal surfaces. This allows the application to walls with sufficient contact time to ensure that the CB agent is effectively treated. In this category, three technologies are evaluated – Sandia Foam and Decon Green, CASCAD, and L-Gel.

Hypochlorite: Historically, chlorine-based decontamination systems have been effectively employed against chemical and biological agents. The use of hypochlorite solutions (aqueous and non-aqueous) or solid/slurry hypochlorites has been wide spread for military applications. Hypochlorite is a standard decontaminant in military applications, excluding shipboard use. This general purpose decontaminant has been used on personnel, equipment, clothing, building surfaces, and soil. It is relatively easy to obtain and inexpensive. While an effective decontaminant, it is corrosive, can form toxic by-products, and has irritant properties that are undesirable. The military typically uses HTH (high test hypochlorite) and STB (super topical bleach), along with household bleach solutions, for agent spills and personnel decontamination. In addition, EPA evaluated data on one hydrogen peroxide and four hydrogen peroxide/peracetic acid mixtures. Based on efficacy at contact times ranging from 10 to 30 minutes, EPA issued a crisis exemption for the use of these products on building surfaces. Because of the wide

experience in its application and its commercial availability, this technology was further evaluated in this report.

Aqueous hydrogen peroxide: There are several sterilization products on the market which contain hydrogen peroxide. These have applications in the food and medical industries for general hard surface cleaning of biological organisms as well as food preparation. Additionally, there are specialized formulations available which have been developed specifically for building or warfare decontamination. Because of the potential for application to building decontamination, this technology is evaluated further in this report.

Aqueous chlorine dioxide: As a biological sterilizer, chlorine dioxide (ClO_2) is an oxidant for biological organisms and the exact method of destruction is not known. Unlike Chlorine (Cl_2), chlorine dioxide is a single-electron transfer-oxidizing agent and does not react with organics to form harmful chlorinated products such as trihalomethane and chloramines. Chlorine dioxide has extensive use in drinking water treatment, generated from sodium chlorite and fed into the water. Sodium chlorite-based cleaners are used in the food processing industry for cleaning of surfaces and of food itself. EPA has data showing the efficacy of aqueous chlorine dioxide against *Bacillus* spores on hard, non-porous surfaces when applied at a concentration of 500 ppm for a 30-minute contact time. A crisis exemption for use of this agent against *B. anthracis* on building surfaces was issued by EPA on the basis of these data. This technology has the potential for application in buildings and is commercially available. As a result, it is further evaluated in this document.

HPO2[®]: EAI Corporation patented a variation of the aqueous hydrogen peroxide system called HPO2, in which hydrogen peroxide is added to Oxone[®]. The technology is reported to work for bulk treatment of chemical agents. Variants of hydrogen peroxide have promise, but no data could be located on this technology. Further, its commercial availability is unknown. As a result, this technology was not addressed in this report.

DS2: DS2 is recognized as the military bench mark for effective chemical and biological decontamination. DS2 was developed to destroy VX and reacts with G agents and mustard gas at ambient temperatures. It is a mixture of 70 percent diethylenetriamine (DETA), 28 percent ethylene glycol monomethyl ether (also known as 2-methoxyethanol), and two percent sodium hydroxide (NaOH). The sodium hydroxide reacts with 2-methoxyethanol to form ethoxide. As DETA is added, free sodium radicals are bound in the mixture. DS2 is highly reactive, yet stable in storage under a broad range of temperatures and times. DS2 is no longer manufactured and is not used at chemical agent destruction facilities because of its corrosive nature to rubber, paint and plastics and its environmental effects. Sorbents, enzymatic foams, other foams, oxidative and reactive formulations, and BX24 (a powder that is mixed with water) are under investigation as replacements. Because replacements for DS2 are being actively investigated and DS2 is recognized to have corrosive properties, it was not evaluated in this report.

TechXtract[®]: TechXtract is designed to remove organics, heavy metals and radionuclides from the surface and subsurface of porous and nonporous solid materials such as concrete, brick, wood, and steel. Active Environmental Technologies, Inc. calls TechXtract a "contaminant extraction technology." The technology uses proprietary chemical mixtures to treat surfaces including floors, walls, ceilings, and equipment. The mixtures may include macro-

and micro-emulsifiers, buffered organic and inorganic acids, and hydrotropic, electrolyte, flotation, wetting, and sequestering agents that extract the contaminants and bring them to the surface. The chemical mixtures are applied sequentially, in successive cycles. Each treatment cycle includes application, penetration, and extraction. Wet vacuuming is used to remove the solutions from the treated substrate. This low-tech, but innovative, aspect of the technology is an important element of its effectiveness for porous substrates. Effective decontamination of a porous surface will be one of the more challenging aspects of building decontamination. TechXtract is effective for porous surface decontamination because wetting agents are used to increase permeation into pores and wet vacuuming is used to get treatment solutions back out of pores. While effective on porous surfaces, some abrasion or dissolution of the surface occurs. The proprietary mixtures may include fluorides or other chemicals that present worker health and safety issues. Because TechXtract was tested and demonstrated in hazardous waste building remediation, it was selected for further evaluation in this document.

Nanoemulsions: A generic nanotech emulsion is a mixture of detergent, buffer, oil and water. The combination is emulsified and stable for many months. This material is not toxic and can be applied to personnel as well as equipment. Current applications require manual application, but the technology could be modified for spraying for wide application. Nanotech emulsions are reported to be effective against both chemical and biological agents. Nanotech technologies under development include a line of virus and pathogen Nanofilters[®] developed by US Global Nanospace for use in aircraft and buildings. However, nanotech emulsions are in the early development stages with additional research still underway. While the technology shows promise, its near term applications are limited, and it was not evaluated for building remediation applications.

Enzymes: Enzymatic systems are reported to have been developed and tested successfully against chemical agents. Researchers at Edgewood Chemical Biological Center are actively engaged in these efforts. They identified and characterized enzymes that are effective against chemical and biological agents and cloned the enzymes' genes. These enzymes decontaminate chemical and biological agents through catalysis. The researchers developed a powder form of the enzymes that requires the addition of water for decontamination. The powders are designed to attack specific contaminants, such as VX and mustard gas. This technology shows promise but is at the research stage. At the current time, little data on these systems with respect to building decontamination are available; additional information would be needed to consider this emerging technology. Further, the technology is not yet in commercial production. As a result, this technology was not addressed in this report.

Sandia Foam/Decon Green: Peroxide-based systems are one of the more visible chemical agent decontamination systems in the market today. Sandia National Laboratories developed "Sandia Foam," which is marketed under the trade names EasyDecon[®] and Modec Decon Formula (MDF) 200[®]. The Sandia foam uses a combination of surfactants and oxidizers to inactivate both biological and chemical agents. Edgewood Chemical Biological Center patented a similar system called Decon Green. These systems are claimed to be effective against all chemical agents, be easily applied, and not produce toxic residues or byproducts. Both Sandia and the West Desert Test Center at Dugway Proving Ground have reported six-log kills of *Bacillus anthracis* spores within one hour. EPA issued a crisis exemption for the use of these foams in building remediation for *B. anthracis*. These were later withdrawn when, in separate

testing conducted by EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), one of the foams did not pass testing to be listed as a sterilizing agent for *B. anthracis*. Because these technologies have potential, they were selected for further evaluation in this document.

CASCAD®: The Canadian Aqueous System for Chemical Agent Decontamination (CASCAD) is a chlorine-based system that delivers an aqueous foam designed to contain and eliminate chemical and biological warfare agents and remove radioactive particle contamination. The immediate isolation and containment of the contamination is its most significant advantage. The active decontaminating ingredient is sodium dichloroisocyanurate (fichlor). Fichlor is used extensively in the food and beverage industry as antibacterial detergent. CASCAD has been tested in Canada, the U.S., and the U.K. For surface decontamination, the biodegradable foam is easily applied and sticks to vertical surfaces. CASCAD is intended for exterior applications on tanks and military equipment. Its use on building interiors has not been tested. Because there is a body of data on decontamination of biological agents, CASCAD is being evaluated as a building remediation alternative.

L-Gel: Lawrence Livermore National Laboratories has developed the L-Gel system using Oxone®, with fumed silica as a gelling agent. Oxone is a non-chlorine alternative used as a decolorizer and disinfectant. The active ingredient in Oxone is potassium peroxy monosulfate, KHSO₅. Similar in formulation to the Sandia Foam, this material combines oxidants with surfactants to destroy biologicals by disrupting the lipid component. Oxone has been shown to effectively react with chemical agents. Mechanisms for inactivation of chemical agents are less well known, but the compound is effective against both classes of agents. L-Gel can penetrate polymeric coatings such as paint and varnish. It is relatively inexpensive (about \$1 for materials only to treat 1 square meter). However, L-Gel is not commercially available (although licensing discussions are underway). Additionally, the silica gelling agent increases the amount of waste requiring management after remediation. However, because of its potential applicability to both chemical and biological agents and its near-term commercial production status, this technology is further evaluated in this report.

2.2.2 Gas- and Vapor-Phase Technologies Considered

Gas and vapor phase technologies require that the area to be contaminated be completely sealed to prevent the escape of the gas or vapor. This may require tenting the entire structure, or comprehensive sealing of shell openings throughout the entire building (or in a particular zone that is to be treated within a larger building). The gas or vapor is injected into the sealed area and allowed to remain in place for the period of time required to ensure treatment. Gas and vapor technologies are more susceptible to variations in temperature and humidity than liquid and foam and gel technologies. Therefore, ways to control these variables must be considered. Five gas and vapor phase technologies were considered – ethylene oxide, gaseous chlorine dioxide, hydrogen peroxide vapor, paraformaldehyde, ozone, and methyl bromide.

Ethylene oxide: Ethylene oxide, an odorless gas at room temperature, can be used for in several applications, including walk-in sized chambers. It is widely used in hospital and biomedical sterilization applications because it is highly penetrating. Off-site ethylene oxide chambers were used for the successful sterilization of critical items for re-use, during anthrax remediation

efforts on Capitol Hill and in other federal mail facilities as well as at the National Broadcasting System (NBC) offices in New York City. Ethylene oxide is a highly reactive molecule with vapors that are flammable and explosive. As little as three percent ethylene oxide in air can be flammable (NIOSH, 1994). Toxicity data indicate that ethylene oxide is irritating to the skin, eyes, and mucous membranes of respiratory tract. Toxicity data indicate that acute exposure to ethylene oxide can cause nausea, vomiting, and death. Chronic exposure can cause irritation of eyes, skin, and mucous membranes, cataracts, and problems in brain function. Exposure to ethylene oxide may result in lung, liver, and kidney damage (U.S. Department of Health and Human Services, 1993). Ethylene oxide is rated as a Group B1 (probable) human carcinogen. Health concerns for subsequent off gassing resulted in an additional heating step to aid in the release of ethylene oxide from the critical items treated during the remediation efforts in Washington, D.C. and New York City. Due to the human health issues and the flammability of ethylene oxide – limiting its use to carefully controlled chambers – this technology is felt to have no applicability for the fumigation of buildings, other than possible use off-site for sterilization of critical items. Hence, it was not evaluated in this study.

Chlorine dioxide gas: Chlorine dioxide was discussed earlier under surface applied (aqueous) technologies. Here, chlorine dioxide is considered in its gaseous form. The chlorine dioxide gas must be generated on site where remediation occurs using commercially available generators due to the instability of the gas. Gas replacement during remediation is required due to the instability. However, this instability has a benefit in that the gas rapidly decomposes after treatment. The gas has better penetrability than hydrogen peroxide vapor, and thus may more likely be effective on porous surfaces, although this has yet to be demonstrated. Temperature and humidity need to be controlled; effective performance may be very difficult to achieve if the relative humidity drops below 60%. Because this technology was employed successfully for the remediation of the Hart Senate Office Building and the Brentwood (Washington, D.C.) and Trenton, New Jersey, U.S. Postal Facilities, it is further evaluated in this report.

Hydrogen peroxide vapor: Hydrogen peroxide vapor is used to treat pharmaceutical manufacturing clean rooms and laboratory toxicology rooms. Hydrogen peroxide vapor was used in the remediation of two federal mail facilities following the 2001 incident. It was demonstrated to be effective against *Bacillus* spores, including the *anthracis* strain. This technology is mature and commercially available. Because of its use in building remediation, this technology is further evaluated in this report.

Paraformaldehyde: Paraformaldehyde is used for routine decontamination of labs and biosafety hoods in clinical and research laboratories for a broad spectrum of biological agents, including *Bacillus anthracis* spores. Paraformaldehyde is heated to generate formaldehyde gas for use as a sterilizing agent. This gas has been used by the U.S. military for the successful remediation of numerous laboratories and buildings. Formaldehyde is an animal carcinogen and probable human carcinogen, and it is genotoxic in a number of assays. This technology is mature and commercially available. Because it has been used by the U.S. Army Medical Research Institute of Infectious Diseases to decontaminate buildings, and was used for treating a mail processing machine in the Department of Justice mail room following the 2001 *B. anthracis* mail attacks, it is further evaluated in this report.

Ozone: Ozone is a reactive form of oxygen that is a strong oxidant with documented ability to kill spores, bacteria and viruses. Ozone generation systems are commercially available. However, ozone has not been used for remediation of buildings. While this technology is promising and could be considered for further evaluation in the future, it is not further evaluated in this report.

Methyl bromide: Methyl bromide is approved for use as a pesticide under controlled conditions. Its most common use is to kill termites in buildings, and in soil treatment for agricultural pest control. Recent demonstrations show its potential for killing *Bacillus* spores. As a result, the technology is further evaluated in this report. However, methyl bromide is an ozone-depleting compound. In addition, it has potential human health effects. It has cumulative, delayed effects on the central nervous system, which may appear as long as several months after exposure. High concentrations can produce fatal pulmonary edema. Chronic exposure can cause central nervous system depression and kidney injury. It may cause severe and permanent brain damage. Severe neurological signs may appear when there is a sudden exposure to high concentrations following continuous slight exposure. Methyl bromide has practically no odor or irritating effects and therefore no warning, even at hazardous concentrations (EPA, 2003).

2.2.3 Other Technologies Considered

Directed energy alternatives: Directed energy methods for decontamination, such as electron beam, x-ray, gamma ray, ultra violet radiation, and microwave radiation, have all been demonstrated to disinfect surfaces. As energy transfer methods, all of these systems can kill bacteria, bacterial spores, and viruses, given sufficient time and power. However, their use for building remediation is questionable. While technically possible, it is probably not reasonably feasible. Two of the major concerns are shadowing and control of the directed energy. Contamination within a building will most likely spread to multiple surfaces, many of which might not be easily accessible to directed energy approaches. While penetrating energy such as electron beam, gamma, and x-rays might overcome many of the shielding issues, their cost and secondary damage when applied to buildings could make them undesirable alternatives. As such these technical alternatives were not reviewed in this document.

Photochemical: Clean Earth Technologies, LLC, located in St. Louis, MO, has developed the Electrostatic Decontamination System (EDS) for the Technical Support Working Group (TSWG). Their two step process works on both biological and chemical agents. The EDS is configured with a photosensitizer sprayer unit (pressurized or battery powered), a photosensitizer (PS) storage unit, and a light source unit (210 – 310 nm UV light source) for activation. The unit weighs under 50 pounds and is contained on a cart for portability. Clean Earth Technologies claims the system is effective at rapidly neutralizing chemical agents and toxic industrial chemicals (TICs) to levels below their Immediately Dangerous to Life and Health (IDLH) concentrations, as well as disinfecting biological agents. The photosensitizer is sprayed onto the surface from a distance of 24 inches, and the UV light can reportedly then decontaminate approximately 1,000 square feet of surface area in 15 minutes. The system has been tested on vertical, horizontal, porous, and non-porous surfaces. The photosensitizer solution is claimed have a shelf life of 10 years and is non-corrosive. This technology is still subject to research and is not commercially available. As a result, this technology was not further evaluated in this report.

Plasma: Plasmas can be generated at atmospheric pressures for the destruction of biological organisms. By passing energy through air, the molecules are ionized generating both positively and negatively charged reactive species. The interaction of these ions, along with the associated ultraviolet light, kills the microorganisms. This technique is applicable to the cleaning, and perhaps disinfection, of small areas and electronic equipment. Because of the relatively labor intensive method of employment and its questionable activity on spores, it was not considered as a candidate for technical evaluation for building remediation alternatives.

Physical Technologies: There are time-tested, proven technologies for physical remediation of chemical spills. For example, there are a variety of sorbent materials (simple, reactive and catalytic) on the market for spot surface decontamination. However, after use, the contaminated sorbent must be recovered and removed for treatment. Hot air and steam jet systems can also be considered as physical removal systems for chemical threat agents. But the chemical agent that is thus driven from the surface must be collected and subsequently treated. This report does not cover the standard spill remediation solutions that a responder may need to include in a remediation effort. At sufficient temperature and exposure time, heat and steam have long been utilized for killing biological organisms; however, the temperatures involved are probably too high for practical use in a building. These technologies are not evaluated here.

2.3 Broad Review of Categories of Alternatives with Potential Applications

Based on the comparative analysis described in Section 2.1, eleven technologies were selected for analysis. The technologies presented in this document include:

Liquid systems

- Hypochlorite
- Aqueous chlorine dioxide
- Aqueous hydrogen peroxide
- TechXtract

Foam/gel systems

- Sandia Foam and Decon Green
- CASCAD
- L-Gel

Gaseous and vapor systems

- Chlorine dioxide gas
- Hydrogen peroxide vapor
- Paraformaldehyde
- Methyl bromide

An overview of these technologies was presented in Section 1.

In Chapters 3, 4, and 5, the technologies are discussed in detail. For each technology evaluated, a description of the technology is presented, along with an assessment of its technical maturity and an evaluation of the existing data. To the extent possible, efficacy data are supplemented by information and data on material compatibilities, residuals generated, and hardware performance. The current uses of the technology outside building remediation are discussed, and information regarding user concerns, such as health and safety concerns, is addressed. Finally, the advantages and disadvantages of each technology is discussed and future research areas are identified.

As discussed in Section 2.2, some technologies were not selected for evaluation in this report. The determination not to evaluate a technology does not imply that the technology is not effective. In many cases, the outlook for these technologies appears to be quite favorable. However, at this time, they generally are not close enough to commercialization (nanotech nanoemulsions, enzymes, photochemical systems), present human health hazards (ethylene oxide), or are untested in building applications (ozone, plasma, directed energy). As a result, they are not covered in this document.

2.4 References for Section 2

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3. LIQUID-BASED TECHNOLOGIES

3.1 Hypochlorite

3.1.1 Technology Description

Historically, chlorine-based decontamination systems have been effectively employed against chemical agents. The use of hypochlorite solutions (aqueous and non-aqueous) or solid/slurry hypochlorites has been widespread for military applications. This general purpose decontaminant class has been used on personnel, equipment, clothing, building surfaces, and soil, as shown in Table 3.1-1. While an effective decontaminant, its corrosive properties, formation of toxic by-products, and irritant properties are undesirable. The military typically uses HTH (high test hypochlorite) and STB (super tropical bleach) along with household bleach solutions for agent spills and personnel decontamination. The compositions of these materials include oxides which assures high pH in aqueous solution and provides a hydrolysis reaction for additional decontamination.

Table 3.1-1. Hypochlorite Decontaminants

Decontaminant	Composition	Application
Bleach*	2-6% NaOCl in water	skin and equipment
HTH (high test hypochlorite)*	Ca(OCl)Cl + Ca(OCl) ₂ as a solid powder or a 7% aqueous slurry	equipment and terrain
STB (super tropical bleach)*	Ca(OCl) ₂ + CaO as a solid powder or as a 7, 13, 40, and 70 wt% aqueous slurries	equipment and terrain
Dutch powder	Ca(OCl) ₂ + MgO	skin and equipment
ASH (activated solution of hypochlorite)	0.5% Ca(OCl) ₂ + 0.5% sodium dihydrogen phosphate buffer + 0.05% detergent in water	skin and equipment
SLASH (self-limiting activated solution of hypochlorite)	0.5% Ca(OCl) ₂ + 1.0% sodium citrate + 0.2% citric acid + 0.05% detergent in water	skin and equipment

* Currently used by DoD

Bleach

Sodium hypochlorite. An aqueous solution of sodium hypochlorite, NaOCl, is often used as a general purpose decontaminant. Improvements in the effectiveness of the hypochlorite reaction have been achieved by introducing stronger oxidants to the system. Developed in the 1940's, calcium hypochlorite (solid) [Ca(OCl)₂], STB, and HTH are found to be more effective decontaminants over a broader range of pH. More recently, in the early 1990's, the U.S. Army evaluated the application of hydantoin (specifically dichlorodimethylhydantoin, DCDMH) as an alternative reactant for chemical destruction of chemical agents. The chlorinating power of DCDMH is greater than that of HTH and STB, and has been used successfully to detoxify mustard, nitrogen mustard, lewisite, and phosgene. However, reaction mechanisms are similar to hypochlorite, producing the same decomposition products. The exact reaction mechanism of DCDMH has not been fully developed.

Calcium hypochlorite. $\text{Ca}(\text{OCl})_2$ is a powerful oxidizing agent, and is an active component of both STB and HTH. The hypochlorite ion (OCl^-) generated by an aqueous solution of $\text{Ca}(\text{OCl})_2$ is effective in the decontamination of G-agents [Sarin (GB), Soman (GD), Tabun (GA)], VX [O-ethyl-S-(2-diisopropylaminoethyl)methylphosphono-thioate] in acidic solutions, and HD [sulfur mustard, bis(2-chloroethyl)sulfide]. Hypochlorite ions in high pH (basic) solutions are not very effective in the decontamination of VX for reasons including: 1) reduced solubility; 2) factor of 10 mole excess; and 3) generation of toxic byproducts. The detoxification of HD by hypochlorite is a simple process that forms several different products. Both sulfoxide (one S-O double bond) and sulfone (two S-O double bonds) species are formed, each of which undergo elimination reactions to form monovinyl and divinyl sulfoxides and sulfones. It was found that VX reacts with OCl^- ions at low pH (acidic). However, at high pH, the solubility of VX is greatly reduced, and a greater than 10:1 ratio of active chlorine to VX is required to oxidize VX as compared to a 3:1 ratio under acidic conditions. In the detoxification of VX, the P-S bond is broken and P-O, S-O, and S=O bonds are formed. When $\text{Ca}(\text{OCl})_2$ dissolves, the result is a solution that also contains hydroxide ions. The hypochlorite behaves as a catalyst in a detoxification of G agents by the hydroxide ion.

High Test Hypochlorite (HTH[®]). The first commercial high-assay calcium hypochlorite product marketed in the U.S., HTH is a solid powder consisting of calcium hypochlorite, and is a powerful oxidizing agent. The hypochlorite ion (OCl^-) generated by an aqueous solution of $\text{Ca}(\text{OCl})_2$ is effective in the decontamination of G agents, VX in acidic solutions, and HD. Hypochlorite ions in high pH solutions are not very effective in the decontamination or detoxification of VX for a variety of reasons.

Super tropical bleach (STB). STB is a combination of a powerful oxidizers, calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, and a strong base, calcium oxide, CaO. STB is effective in the decontamination or detoxification of HD, G agents and VX. The hypochlorite ion (OCl^-) generated by an aqueous solution of $\text{Ca}(\text{OCl})_2$ and the hydroxide ion formed by the dissolution of CaO [which produces $\text{Ca}(\text{OH})_2$] is effective in the decontamination or detoxification of G agents, VX in acidic solutions, and HD. Hypochlorite ions in high pH solutions are not very effective in the decontamination of VX for a variety of reasons.

3.1.2 Technical Maturity

Sodium hypochlorite (standard bleach) is the most effective disinfectant for industrial applications, swimming pools, and household cleaning. Its production is based on very pure chlorine gas and high quality caustic soda (lye). Similar to chlorine, sodium hypochlorite was initially used as a bleaching agent in the textile industry.

The principal form of hypochlorite produced, sodium hypochlorite (NaOCl), is used as an aqueous solution (Kirk-Othmer, 1992). Sodium hypochlorite was first registered for use in the United States as an antimicrobial pesticide in 1957 (EPA, 2004). Sodium hypochlorite has proven to be effective against a wide range of bacteria, fungi, and viruses. It is registered by the EPA for use in the sanitization and disinfection of household premises, food processing plants, and agricultural settings. It is also used in animal facilities, hospitals, human drinking water supplies, chemical pulp and textile bleaching, as a commercial laundry and household bleach, as a sanitizer for swimming pools, and as a disinfectant for municipal water and sewage (Kirk-

Othmer, 1993; EPA, 2004). Sodium hypochlorite solutions are sold for household purposes at 5-6 percent concentrations, while 10-15 percent concentration solutions are sold for swimming pool disinfection, institutional laundries, and industrial purposes (Kirk-Othmer, 1992).

In food processing, sodium hypochlorite is used as a disinfectant and sanitizer (Kirk-Othmer, 1993). NaOCl may be used in washing and lye peeling of fruits and vegetables, and both sodium and calcium hypochlorite may be used as a final sanitizing rinse on food processing equipment (EPA, 1991). Hypochlorite is still used in pulp bleaching, but its use is decreasing because the bleaching reaction generates chloroform (Kirk-Othmer, 1992).

Synonyms and trade names for sodium hypochlorite include Clorox[®], bleach, liquid bleach, sodium oxychloride, Javex[®], antiformin, showchlon, Chlorox, B-K, Carrel-Dakin solution, Chloros, Dakin's solution, hychlorite, Javelle water, Mera Industries 2MOM3B[®], Milton, modified Dakin's solution, Piochlor[®], and 13 percent active chlorine.

Sodium hypochlorite is generally sold in aqueous solutions containing 5 to 15 percent sodium hypochlorite, with 0.25 to 0.35 percent free alkali (usually NaOH) and 0.5 to 1.5 percent NaCl. Solutions of up to 40 percent sodium hypochlorite are available, but solid sodium hypochlorite is not commercially used. Sodium hypochlorite solutions are a clear, greenish yellow liquid with an odor of chlorine. Odor may not provide an adequate warning of hazardous concentrations. Sodium hypochlorite solutions can liberate dangerous amounts of chlorine or chloramine if mixed with acids or ammonia. Anhydrous sodium hypochlorite is very explosive. Hypochlorite solutions should be stored at a temperature not exceeding 20 °C away from acids in well-fitted air-tight bottles away from sunlight.

Calcium hypochlorite, Ca(OCl)₂, is the principal form of solid hypochlorite produced commercially. Water treatment is the largest use of calcium hypochlorite. Calcium hypochlorite was first registered for use as a pesticide in 1957. Calcium hypochlorite (65-70 percent available Cl₂) is used for disinfection in swimming pools, drinking water supplies, and for treatment of industrial cooling water. Its cooling water applications include slime control of bacterial, algal, and fungal origin. Calcium hypochlorite is also used for disinfection, odor control, and biological oxygen demand (BOD) reduction in sewage and wastewater effluents. It is used as a sanitizer in households, schools, hospitals, and public buildings, and is used for microbial control in public eating places. Calcium hypochlorite is used for bacterial and odor control, and general sanitation in many food-related industries including dairies, wineries, breweries, canneries, food processing plants, and beverage bottling plants (Kirk-Othmer, 1993). High assay calcium hypochlorite (70-74 percent available Cl₂) was first commercialized in the United States in 1928 under the trade name HTH. It is now produced by two additional manufacturers in North America (Kirk-Othmer, 1993).

Calcium hypochlorite is a white crystalline solid, decomposes at 100°C, decomposes in water and alcohol, is not hygroscopic, and is practically clear in water solution. It is toxic by ingestion, skin contact, and inhalation. Calcium hypochlorite is generally available as a white powder, pellets, or flat plates. It decomposes readily in water or when heated, releasing oxygen and chlorine. It has a strong chlorine odor, but odor may not provide an adequate warning of hazardous concentrations. Calcium hypochlorite is not flammable, but it acts as an oxidizer with combustible material and may react explosively with ammonia, amines, or organic sulfides. It becomes a dangerous fire risk in contact with organic material. Calcium hypochlorite should be

stored in a dry, well-ventilated area at a temperature below 120 °F (50 °C), separated from acids, ammonia, amines, and other chlorinating or oxidizing agents.

Synonyms and trade names for calcium hypochlorite include losantin, hypochlorous acid, calcium salt, B-K Powder, Hy-Chlor[®], chlorinated lime, lime chloride, chloride of lime, calcium oxychloride, HTH, mildew remover X-14[®], Perchloron[®], and Pittchlor[®].

Super tropical bleach was standardized in the 1950s. It is a mixture of 93 percent calcium hypochlorite and 7 percent sodium hydroxide and is more stable than bleach in long-term storage and easier to spread (Modec, 2003). This stability makes super tropical bleach useful for application in hot, humid climates (Kirk-Othmer, 1992).

Sodium and calcium hypochlorite are extremely corrosive, causing severe damage to the eyes and skin upon contact. Because of these acute effects, they have been assigned to Toxicity Category I, the highest degree of toxicity, by EPA. Residues of sodium and calcium hypochlorite that may remain on certain food crops disinfected with the chemicals pose no known human health hazard (EPA, 1991).

Due to the acute toxicity of these products, protective clothing, safety glasses or goggles, and chemical-resistant gloves are required while handling and applying products that contain sodium or calcium hypochlorite as the active ingredient. Re-entry levels must be met before entering swimming pools, hot tubs, or spas treated with sodium or calcium hypochlorite, and reentry intervals must be observed before using food and non-food contact surfaces that have been sprayed or fogged with either chemical (EPA, 1991).

3.1.3 Applications of the Technology

Chlorine-based aqueous solutions have been considered as general purpose decontaminants since World War I. Many studies have been performed to evaluate their effectiveness on chemical agents. Chemical oxidation is applicable to the decontamination process. The reaction chemistry is very complex and varies between the different chemical agents. The reactions process is highly dependent on the pH of the solution, solubility of the agent, and competing hydrolysis reactions producing undesired reaction products in some cases.

The requirement for chemical agent decontamination dates back to World War I when Germany unleashed HD on Allied troops at Ypres, France in 1915. Prior to that time, the poisonous chemicals used on the battlefield, such as chlorine, were non-persistent gases and required no decontamination. The first decontaminants used were bleaching powders and, to a lesser extent, potassium permanganate. The reactions of chemical agents with excess bleach are so vigorous that both neat and thickened agents can be converted to less or nontoxic products at the liquid-liquid (bleach solution) or liquid-solid (bleach powder) interface in a few minutes. Solubilization of the agents in the same medium as the bleach is not required. HD is converted into a series of oxidation and elimination products. It is believed that the sulfoxide is formed first, followed by sulfone formation. Subsequently, both oxidation products undergo elimination reactions in the strongly basic solution to produce the corresponding monovinyl and divinyl sulfoxides and sulfones, although small amounts of additional unidentified products are also present in the final solution (Yang, 1992).

By World War II, superchlorinated bleaches, shown in Table 3.1-1, were used as the most common general purpose decontaminants. However, there are some disadvantages to using bleach as a decontaminant: 1) the active chlorine content of the bleach gradually decreases with time so that a fresh solution must be prepared prior to each use; 2) a large amount of bleach is required for the oxidation of the agents; and 3) bleach is corrosive to many surfaces.

Common oxidants used for decontamination are bleaches that produce active chlorine. Active chlorine exists in water in equilibrium with the hypochlorite ion, $3\text{ClO}^- = 2\text{Cl}^- + \text{ClO}_3^-$. STB [$\text{Ca}(\text{OCl})_2 + \text{CaO}$] and HTH [$\text{Ca}(\text{OCl})\text{Cl} + \text{Ca}(\text{OCl})_2$], are prepared as slurries that are a mixture of water and solid bleach powders.

During the remediations of several of the buildings that were impacted by the 2001 anthrax mail attack, household bleach – diluted 10:1 (to 0.525% to 0.6% NaOCl), and adjusted to a pH near neutral – was used with apparent success in wiping down surfaces contaminated with *B. anthracis*. This application for *B. anthracis* was authorized by a crisis exemption issued by EPA under Section 18 of FIFRA, following EPA testing of the pH-modified bleach using the AOAC Sporicidal Activity Test (AOAC, 2000). Based upon this testing, the crisis exemption specified that the bleach solution had to be adjusted to a pH near 7, that it be utilized only on hard (non-porous) surfaces, and that the surfaces remain wetted with the bleach solution for no less than 60 minutes. The crisis exemption also required that – following the total remediation process for these buildings, including the bleach wipe-down step – environmental sampling be conducted within the treated areas of the buildings to confirm the efficacy of the total procedure. The results of the sporicidal activity testing are discussed in the following section.

Further discussion of the crisis exemption for the use of bleach against *B. anthracis* can be found on EPA's web site at:
www.epa.gov/pesticides/factsheets/chemicals/bleachfactsheet.htm.

3.1.4 Compilation of Available Data

Chemical agents. The U.S. Army's Field Manual 3-9 recommends the use of hypochlorite for decontamination of chemical agent spills and equipment clean up (U.S. Army, 1990). Field Manual 3-5, NBC Decontamination (U.S. Army, 2002), lists STB and HTH as standard decontaminants, and bleach as a non-standard decontaminant. STB and HTH are not recommended for ship use, whereas bleach is.

Laboratory studies have documented that aqueous solutions of hypochlorite can successfully eliminate chemical agents (HD, GB, GD, GA, and VX) below 1 part per million with reaction half lives of 1.5 minutes or less (Yurow, 1991).

G agents can be rapidly detoxified in bleach solutions. The hypochlorite anion behaves as a catalyst breaking the P-F bond in GB and GD (and P-CN bond in GA), substituting a hydroxyl group to the P atom and releasing the fluoride (or cyanide) ion (Epstein, 1956). The elimination of the fluoride (or cyanide) creates a less toxic phosphono compound.

Bleach can also be used for the decontamination of VX, particularly under low pH conditions. VX readily dissolves in acidic solutions via protonation of the nitrogen while the sulfur is oxidized by HClO. Under such acidic conditions, only three moles of active chlorine are

consumed for each mole of VX. At high pH, the solubility of VX is significantly reduced. The non-protonated nitrogen is oxidized, accompanied by the evolution of chlorine or oxygen gas and the formation of sulfate and carbonate salts. Under basic conditions, more than 10 moles of active chlorine are required to oxidize 1 mole of VX. Despite the long history of alkaline bleach solutions as general purpose decontaminants for the chemical agents, the precise stoichiometry at high pH has not been determined for VX (Yang, 1992).

Biological agents. Decontamination of biological simulant (*bacillus subtilis* var. *niger*, known as Bg) with sodium hypochlorite was reported in a Battelle report (Battelle, 1999). The effectiveness of three decontaminants was compared. The decontaminants were: 1) pH-adjusted sodium hypochlorite (ASH) composed of household bleach (5.25 percent by weight), white vinegar for pH adjustment (5 percent acid strength), and dilution water; 2) diluted bleach (5.25 percent by weight sodium hypochlorite), diluted with water; and 3) plain water. The results (Table 3.1-2) indicate that ASH was the most effective decontaminant against the Bg, effectively reducing the spore count by 99.6 percent.

The conclusions reached from this study were: 1) ASH performed better than either diluted bleach or plain water; 2) the presence of dirt, mud, and foreign material will greatly reduce the germicidal power of ASH; and 3) the decontamination process is limited to small areas and easily reachable locations. Subsequent studies report that hypochlorous acid (2.5 percent aqueous solution) had a 100 percent Bg spore kill rate at relative humidity (RH) of 100 (CBIAC and AD - A084392, as referenced in Battelle, 1999).

Table 3.1-2. Residual Agent after Decontamination

Decontamination Solution	Sample #	Total Spores on Strip After Spray	Average Percent Reduction
Water	1	8.9×10^4	96.8
	2	6.2×10^4	
	3	3.6×10^4	
Bleach	1	4.5×10^4	98.0
	2	4.0×10^4	
	3	4.0×10^4	
ASH	1	1.1×10^4	99.6
	2	5.3×10^3	
	3	5.6×10^3	

Diluted sodium hypochlorite was tested by EPA for its sporicidal activity following the 2001 anthrax mail attacks, to support a crisis exemption under FIFRA that would allow the use of this product against *B. anthracis* spores in some of the affected buildings. Tests were conducted using the AOAC Sporicidal Activity Test (AOAC, 2000). The product tested was household bleach (6% NaOCl) that had been diluted with water by a 10:1 ratio, resulting in a 0.525% solution. Two such dilute solutions were tested: bleach that had been diluted with pure water (resulting in a pH of 10.2); and bleach that had been diluted with water and with white vinegar, in order to achieve a final solution pH of 6.5, near neutral. Consistent with the AOAC protocol, the sporicidal efficacy of these two solutions was tested using two surfaces inoculated with 10^6 to 10^7 *B. subtilis* spores: porcelain penicylinders (representing hard, non-porous surfaces) and silk suture loops (representing porous surfaces). The AOAC test does not determine the

quantitative log kill of the spores; it measures qualitatively whether or not all the spores on the surface were killed.

The results of the testing on the porcelain penicylinders showed that – with the pH-adjusted 0.525% NaOCl – more than 90% of the penicylinders had complete kill after 30 minutes of exposure time, and every cylinder showed complete kill after 60 minutes. By comparison, the non-adjusted (high-pH) bleach still showed live spores on 40% of the penicylinders after 30 minutes.

The results of the testing with the silk suture loops showed live spores on essentially all of the loops, even after 90 minutes of exposure time.

On the basis of these efficacy results, EPA issued a crisis exemption for the use of sodium hypochlorite solutions in the *B. anthracis* remediation activities, with the following provisions: it is for use only on hard surfaces; the solution must be pH-neutral, with a NaOCl concentration between 0.5% and 0.6%; and the contact time of liquid solution on the surface must be no less than 60 minutes (with the solution having to be re-applied if the surface dries prior to that time). Additionally, post-remediation sampling must be performed to confirm that the remediation process – including the bleach application step, and any other steps that are performed (e.g., including fumigation) – has in fact been efficacious.

Issuance of a crisis exemption requires that EPA consider the safety of a product, as well as the product's efficacy. The Agency's review deemed this product to be safe for use with proper protective measures, since it is already registered under FIFRA for other (disinfection) applications.

3.1.5 Concerns for the User (Applicability)

Calcium hypochlorite is a white, crystalline, and oxidizing solid material which looks much like table salt. The solid material has a faint odor of chlorine, and can be toxic by ingestion, skin contact, and inhalation. Calcium hypochlorite is used as a disinfectant in swimming pools, sewage treatment operations, and in water treatment operations.

Solid calcium hypochlorite should not be stored near reactive or combustible materials. Fires involving calcium hypochlorite may be difficult to put out because if calcium hypochlorite is not kept completely dry, it will decompose liberating oxygen and chlorine. A spontaneous fire or explosion could result if solid $\text{Ca}(\text{OCl})_2$ is not kept dry and is stored with organic or other flammable material(s). Therefore, calcium hypochlorite must be stored in a completely dry location, isolated from combustible materials, or fully dissolved to prevent creating a hazardous condition.

Hypochlorites should be used as aqueous solutions. Contact with organic materials in the dry form may cause fires or generation of toxic gases. The MSDSs for different forms of bleach and calcium hypochlorite are available on the web.

3.1.6 Availability of the Technology for Commercial Applications

Sodium- and calcium-based hypochlorites are commercially available under a range of brand names, as discussed in the preceding sections.

Historically, hypochlorite decontamination solutions have been used to decontaminate biological organisms in small areas, personal protective equipment, and contaminated floor/ground/wall surfaces. The systems are "low tech", that is, hand sprayers, buckets, mops, rags, brushes, etc. are used to apply the solution to the contaminated surfaces with vigorous scrubbing followed by a water rinse. EPA's testing using the AOAC Sporocidal Activity Test has shown that diluted household bleach (NaOCl) is effective in achieving a six- to seven-log reduction in *Bacillus subtilis* spores when applied to hard, non-porous surfaces, if the sodium hypochlorite is adjusted to a pH of 7, and is allowed to contact the surface for 60 minutes. Diluted bleach was not found to be effective on porous surfaces (silk suture loops) in the AOAC test.

Hypochlorites are also used by the military to decontaminate spills of G and VX chemical agents. For VX decontamination to be effective, the pH of the bleach must be low.

3.1.7 Advantages and Disadvantages

Hypochlorite solutions are relatively available (household bleach is available in any grocery store, HTH is available from swimming pool supply and chemical companies), low-cost, and easy to obtain. The application is low tech and requires little knowledge of equipment operation. However, the user must be aware of the dilution, pH adjustment, and contact time requirements for treatment to be effective, as defined by EPA's AOAC testing.

The corrosive nature of hypochlorite solutions requires care to be taken to ensure materials treated are resistant to the oxidative process. Attention to waste containment and recovery is required. The waste generated from the use of high-concentration, non-pH-adjusted hypochlorites should be considered to be hazardous and handled accordingly. However, the wastewater may be declared non-hazardous if when bleach is used in accordance with the EPA crisis exemption (i.e., it is diluted to 0.5 to 0.6% NaOCl concentration, and the pH is adjusted with vinegar to be near neutral).

3.1.8 Potential Areas for Future Research (Uncertainties)

Further research is needed to systematically quantify the concentration, solution pH, and length of contact time required for hypochlorites (in particular, NaOCl) to be effective on a variety of biological agents (in addition to *B. subtilis* spores) on both non-porous and porous surfaces. Similar testing is needed for the range of hypochlorites, quantifying concentration, pH, and contact time required for efficacy against chemical agents.

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3.2 Aqueous Chlorine Dioxide

3.2.1 Technology Description

Chlorine dioxide possesses disinfection properties in both its aqueous and gaseous states. The focus of this section is an evaluation of aqueous chlorine dioxide.

Chlorine dioxide (ClO_2) is unstable and therefore must be generated at the use site, typically using sodium chlorite as a reactant. Aqueous chlorine dioxide is generated for use as a hard surface cleaner by adding gaseous chlorine dioxide to water. Gaseous chlorine dioxide is generated via the mechanisms and equipment described in Section 5.1 of this document. Gas generated in this manner can be subsequently dissolved in water. For example, gas generators discussed in Section 5.1 can generate both gaseous and aqueous chlorine dioxide.

Aqueous chlorine dioxide can also be generated by acidifying an aqueous sodium chlorite (NaClO_2) solution. So-called “stabilized chlorine dioxide” is a commercially available solution of sodium chlorite, pH-adjusted to be slightly basic. This basic sodium chlorite forms a chlorine dioxide solution with the addition of acid, and is thus sold as a ‘two-part’ formulation (Purogene, 2003). However, the apparent instructions for at least one product is to dilute the concentrated product in water and apply to surfaces (Neways, 2001). In this case, the precise mechanism by which the sodium chlorite forms chlorine dioxide is unclear.

Regardless of whether aqueous chlorine dioxide solutions are generated onsite from gaseous chlorine dioxide, or from sodium chlorite or stabilized chlorine dioxide solutions, they are applied manually to hard surfaces for disinfection with a sponge or mop, or as a spray.

3.2.2 Technical Maturity

Aqueous chlorine dioxide has been recognized for its disinfectant properties since the early 1900’s, and was first registered by EPA as a disinfectant and sanitizer in 1967. Sodium chlorite-based cleaners are used in the food processing industry for cleaning of surfaces and of food itself. Chlorine dioxide has extensive use in drinking water treatment, generated from sodium chlorite and fed into the water. These applications, and the biological organisms commonly present in these industries, are reflected in the available data regarding chlorine dioxide’s effectiveness.

3.2.3 Applications of Aqueous Chlorine Dioxide

Wood pulp bleaching is the largest use of aqueous chlorine dioxide. Other aqueous chlorine dioxide applications include, but are not limited to, textile bleaching, treatment of municipal water supplies, and disinfection of food and food processing equipment. Specific examples of such applications are discussed in Section 5.1.3 of this document.

3.2.4 Evaluation of Available Data

Various research has been conducted to test the disinfection capabilities of aqueous chlorine dioxide. Much research has been conducted on the use of aqueous ClO_2 in water distribution

systems. There has also been a significant amount of data generated on the effectiveness of aqueous ClO₂ as a food disinfectant. Aside from these uses, there is little experimental data regarding aqueous chlorine dioxide surface disinfection applications. The majority of the research conducted has been laboratory scale, aimed at determining the efficacy of ClO₂ in the destruction of pathogens and viruses deemed likely to be contaminants in those applications.

This section discusses available data concerning the effectiveness of chlorine dioxide in destroying bacteria, fungi, and viruses. Based on the data presented, the following general conclusions can be drawn regarding chlorine dioxide performance:

- All data pertain to biological organisms. No data are available regarding chemical agents.
- Aqueous solutions of stabilized chlorine dioxide (slightly basic NaClO₂) must be properly activated with acid prior to use. Sodium chlorite has very few biocidal properties by itself.
- Chlorine dioxide reacts very fast with the target organism; after 5 minutes no significant additional reaction is typically expected.
- Chlorine dioxide is effective against certain types of bacteria, fungi, and viruses. However, the chemical performs better against some organisms than others. As a result, there is uncertain predictive capability in applying results to untested organisms.

In November 2001, EPA's Office of Solid Waste and Emergency Response issued a crisis exemption under Section 18 of FIFRA allowing the limited sale, distribution, and use of products containing aqueous chlorine dioxide for surface cleaning of buildings contaminated with spores of *Bacillus anthracis*. On March 28, 2002, this crisis exemption was amended to specify the conditions for use of aqueous chlorine dioxide for decontamination. This amendment allowed for the disinfection of hard surfaces only. Furthermore, the amendment specified the concentration of aqueous chlorine dioxide to be 500 mg/L, to be applied at room temperature (68 °F), with a minimum contact time of 30 minutes (EPA 2001, EPA 2002).

Further discussion of the crisis exemption for the use of aqueous ClO₂ against *B. anthracis* can be found on EPA's web site at:

www.epa.gov/pesticides/factsheets/chemicals/chlorinedioxidefactsheet.htm

Disinfection/Sterilization for Bacteria and Spores

Several tests have been conducted to determine the effectiveness of commercially available cleaners to destroy bacteria or other organisms. One test assessed the ability of various commercially available cleaners and sanitizers to remove bacteria from various surfaces including stainless steel and plastic (Krysinski, 1992). Material contaminated with *Listeria monocytogenes* organisms were submerged in solutions for 10 minutes and then evaluated for efficacy. Results are presented in Table 3.2-1. Stainless steel was the 'easiest' material to disinfect, while a polyester/polyurethane conveyer belt was the 'hardest.' The log kill is modest at these concentrations and exposure times.

Table 3.2-1. Deactivation of *Listeria monocytogenes* Using Chlorine Dioxide Solutions

Sanitizer or Cleaner	Log Kill and Final Organism Count		
	Etched Stainless Steel	Polyester	Polyester/ Polyurethane
Chlorine dioxide (5 ppm) sanitizer	Log kill >3.3 (Final < 20 CFU/cm ²)	Log kill >3.2 (Final < 20 CFU/cm ²)	Log kill 0.7 (Final 9,000 CFU/cm ²)
Chlorine dioxide (5 ppm) + acidic quaternary ammonium compound (QAC) sanitizer	Log kill >3.3 (Final < 20 CFU/cm ²)	Log kill >3.2 (Final < 20 CFU/cm ²)	Log kill 2.0 (Final 500 CFU/cm ²)
Detergent/chlorine dioxide blend of cleaner	Log kill >3.2 (Final < 20 CFU/cm ²)	No data	Log kill 1.4 (Final 2,000 CFU/cm ²)

Source: Krysinski et al., 1992.

Log kill calculated as the ratio of the final counts following treatment with solution versus the final counts of the control (no cleanser). Ten minute contact time.

Harakeh (1988) evaluated a solution of a commercially available stabilized chlorine dioxide solution (Purogene) for the destruction of various bacteria as a function of time and pH. Bacteria were mixed with the chlorine dioxide solution. The concentration of chlorine dioxide evaluated was very low (0.75 mg/L) in comparison to the use levels of 500 mg/L cited in the EPA memoranda. Nevertheless, the following conclusions and observations were identified:

- Based on tests with *E. coli*, pH had a significant effect on destruction. The product was acidified to varying degrees; the greatest inactivation occurred at the lowest pH tested (3.5). Essentially, no inactivation occurred in the pH range of 5 to 8.7. Results are illustrated in Table 3.2-2.
- The degree of inactivation is dependent on the specific organism, as shown in Table 3.2-3.
- The highest degree of inactivation occurred within 60 seconds. Inactivation ‘flattened out’ between 1 and 15 minutes. For example, Table 3.2-3 illustrates that the inactivation measured after 5 minutes is not significantly more than the inactivation measured after 15 minutes. A similar observation has been noted in other tests using sodium chlorite-containing disinfectants (Mullerat et al., 1995).

Table 3.2-2. Effect of Adding Acid to Stabilized Chlorine Dioxide Solution

pH	Log Inactivation of <i>E. coli</i> After 5 Minutes
8.7 (initial product pH)	0.0
7	0.0
6	0.0
5	0.4
3.5	3.8

Source: Harakeh (1988). Tests conducted on stabilized chlorine dioxide product at 23 °C. Chlorine dioxide concentration of 0.75 mg/L.

Table 3.2-3. Effectiveness of Acidified Stabilized Chlorine Dioxide on Bacteria

Bacteria	Log Kill After 5 Minutes	Log Kill After 15 Minutes
<i>Escherichia Coli</i>	5.6	5.6
<i>Pseudomonas aeruginosa</i>	5.2	5.4
<i>Yersinia enterocolitica</i>	5.2	5.2
<i>Klebsiella pneumoniae</i>	5.0	5.0
<i>Streptococcus pyogenes</i>	1.9	1.9
<i>Salmonella typhimurium</i>	9.0	9.9
<i>Bacillus subtilis</i>	4.5	4.5

Source: Harakeh et al., 1988. Tests conducted on stabilized chlorine dioxide product adjusted to pH 3.5 at 23 C. Chlorine dioxide concentration of 0.75 mg/L.

With the rising use of chlorine dioxide in water distribution systems, much research has been conducted to verify the disinfectant abilities of chlorine dioxide as used in water treatment facilities. For example, Tarquin and Rittmann (1993) have reported a chlorine dioxide disinfection study conducted in El Paso, Texas, in which chlorine dioxide was tested for its ability to reduce coliforms and total plate counts at El Paso's 20 million gallon per day surface water treatment plant. Chlorine dioxide was generated onsite and injected into the treatment plant's second set of settling tanks at a concentration of 1 mg/L. Samples were collected before and after treatment to measure coliform bacteria and total plate counts. Table 3.2-4 presents the results of the coliform analyses. The average coliform reduction was 83 percent.

Table 3.2-4. Coliform Reduction in Drinking Water Treated with Chlorine Dioxide

Date	Coliform Count/100 ml (before ClO ₂)	Coliform Count/100 ml (after ClO ₂)	Percent Reduction
7/31	860	43	95
8/07	360	12	97
8/14	620	360	42
8/21	230	0	100
8/28	385	0	100
Average	491	83	83

Source: Tarquin and Rittmann, 1993.

Chlorine dioxide administered continuously at 1 mg/L.

Similar reductions were reported for total plate counts. Plates for samples that had been subjected to chlorine dioxide disinfection had approximately 85 percent less growth than those samples that were not subjected to ClO₂ treatment.

Tanner (1989) tested the biocidal activity of commercial disinfectants containing chlorine dioxide. Three organisms were tested using a modified version of the Association of Official Analytical Chemists (AOAC) use-dilution method in which a disinfecting material is combined with a test organism in a solution. *Pseudomonas aeruginosa*, *Staphylococcus aureus*, and

Saccharomyces cerevisiae samples were added into the chemical solutions. Samples were drawn after 30 seconds and 60 seconds of contact time. Chlorine dioxide was used at a concentration of 500 mg/l and diluted to lower levels. Table 3.2-5 presents the concentration required to achieve a 5 log reduction (99.999 percent) in viable cell counts after one minute of contact time.

Table 3.2-5. Chlorine Dioxide Concentration for 5-log Reduction in Cell Count at 60 Seconds

Species	Concentration (mg/L)	
	ClO ₂	Acidified Sodium Chlorite
<i>Pseudomonas aeruginosa</i>	48	310
<i>Staphylococcus aureus</i>	93	1300
<i>Saccharomyces cerevisiae</i>	95	640

Tanner, 1989.

Tests conducted at 22°C.

Ten other chemicals (including sodium hypochlorite and hydrogen peroxide) were also subjected to the same biocidal activity tests. According to Tanner's results, while other chemicals such as these similarly achieved 5-log reduction against the three organisms, lower levels of chlorine dioxide were required than for other products.

The effectiveness of chlorine dioxide for inactivating other bacteria was determined by Chauret et al. (2001). *B. subtilis* spores, *Clostridium sporogenes* spores, and *C. parvum* oocysts were evaluated. A 99 percent pure chlorine dioxide solution (generated onsite) was introduced into an aqueous suspension of the organisms. Samples were extracted at various time intervals to determine the remaining organism counts. Results were presented for various concentrations and time intervals and are summarized in Table 3.2-6. A lower concentration-time value corresponds to quicker reaction time or lower required solution concentration.

Table 3.2-6. Inactivation of Bacteria with Chlorine Dioxide

Organism	Concentration·time (mg·min/L)	Log inactivation
<i>C. parvum</i>	75 – 1,000	2.0
<i>B. subtilis</i>	~ 75	2.0
<i>C. sporogenes</i>	~ 75	2.0

Source: Chauret et al., 2001.

Results are given using the most probable number (MPN)-cell infectivity method.

Deactivation of *C parvum* was determined for oocysts purchased from several different suppliers; a range is presented here.

Aqueous chlorine dioxide was tested by EPA for its sporicidal activity following the 2001 anthrax mail attacks, to support a crisis exemption under FIFRA that would allow the use of this product against *B. anthracis* spores in some of the affected buildings. Tests were conducted using the AOAC Sporicidal Activity Test (AOAC, 2000). The product tested contained either

500 or 1,000 mg/L ClO₂, with 0.1% v/v surfactant. The sporicidal efficacy was tested using two surfaces inoculated with 10⁶ *B. subtilis* spores: porcelain penicylinders (representing hard, non-porous surfaces) and silk suture loops (representing porous surfaces). The AOAC test does not determine the quantitative log kill of the spores; it measures qualitatively whether or not all the spores on the surface were killed.

The results of the testing on the porcelain penicylinders showed that, with the 500 mg/L solution, only one of the 60 penicylinders failed to have complete kill after 10 minutes of exposure time, and every cylinder showed complete kill after 30 minutes. By comparison, with the silk suture loops, every one of the loops contained live spores even after 90 minutes of exposure time to a solution containing 1,000 mg/L.

On the basis of these efficacy results, EPA issued a crisis exemption for the use of aqueous ClO₂ solutions in the *B. anthracis* remediation activities, with the following provisions: it is for use only on hard surfaces; the solution must have a ClO₂ concentration of 500 mg/L; the contact time of liquid solution on the surface must be no less than 30 minutes; and applications should be made at room temperature (about 68 °F, or 20 °C). Additionally, post-remediation sampling must be performed to confirm that the remediation process – including the aqueous ClO₂ application step, and any other steps that are performed (e.g., including fumigation) – has in fact been efficacious. Any remaining aqueous ClO₂ must be removed from the treated areas before persons without protective equipment are allowed to re-enter.

Fungicidal Activity

The effectiveness of chlorine dioxide as a fungicide was tested on post-harvest decay fungi and filamentous fungi. Griffith et al. (1999) reported a 1994 study by Roberts and Reymond where *in vitro* tests on *Mucor piriformis*, *Botrytis cinerea*, *Penicillium expansum*, and *Cryptosporiopsis perennans* were conducted. Conidial suspensions of each pathogen were pipetted into test tubes containing ClO₂ at concentrations of 1, 3, and 5 mg/l. Samples were drawn at 30 second intervals and the number of viable colony forming units/ml (CFU) was determined. The results of the tests are presented in Table 3.2-7.

These experimental results indicate that deactivation is influenced by time, concentration, and organism type. Complete deactivation (to the limits of the test) was recorded for each organism at the highest concentrations and time identified (5 mg/L and 4 minutes); lower concentrations or lower contact times resulted in poor results for some organisms.

Table 3.2-7. Mortality of Fungi After *in vitro* Contact with ClO₂ at Various Concentrations and Contact Times

Fungus	ppm ClO ₂	Percent spore mortality				
		30 sec.	60 sec.	120 sec.	180 sec.	240 sec.
<i>Cryptosporiopsis perennans</i>	1	100	100	100	100	100
	3	100	100	100	100	100
	5	100	100	100	100	100
<i>Mucor piriformis</i>	1	85	93	99.9	99.9	100
	3	100	100	100	100	100
	5	100	100	100	100	100
<i>Penicillium expansum</i>	1	42	77	99	99.6	99.8
	3	99	99.9	100	100	100
	5	100	100	100	100	100
<i>Botrytis cinerea</i>	1	35	49	94	98	99
	3	94	99	99.7	99.9	99.9
	5	99	99.5	100	100	100

Griffith et al., 1999.

Samples were diluted and placed onto malt extract agar. CFU determined after a 2-3 day incubation period.

Virucidal Activity

In a 1981 publication by Roberts as reported by Griffith et al. (1999), the virucidal activity of chlorine dioxide was tested for the inactivation of human infectious viruses in the effluent of three municipal waste treatment, sewage sludge facilities in the San Francisco Bay area. *Poliovirus I LSC* was used in these experiments due to its potential as an indicator for the *Hepatitis* viruses. These experiments were conducted using coliphage of *Escherichia coli* and inoculum of the *Poliovirus I* in secondary effluents. Samples were taken at various time intervals following 2 ppm and 5 ppm dosing of ClO₂. Based on the authors' determination that phage survival would be indicative of the inoculum survival, coliphage survival was determined using the Kott Method and Reverse Phage Titer Rise Reaction (RPTRR) Method. Table 3.2-8 represents the results of the experiments, as extrapolated from a graph presented in the 1981 Roberts publication. The values are indicative of the reduction in viable organism count.

Table 3.2-8. ClO₂ Control of Poliovirus I. in Treated Sewage

ClO ₂ Dosage	Log Reduction of Viruses			
	2 minutes	5 minutes	10 minutes	30 minutes
2 ppm	1.2	2.0	2.4	2.5
5 ppm	3.2	3.7	4.0	4.7

Griffith et al., 1999

Table 3.2-8 shows that virus reduction is significantly increased with only slightly higher chlorine dioxide levels. Griffith et al. (1999) identified that the mortality of coliform bacteria was similar to the results in Table 3.2-8.

Biofilm Control

Mayack et al. (1984) tested the effectiveness of using chlorine dioxide for the control of biofilm. Table 3.2-9 presents data extrapolated from a graph in the Mayack document, showing the dry weight and total organic carbon (TOC) reductions after chlorine dioxide use. Table 3.2-9 shows an 82-91 percent reduction of dry weight biofilm and a 92-96 percent reduction of TOC in biofilm at these conditions.

Table 3.2-9. ClO₂ Bio-Fouling Control

Chemical	1 ppm 1 hr/day		1 ppm 15 minutes/4 times daily	
	Dry wt. mg/cm ²	TOC mg/cm ²	Dry wt. mg/cm ²	TOC mg/cm ²
Control	2.10	0.75	2.10	0.75
ClO ₂	0.38	0.06	0.18	0.03

Source: Mayack et al., 1984.

An example of the importance of biofilm control is in the control of *Legionella pneumophila*, the bacteria identified in 1976 as responsible for Legionnaires' Disease. This disease is thought to be caused by the inhalation of bacteria contained in water mists from cooling towers and other air handling equipment, such as a building's ventilation system. Biofilm may be the growth media for *L. pneumophila* bacteria, as well as other airborne infectious bacteria.

3.2.5 Concerns for the User

The Occupational Safety and Health Administration's guidelines for the use and storage of ClO₂ is available at www.osha-slc.gov/SLTC/healthguidelines/chlorinedioxide/recognition.html.

Chlorine dioxide is a severe respiratory and eye irritant and therefore must be handled with great care. Protective clothing such as gloves should be worn at all times while handling liquid chlorine dioxide.

Because aqueous chlorine dioxide is essentially gaseous chlorine dioxide in solution, there exists the safety hazard of ClO₂ volatilization. It is important that the ClO₂ generation system be equipped with safety features designed to prevent the concentration of chlorine dioxide from exceeding its solubility limit (Simpson, undated).

3.2.6 Availability of the Technology for Commercial Applications

There are numerous commercial vendors for the supply of ClO₂. Data for domestic and foreign manufacturers of chlorine dioxide gas generators and liquid stabilized ClO₂ are presented in Section 5.1 of this document in the discussion of gaseous chlorine dioxide. In addition to ClO₂ generators, some of these vendors also offer stabilized chlorine dioxide (SCD) products, such as Radicate. Radicate is available in concentrated form for \$50/liter (makes about 2 gallons). (<http://www.neways.com/usa/products>).

The cost of generating aqueous chlorine dioxide from chlorine dioxide gas is dependent upon a number of factors, including the price of the generating equipment and the base chemicals used. The cost of generating chlorine dioxide using sodium chlorite is estimated as approximately two to four times higher than the cost of generating chlorine dioxide from sodium chlorate (a raw material used for extremely large scale production of chlorine dioxide). The estimated cost of generating one metric ton of chlorine dioxide using sodium chlorate ranged from \$1,100 to \$1,800 in 1992 (Kirk-Othmer, 1993).

3.2.7 Advantages and Disadvantages

Advantages of using aqueous ClO₂ in remediation operations include the following:

- It has been shown to be effective in other applications, specifically water distribution system disinfection
- It is easily applied (i.e., applied directly to the surface to be disinfected with a sponge or mop).
- It is effective in relatively low concentrations; thereby, presenting less of an occupational hazard during use.
- It is quick acting.

Disadvantages of using aqueous ClO₂ in remediation operations include the following:

- There is a potential for bleaching of surfaces to which it is applied. Weaver-Meyers et al. (2000) reported that a <0.02 percent (<200 ppm) aqueous chlorine dioxide solution used to repeatedly wipe moldy books in the University of Oklahoma Libraries had a slight bleaching effect on the spines of the books. Items wiped once showed no detrimental effects.
- The chemical is unstable. Once prepared, the solution must be used quickly and it is likely that certain conditions (e.g., sunlight) would accelerate its decomposition.
- Chlorine dioxide is not effective on porous surfaces. The March 2002 crisis exemption was issued for non-porous surfaces only.

3.2.8 Potential Areas for Future Research

Areas for potential research specifically regarding the use of aqueous chlorine dioxide in remediation operations include the following:

- Although the effectiveness of aqueous chlorine dioxide to decontaminate biological agents has been widely investigated, there are no demonstrations of the use of aqueous ClO₂ against chemical contaminants (agents).
- A data gap exists regarding the use of aqueous ClO₂ against *Bacillus anthracis* spores. Currently, the susceptibility of *B. anthracis* spores to aqueous ClO₂ is based on its biological similarity to other species of *Bacillus* which have been the subject of experiments. There is a need for systematic testing to quantify the sensitivity of *B. anthracis* to ClO₂ disinfection specifically, as a function of concentration and exposure time. Likewise, the product's efficacy against other biological threat agents could be studied.
- Further testing is needed to better determine the effectiveness of aqueous chlorine dioxide on non-porous materials.

3.2.9 References for Section 3.2

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3.3 Aqueous Hydrogen Peroxide

3.3.1 Technology Description

Hydrogen peroxide is a strong oxidizing agent. It is commercially available in aqueous solution, ranging in concentrations from 3 to 86 percent. Its principal uses include wood pulp and textile bleaching, waste and wastewater treatment, and use as a chemical intermediate (Kirk-Othmer, 1995). It is also used as a household disinfectant. It has been in use in industrial and commercial applications for over 100 years. It has been registered by EPA since 1977, as an antimicrobial pesticide for indoor use on hard surfaces, including use in residences, medical facilities, food establishments, and other commercial and industrial applications.

Another “peroxy” compound that is commonly used – and is often used as a supplemental oxidizing agent in mixtures with hydrogen peroxide – is peroxyacetic acid. Peroxyacetic acid, an organic peroxide, has been registered since 1985 as an antimicrobial pesticide for indoor use.

While hydrogen peroxide (H_2O_2) solution is effective as an oxidizing agent, its effectiveness increases when dissociated into hydroxyl free radicals (i.e., $OH\bullet$). For example, non-dissociated hydrogen peroxide is not fully effective in detoxifying VX, as not all chemical bonds contributing to the potency of this threat agent are broken by peroxide alone. However, hydroxyl free radicals are very effective in detoxifying VX and other chemical agents (Yang, 1999). For this reason, hydrogen peroxide is often combined with other reagents to increase its activity and effectiveness.

Many different formulations containing hydrogen peroxide have been developed and tested on chemical and biological agents. This chapter will include discussions of formulations where hydrogen peroxide is a principal reagent. As discussed below, hydrogen peroxide is often combined with other ingredients which provide synergistic effects in sterilant formulations. For example, Sandia Foam (contains hydrogen peroxide and surfactants) and Decon Green (contains hydrogen peroxide, carbonates, molybdenum, and surfactant), each discussed elsewhere in this report, are foam formulations with hydrogen peroxide as an active ingredient.

Liquid hydrogen peroxide is identified as being much less sporicidal than the vaporized form at low concentrations (Carlsen and Raber, 2002). Nevertheless, data are available regarding the effectiveness of liquid hydrogen peroxide on its ability of detoxifying both chemical and biological agents.

In detoxifying small quantities of chemical agents or agent-contaminated surfaces, a liquid solution containing excess reagents is frequently used (Yang, 1999). The solution contains excess reagents that chemically convert the agent to less toxic reaction products. Hydrogen peroxide can be used in a manner similar to other cleansing agents. The solution is applied to a wipe (e.g., mop, sponge), spread on a surface, and allowed to stand for a period of time. While some hydrogen peroxide residue may be left following evaporation, removal of this residue is not necessarily required depending on the end use application of the surface. Hydrogen peroxide solution may be considered practical for spot decontamination as well as for larger areas that are well contained and easily accessible.

Additional reagents can be mixed with hydrogen peroxide to increase its effectiveness. For example, ultraviolet light and metal catalysts (iron and copper) are effectively used for promoting free radical formation in hydrogen peroxide to increase effectiveness. Reagents such as organic solvents and pH adjusters are needed when detoxifying chemical agents; these reagents increase the solubility of the chemical agent in the cleaning solution and allow for more effective contact between the hydrogen peroxide and the toxic agent. Peroxyacetic acid and similar organic acids – strong oxidizing agents in their own right – can be added specifically to increase the oxidizing capability of the hydrogen peroxide in such solutions.

Solutions containing hydrogen peroxide may have a limited shelf-life. Hydrogen peroxide is known to destabilize and decompose into water and oxygen over time (Kirk-Othmer, 1995). In addition, the stability of a dilute solution such as one used for cleaning is typically less than that of a concentrated material (Kopis, 2000). This is particularly the case for oxidizing chemicals. Therefore, it is expected to be more effective to dilute hydrogen peroxide solutions at the use site rather than to purchase ‘ready to use’ diluted formulas.

3.3.2 Technical Maturity

There are several sterilization products on the market that contain hydrogen peroxide. These have applications in the food and medical industries for general hard surface cleaning of biological organisms as well as food preparation. Some of these products are discussed in Section 3.3.4.

Additionally, there are specialized formulations available which have been developed specifically for building or warfare decontamination. These include, among others, Sandia Foam and Decon Green, discussed elsewhere in this report.

Other formulations have been patented, although their applications are not known. A mixture of hydrogen peroxide and a bleach activator (e.g., tetra-acetyl ethylenediamine) forms a peroxycarboxylic acid (in the same family as peroxyacetic acid), which is a strong oxidizer. The solution is applied to contaminated surfaces for removal of chemical agents (Brown, 2002). As discussed later in this section, other applications of hydrogen peroxide and peroxyacetic acid are commercially available for biological disinfection.

3.3.3 Applications of the Technology

The greatest application for liquid hydrogen peroxide is in the bleaching of pulp and paper. Its demand is due to its application as a more environmentally-friendly alternative to chlorine compounds. In 1991, 49 percent of the total North American hydrogen peroxide demand was in the pulp and paper market (Kirk-Othmer, 1995). By 2000, this use increased to 57 percent. Hydrogen peroxide is also used in textile bleaching, waste and wastewater treatment, and use as a chemical intermediate (Kirk-Othmer, 1995).

Hydrogen peroxide is used as an over-the-counter biological disinfectant for indoor hard surfaces in residential, commercial, and industrial applications.

3.3.4 Evaluation of Available Data

Performance data for aqueous solutions containing hydrogen peroxide – in detoxifying both chemical and biological agents – are frequently available only from laboratory experiments, such as liquid-phase chemical reaction data or test strip applications. Data obtained from laboratory measurements are effective for screening or for making comparisons (Kopis, 2000). However, there is some uncertainty in applying laboratory data towards the decontamination of surfaces in the field; ‘field test’ data are the preferred indicator of performance. Some field data for the hydrogen peroxide-containing Sandia foam are available for a simulated building environment, as discussed in Section 4.1 of this document.

Based upon lab tests using the AOAC Sporicidal Activity Test, EPA has issued crisis exemptions under FIFRA Section 18 for several aqueous products containing hydrogen peroxide, for use in the cleaning of buildings contaminated with *Bacillus anthracis* (Horinko, 2002). Some of these products are concentrated formulations which are diluted immediately prior to use in accordance with product instructions, while others require no dilution. Exemptions have been issued for the following products:

- Oxonia Active, diluted to 2.1 percent hydrogen peroxide and 0.45 percent peroxyacetic acid;
- KX-6049, diluted to 0.7 percent hydrogen peroxide and 0.45 percent peroxyacetic acid;
- Actril Cold Sterilant and Spor-Klenz Ready to Use, each applied as an undiluted formulation of 0.8 percent hydrogen peroxide and 0.06 percent peroxyacetic acid;
- Johnson Virex STF, applied as an undiluted formulation of 7.5 percent hydrogen peroxide.

As shown, these formulations include hydrogen peroxide in concentrations ranging from 0.7 percent to 7.5 percent, and peroxyacetic acid in concentrations ranging from 0.06 percent to 0.45 percent. Peroxyacetic acid (also known as peracetic acid, CH_3COOOH), like hydrogen peroxide, is an oxidizing agent.

The crisis exemption issued for each of these aqueous peroxide products specifies the conditions under which they must be applied for treatment of *B. anthracis*. All of the products must be utilized only on hard surfaces; must be applied at room temperature (68 °F, or 20 °C); and must have a contact time of at least 10 to 20 minutes, depending upon the specific product. The extent of product dilution prior to use is also specified. Further information is available on EPA’s web site,

www.epa.gov/pesticides/factsheets/chemicals/hydrogenperoxide_peroxyaceticacid_factsheet.htm

Performance Towards Chemical Agents

In some instances, chemical agents react to form toxic end products, depending on the reactants used (Wagner and Yang, 2002). For example, for VX, perhydrolysis (reaction of OOH^- , formed from hydrogen peroxide) minimizes or avoids the generation of a toxic byproduct – S-[2-(diisopropylamino)ethyl] methylphosphonothioic acid, called EA 2192 – which is generated

from simple hydrolysis (reaction of OH⁻). As another example, HD can be hydrolyzed to nontoxic thiodiglycol by simple hydrolysis (although the nucleophilic substitution is slow).

HD can be rapidly oxidized to form two reaction products, a sulfone (which has severe irritating vesicant properties) and sulfoxide (which does not). Hypochlorites and peroxyacids rapidly oxidize HD, but the reaction is non-selective, producing both sulfoxide and sulfone. Hydrogen peroxide, a milder oxidant, selectively yields the nonvesicant sulfoxide, although at a less rapid reaction rate. The rate with hydrogen peroxide can be increased with the addition of peroxide activators (such as bicarbonate and molybdate), discussed further below.

The U.S. Army Edgewood Chemical Biological Center (ECBC) has examined the detoxification of chemical agents (including VX, GB, and HD) with hydrogen peroxide (Wagner and Yang, 2002). Liquid-phase reactions of these chemical agents with hydrogen peroxide-containing reagents were conducted in test tube experiments. The reagents were mixtures of hydrogen peroxide, activators such as sodium bicarbonate (to promote dissociation of the hydrogen peroxide into more chemically-active components), and co-solvents such as t-butanol (to increase the solubility of the chemical agent). Hydrogen peroxide concentrations ranged from 11 percent to 30 percent. Reaction speed was recorded as half-life, which is the time required for half of the chemical agent to react (a lower half-life corresponds to higher reaction speed). On this basis, 10 half-lives would be required to achieve a 3-log reduction, and 20 half-lives to achieve a 6-log reduction (if reaction time is independent of the chemical agent concentration). The results observed by ECBC are presented in Table 3.3-1.

Table 3.3-1. Reaction of Hydrogen Peroxide-Containing Solutions with Chemical Agents

Reagents Present (combination of peroxide, activator, and alcohol)	Observed Half-Life		
	VX	GB	HD
15% Hydrogen peroxide and t-butanol	>> 16 hr	29 days	42 min
15% Hydrogen peroxide, 0.037M sodium bicarbonate solution, and t-butanol	120 min	<1 min	20 min
22-26% Hydrogen peroxide, 0.1M sodium bicarbonate solution, and t-butanol	11 min	<1 min	2.1 min
22-26% Hydrogen peroxide, 0.1M sodium bicarbonate solution, and either ethanol, isopropanol, or polypropylene glycol	No data	No data	1.8 - 1.9 min
30% Hydrogen peroxide, 0.33M sodium bicarbonate solution, and t-butanol	56 sec	No data	No data
11% Hydrogen peroxide, urea, 0.75M sodium bicarbonate solution, and t-butanol	7.5 min	<1 min	1.6 min
28% Hydrogen peroxide, 0.2M potassium bicarbonate, and isopropanol/ Triton X-100 polyether alcohol	2.6 min	No data	2.1 min

Reagents Present (combination of peroxide, activator, and alcohol)	Observed Half-Life		
	VX	GB	HD
28% Hydrogen peroxide, 0.1M potassium bicarbonate/ 0.1M potassium carbonate, and isopropanol/ Triton X-100 polyether alcohol	<1 min	2.4 min at room temperature; 189 min at -30 °C	No data
28% Hydrogen peroxide, 0.1M potassium bicarbonate/ 0.1M potassium carbonate/ 0.01M potassium permanganate, and isopropanol/ Triton X-100 polyether alcohol	<1 min	<<30 sec at room temperature; 5.7 min at -30 °C	No data

Source: Wagner and Yang, 2002.

Earlier results from ECBC examined pH variations and the use of catalysts in chemical agent destruction with hydrogen peroxide. Results regarding the performance as a function of pH are shown in Table 3.3-2. Results regarding the performance of different catalysts are shown in Table 3.3-3.

Table 3.3-2. Effect of pH on VX Detoxification Using Hydrogen Peroxide

Reagent	pH Conditions	Result of VX Detoxification
0.5M Solution of peroxy carbonate (sodium carbonate and hydrogen peroxide)	Slightly basic	'Complete' hydrolysis of VX in less than two minutes
14% Hydrogen peroxide	Slightly acidic (initial pH 4)	Initial rapid reaction; reaction stopped with 47% VX remaining
Hydrogen peroxide and up to 6M of a strong acid such as hydrochloric acid	Strongly acidic	Results in dissolution of VX and subsequent detoxification to an unspecified degree

Source: Yang, 1999.

Table 3.3-3. Effectiveness of Hydrogen Peroxide and Catalysts on Chemical Agents

Chemical Agent	Formulation	Catalyst Added	Result
HD in solution	1% hydrogen peroxide in 50-50% (volume) water/ N-cyclohexyl-2-pyrrolidinone (at 21 °C).	None	Half-life of 6 hours
HD in solution	1 M hydrogen peroxide (about 3 percent) in acetonitrile (at 20 °C).	0.01 M vanadium catalyst, VO[(CH ₃ CO) ₂ CH ₂] ₂	Complete conversion < 2 minutes
VX in solution			“Not effective”
VX or HD	Hydrogen peroxide in unspecified solutions	Iron-containing catalysts	“Not effective”

Source: Yang et al., 1992.

Based on the data in Tables 3.3-1 to 3.3-3 and additional discussions in the source documents (Yang, 1999; Wagner and Yang, 2002; Yang et al., 1992), the following conclusions are available regarding the effectiveness of hydrogen peroxide on chemical agents:

- Most data are available for the agent in solutions or suspensions and therefore there is some uncertainty in extrapolating the results to a surface application.
- Co-solvents (water soluble organic solvents) are needed to increase the contact between hydrogen peroxide and the chemical agent. Chemical agents are typically insoluble in water.
- Hydrogen peroxide alone, or hydrogen peroxide with a solvent, exhibits poor performance for the GX, HD, and VX agents.
- Performance is significantly improved with the addition of a carbonate activator and/ or certain catalysts. Various combinations resulted in a half-life of less than one or two minutes. Assuming that reaction time is independent of agent concentration, a 3-log reduction in concentration is achieved in 20 minutes and a 6-log reduction in concentration is achieved in 40 minutes for formulations in Tables 3.3-1 to 3.3-3 with a half-life of two minutes or less.
- Activators increase the effectiveness of hydrogen peroxide. The reaction speed increases for all three agents (VX, GB, and HD) as the activator concentration increases.
- Chemical agents react differently to activators. GB is deactivated rapidly in all conditions where an activator is present, and therefore is somewhat ‘easier’ to treat. In the case of VX, the fastest reaction results from the use of a mixture of potassium bicarbonate and potassium carbonate. For HD, the fastest reaction results from the use of a mixture of potassium bicarbonate, potassium carbonate, and potassium molybdate.
- None of the chemical agents were tested with a commercially available hydrogen peroxide/peracetic acid product (or similar) such as those identified in the EPA exemption. Due to their low solubility in water, however, significant destruction of these agents in such products would not be expected.

Performance Towards Biological Agents

Whereas chemical agent detoxification data are available solely from the ECBC, data regarding the effectiveness of hydrogen peroxide towards biological agents are available from many different sources.

One study evaluated the effectiveness of hydrogen peroxide in killing bacteria from sponges (Ikawa and Rossen, 1999). Results from this study potentially can be used to assess the penetrating ability of hydrogen peroxide, as well as the effectiveness of ‘off the shelf’ hydrogen peroxide. In this study, bacteria-containing sponges were soaked for five minutes in a commercial three percent hydrogen peroxide solution. Testing was conducted on common household scrubber sponges. Results are presented in Table 3.3-4. The results show that a three percent hydrogen peroxide solution has limited effectiveness in destroying certain types of bacteria present within the sponges. As shown, some bacteria are treated extremely effectively while for others treatment is ineffective. In addition, hydrogen peroxide appears to have the ability to penetrate the porous texture of a sponge.

Table 3.3-4. Reduction of Bacteria in Sponges Following Hydrogen Peroxide Treatment

Sponge Type	Bacterial Reduction	Post-treatment Bacteria Count	Bacteria Type
Laboratory-inoculated household scrubber sponge	99.998%	Not detected (<10 CFU/sponge)	Combination of <i>Escherichia coli</i> , <i>Salmonella choleraesuis</i> , <i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i> , and <i>Shewanella putrefaciens</i>
Consumer-used household scrubber sponge	56.2%	3.2x10 ⁶ CFU/sponge	Bacteria resultant from day-to-day kitchen use; species not determined

Tests conducted by soaking sponge for five minutes in a three percent hydrogen peroxide solution.
Source: Ikawa and Rossen, 1999.

The activity of a hydrogen peroxide formulation was tested by spraying solution onto glass slides inoculated with various organisms and allowing the material to sit for two hours (Elhaik and De Nicola, 2001). The relatively weak formulation consisted of six different individual components, as follows: (1) hydrogen peroxide, (2) organic acid, (3) silver salt, (4) phosphoric acid, (5) a surfactant, and (6) a corrosion inhibitor. The first three components, in combination, provide disinfection properties. The phosphoric acid acts as a stabilizer. Results are shown in Table 3.3-5. The tests showed that the more concentrated solutions displayed a higher kill rate than the less concentrated solutions. Other tests showed that the performance of the solution was lower when either the organic acid or the silver salt was removed; hydrogen peroxide performance improved with the addition of these components.

Table 3.3-5. Performance of Hydrogen Peroxide-Containing Formulation Sprayed Onto Glass Slides

Strain	Log Kill Rate	
	Solutions consisting of: 1.6 - 4% Hydrogen peroxide 1 - 2.8% acetic acid/peracetic acid 16-25 ppm silver 16-25 ppm phosphoric acid 80-200 ppm surfactant 64-160 ppm corrosion inhibitor	Solutions consisting of: 0.8% Hydrogen peroxide 0.5% acetic acid/peracetic acid 2-10 ppm silver 4-10 ppm phosphoric acid 20-40 ppm Surfactant 20-32 ppm corrosion inhibitor
<i>Staphylococcus aureus</i>	6.3	5.2-5.3
<i>Pseudomonas aeruginosa</i>	6.2	5.1-5.2
<i>Enterococcus faecium</i>	5.2	5.1-5.2
<i>Mycobacterium smegmatis</i>	5.1	5.1-5.2
<i>Candida albicans</i>	5.3	4.2-5.0
<i>Penicillium verrucosum</i>	5.1-5.2	3.8-4.1
<i>Bacillus subtilis</i>	3.6	3.6

Source: Elhaik and De Nicola, 2001.

Note: 1% = 10,000 ppm

Solution was allowed to set on glass slides for two hours following spray application.

Conditions: 80% humidity, 24 °C.

A synopsis of available data regarding the effectiveness of hydrogen peroxide on *B. anthracis* is available (Spotts-Whitney et al., 2003). A 100 percent kill rate was reported for a 0.88 M (about 3 percent) hydrogen peroxide solution at pH of 4.3 to 5. Results of 100 percent kill were reported after 3 hours for a spore suspension of 10⁶ CFU/mL, and 100 percent kill was reported after 6 hours for a stainless steel carrier coated with a spore suspension (initial challenge dose not specified).

Another study examined the effectiveness of mixtures of hydrogen peroxide and other additives towards killing viruses and bacteria (Sagripanti, 1992). These results were conducted in suspensions. The results showed that hydrogen peroxide alone was relatively ineffective at low concentrations, but when combined with copper there was a far greater degree of virus inactivation. Results are shown in Table 3.3-6.

Table 3.3-6. Effectiveness of Hydrogen Peroxide on Biological Agents

Biological Agent	Hydrogen Peroxide Concentration	Other Additives	Result
Junin virus	110 mg/L (about 0.01%)	None	50% reduction
	170 mg/L (about 0.02%)	10 mg/L copper	3.5 log reduction after 30 minutes
<i>B. subtilis</i>	5%	0.2% copper	3-log reduction after 35 minutes; >5-log reduction after 60 minutes

Results at 21 °C.

Source: Sagripanti, 1992.

In contrast to the above apparent effectiveness of copper, one study examined the effectiveness of hydrogen peroxide on *B. globigii* spores (Cross et al., 2003). A spore suspension was exposed to a solution of 0.1 M hydrogen peroxide (about 0.3 percent) and 0.6 M copper (II) for 30 minutes. The tests were repeated with the addition of 0.1 M ascorbic acid. All tests using the above mix of reagents resulted in only a 1-log kill (i.e., ten percent of the spores survived). The reagents selected for these tests were intended to result in the formation of hydroxyl free radicals.

Based on the above data regarding the performance of hydrogen peroxide towards biological organisms, the following conclusions are available:

- Most data are available for the agent in solutions or suspensions and therefore there is some uncertainty in extrapolating the results to a surface application.
- A solution of 3 percent hydrogen peroxide is sufficiently effective towards destroying *B. anthracis* and several types of bacteria. For another type of virus (Junin virus), results are inconclusive because a low hydrogen peroxide concentration (0.01 percent) resulted in low kill rate (50 percent); data for higher concentrations are not available.
- Very effective destruction (5 to 6 logs after 2 hours) for various strains was found for peracetic acid/hydrogen peroxide formulations when combined with other reagents, including silver. EPA evaluated confidential testing results of peracetic acid/hydrogen peroxide formulations on hard nonporous surfaces and issued its product-specific crisis exemptions, in part, on the basis of these results.
- Metals (in particular copper and iron) have mixed results in increasing the effectiveness of hydrogen peroxide. These metals have well documented effects in transforming hydrogen peroxide into free radicals and therefore in theory would be expected to increase performance. It is possible that the degree of this increased performance depends on the particular organism.

3.3.5 Concerns for the User

Hydrogen peroxide is a strong oxidizer; therefore, precautions for skin, inhalation, and eye protection are needed when handling products containing this chemical in any concentration. Most formulations for use are relatively dilute and present less of a risk than more concentrated solutions, such as those used for vapor hydrogen peroxide. Some other precautions regarding vapor hydrogen peroxide, as discussed in Section 5.3.5, are also applicable to liquid hydrogen peroxide.

Significant additional shipping fees are required when purchasing any product containing concentrated hydrogen peroxide. Hydrogen peroxide in concentrations of 8 percent or more requires hazardous material shipping. Solutions containing hydrogen peroxide at concentrations less than this may or may not require hazardous material shipping designation depending on the other ingredients present.

3.3.6 Availability of the Technology for Commercial Applications

Many different hydrogen peroxide-containing products are on the market. In addition, hydrogen peroxide alone can be purchased. The availability and cost of several of these alternatives are as follows:

- Actril Cold Sterilant (supplied by Minntech). This formulation contains 0.8 percent hydrogen peroxide and 0.06 percent peracetic acid. Based on 2003 correspondence with the supplier, the cost for a case of four 1-gallon containers is \$70.70 (with test strips included) or \$51.25 (for the formulation only).
- Concentrated hydrogen peroxide (many suppliers possible). This is technical grade 35 percent hydrogen peroxide. Based on a supplier's 2003 web page (Clyde Co-Op), the cost for a 1-gallon container is \$49.38. (As discussed in Section 5.3, this is the concentration used for vapor hydrogen peroxide applications.)

Several of the formulations described in Section 3.3.4 have uncertain availability. For example, combinations of hydrogen peroxide, carbonates, and metals were prepared using the individual chemicals. While these chemicals are readily available, it is inconvenient and probably impractical to prepare such formulations at a use site.

3.3.7 Advantages and Disadvantages

A principal advantage for hydrogen peroxide is that it breaks down into environmentally benign products --- water and oxygen. As a liquid solution, it is easy to apply (e.g., sponge, mop, spray). Another advantage cited for liquid hydrogen peroxide is that it does not freeze under most conditions. However, at low temperatures, the reaction time is slowed considerably (Wagner and Yang, 2002).

Hydrogen peroxide is an oxidant; therefore, it is expected to detrimentally affect color in textiles, carpet, etc. In addition, its effectiveness towards porous materials, such as textiles and carpets, has not been demonstrated.

Like other liquid phase decontaminants and sterilants, the surface must remain wet for the active ingredient to be efficacious against the target organism. In addition, for most products, the surface to be treated should be pre-cleaned. The correct concentration, contact time, and temperature for application of each product are determined by the results of the efficacy testing for that product.

The effectiveness of hydrogen peroxide in destroying G agents, such as GB, is identified as about equal to the performance of an unmodified base solution (e.g., of NaOH), having a pH just above 7. For the G agents, there is little advantage to using hydrogen peroxide. However, for VX, the use of base solutions result in the formation of a toxic byproduct, which does not result from the use of hydrogen peroxide (Wagner and Yang, 2002).

3.3.8 Potential Areas for Future Research

Additional data are desirable in several areas. More data regarding the effectiveness of hydrogen peroxide and/or peracetic acid is desirable, particularly with regard to porous and nonporous surfaces. There may be difficulties in the practical building decontamination application of some of the peroxide formulations that have been found to be effective in the lab. Therefore, formulations or on-site recipes may need further development.

3.3.9 References for Section 3.3

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3.4 TechXtract® Contaminant Extraction Technology

TechXtract is a decontamination technology that chemically extracts hazardous substances from solid materials such as concrete, brick, steel, and wood. It is a proprietary process with a proprietary set of chemical mixtures used for treatment. TechXtract is designed to remove organics, metals, or radionuclides from the surface and subsurface of porous and nonporous solid materials in a series of application, penetration, and extraction steps.

3.4.1 Description of the Technology Alternative

Environmental Extraction Technologies, Inc. (EET) is a division of Active Environmental Technologies, Inc. (ACT). EET calls their TechXtract a "contaminant extraction technology". The technology can be used for treating floors, walls, ceilings, and equipment. The mixtures may include emulsifiers, buffered organic and inorganic acids, and hydrotropic, electrolyte, flotation, wetting, and sequestering agents that extract the contaminants and bring them to the surface. The chemical mixtures are applied sequentially, in successive cycles. Each treatment cycle includes application, penetration, and extraction. Wet vacuuming is used to remove the solutions from the treated substrate.

Effective decontamination of a porous surface is one of the more challenging aspects of building decontamination. TechXtract's effectiveness in decontamination of porous surfaces is, in part, because it uses wetting agents to increase permeation into pores, and because it uses wet vacuuming to get treatment solutions back out of pores.

Although TechXtract is a proprietary process, EET describes the types of chemicals used in their process generically in their advertising literature and on their Internet web site. More detail on specific chemicals used in TechXtract formulations is provided in their patents (Borah, 1995, 1996, 1998; Tyerech, 1998).

How TechXtract Is Used

EET uses and sells chemical formulations called TechXtract 100, 200, and 300. TechXtract 100 is used in one type of treatment cycle. It contains macro- and micro-emulsifiers, as well as electrolyte, flotation, wetting, and sequestering agents. It is applied to the surface being treated as a fine mist, then worked into the surface using an abrasive pad. Then the TechXtract is allowed at least 45 minutes to penetrate into the subsurface. A rinse formula, of ten percent TechXtract 300 mixed with water, is sprayed onto the surface being treated. Then the treatment chemicals and contaminants are removed using a wet vacuum.

The other type of treatment cycle uses TechXtract 200 and 300, and often follows a TechXtract 100 cycle. TechXtract 300 is applied first, and worked into the surface using an abrasive pad. Then TechXtract 200 is immediately applied using the same procedure. EET claims that TechXtract 200 and 300 work together synergistically. They contain buffered organic and inorganic acids, sequestering agents, wetting agents, and hydrotropic chemicals.

The number of TechXtract 100 and 300/200 cycles used for a given decontamination situation will depend on the contamination levels, the difficulty of removal of the contaminant from the matrix, and the depth of the contamination.

TechXtract formulations are applied with abrasive scrubbing, such as with a scrub brush, abrasive pad, or electric floor polisher. This helps remove surface contamination, allowing access by the formulations to the subsurface, and mechanically enhancing penetration.

TechXtract usually solubilizes and extracts, rather than destroying the target compound. Therefore, the liquid wastes contain the extracted contaminants, and must be discarded. In some cases, oxidizing agents are used in the formulations, in which case oxidation products are produced as secondary waste. Small amounts of the TechXtract chemicals are likely to remain in the treated matrix, especially if the matrix is porous. EET says that none of the TechXtract constituents, when spent, will be characterized as hazardous wastes under the Resource Conservation and Recovery Act (RCRA).

By design, a very small amount of the substrate is leached or removed by TechXtract to facilitate release of contaminants. This may result in an unacceptable effect to the surfaces of expensive or sensitive materials.

Functions of the TechXtract Formulation Components

The chemical warfare agents and industrial chemicals most likely to be used in a terrorist scenario would probably be organic chemicals. Therefore, the functions of the treatment chemicals used in TechXtract formulations are discussed here in the context of remediating buildings contaminated with hazardous organics.

Emulsifiers are surface-active chemicals that, in TechXtract applications, stabilize suspensions of organics (having low aqueous solubility) in aqueous matrices. They perform like detergents. The emulsifiers mentioned by EET in their patent for removal of contaminants from surfaces were quaternary amines.

Flotation agents are another type of surface-active chemical, that will cause solid metal-containing particles to adhere to air bubbles and float to the surface of liquids. They would be most useful for heavy metal or radionuclide removal from a contaminated matrix. They would also help to open up an inorganic matrix (such as concrete, brick, or stone) to allow organics extraction. Flotation agents are widely used in the mining industry, for separation of metal-containing ore particles from the low metal content ore tailings.

Wetting agents are another type of surface-active chemicals used in TechXtract formulations. They decrease the surface tension of aqueous solutions, enhancing their ability to penetrate into small pores and crevices. This would be expected to greatly increase the decontamination effectiveness of TechXtract formulations for porous matrices such as concrete and wood. Wetting agents are used in agriculture, where they are called soil penetrants, because they enhance the permeation of beneficial chemicals (nutrients and pesticides) through the soil matrix to the plants' roots, where they can be most effective.

Sequestering agents are chemicals that form complexes or chelates with metals, enhancing the extractability of the metal by aqueous formulations. When removing organic contaminants from metal surfaces, and from the boundaries between metal grains in a metal object, sequestering agents will dissolve small amounts of the metal surface, releasing the organics to the extractant formulation and enhancing their removal. Sequestering agents are widely used for cleaning metal surfaces, and for solubilizing nutrient metals for plants in the horticultural and agricultural industries. TechXtract patents mention a variety of sequestering agents, including nitrilotriacetic acid, hydroxyethylene diamine tetraacetic acid, and ethylenediamine tetraacetic acid (EDTA).

Buffered organic and inorganic acids have at least three purposes. They release contaminants from metal surfaces by dissolving some of the metal, analogous to sequestering agents. Ammonium bifluoride, which releases hydrofluoric acid in aqueous solution, is used commercially to remove vitreous enamel from metal surfaces. Its ability to solubilize silica and silicate matrices is probably why it is used in TechXtract formulations. Stone, brick, and glass are silica and silicate types of building materials whose decontamination would be enhanced by ammonium bifluoride to dissolve their surface and open the matrix. Some polyfunctional organic acids used in TechXtract, like oxalic acid and citric acid, are also sequestrants. (Oxalic acid is used commercially to remove rust stains.) Organic acids with aliphatic hydrocarbon chains will also act as co-solvents for organic contaminants and for organic emulsions of contaminants. (See hydrotropic chemicals.) The buffering of the acids helps control the amount of metal that is removed from a surface, so that damage to the surface is minimal or negligible.

Hydrotropic chemicals (also known as co-solvents) increase the solubility of other chemicals in water-based solutions. They typically have both hydrophilic and hydrophobic components in the same molecule, similar to surfactants, but they form solutions rather than suspensions. Ethylene glycol monobutyl ether and glycerine are examples of hydrotropic chemicals used in TechXtract formulations.

Electrolytes may be contained in TechXtract formulations. In its patents, EET makes it clear that de-ionized or distilled water is used in its formulations, to minimize ions in solution that would decrease the effectiveness of the formulations. Tap water tends to contain variable levels of cations, such as the divalent cations magnesium and calcium, which use up the sequestrants. Salts in solution can decrease the effectiveness of the nonionic surfactants in emulsifying target organics. In some cases, however, EET uses monovalent cations (such as Na⁺) to disrupt the links between matrix divalent cations (such as Ca⁺⁺ and Mg⁺⁺) and contaminants, to separate contaminants from surface charged matrices such as concrete or clays (SAIC, 2003).

It is apparent that TechXtract formulations draw on a wide variety of surface cleaning, and contaminant solubilization and mobilization technologies that have been individually proven in other industries. Their integration into a single decontamination technology, or array of decontamination formulation variants, by EET is one of the innovative aspects of TechXtract. The ability of TechXtract formulations to penetrate into porous surfaces by using wetting agents, and the wet vacuuming to get treatment solutions back out of pores, are the other most significant innovations of this technology.

3.4.2 Technical Maturity

TechXtract is an array of technologies that have been integrated into commercial decontamination service. Some elements of the technology, such as the use of surfactants in aqueous solutions to remove organic contaminants, and the use of chelating agents to remove heavy metal contaminants, are mature technologies, used widely in industry for decontamination applications. Other elements of TechXtract, such as the use of Fenton's reagent, wetting agents, ammonium bifluoride, monovalent cations, and flotation agents for decontamination applications are less mature elements of decontamination technology. These technologies are mature for other industrial applications, but their use in building decontamination is innovative and less mature.

None of the decontamination projects performed with TechXtract have involved chemical warfare agents (CWAs). Because most applications of the technology have been removals rather than in-place chemical destructions, and many of the successful applications have been the removal of difficult hydrophobic organics, there is little question that TechXtract will be able to remove VX, HD, and the G-agents from a variety of building material substrates. The CWAs would then have to be treated and disposed as hazardous waste.

Some of the acidic ingredients used in TechXtract formulations might hydrolyze CWAs in place. If the Fenton's reagent version of TechXtract were applied to CWAs, which uses hydroxyl radicals and ozone to oxidize contaminants, it is likely that the CWAs would be, at least partially, destroyed in place (converted to much less toxic products). These applications have not been tested; there is no assurance of their success (See section 3.4.8).

The simplicity of the application and removal of TechXtract formulations to and from a substrate to be decontaminated, in multiple stages depending on the difficulty of the task, makes the technology readily scalable to large and small tasks. The cost per unit area of the decontamination task will be higher for small areas than for large areas, because the cost for mobilization is a relatively fixed cost. For tasks over about 5000 ft², the material and labor costs, which are proportional to the size of the cleanup, will be the dominant costs (see section 3.4.6).

3.4.3 Applications of the Technology

The TechXtract array of decontamination technologies is fully commercialized. It is available as a service performed on site by EET, or as a commercially available set of products, with training services available as well (see section 3.4.6).

EET claims to have used TechXtract decontamination in over four hundred applications, with a 99 percent success rate (EET, 2004). It has been applied to removal of organics from concrete and granite floors and large metal equipment, which are target applications relevant to terrorist contamination of buildings.

TechXtract was tested by the Hanford Site C Reactor Technology Demonstration Group, under the auspices of the U.S. Department of Energy's (DOE's) Federal Energy Technology Center, for the removal of radionuclide contamination from the surface of lead bricks (DOE, 1998).

3.4.4 Evaluation of Available Data

The following paragraphs describe two decontamination projects performed with the TechXtract technologies that illustrate its applicability to building cleanups.

Polychlorinated Biphenyl (PCB) Transformer Oil Extraction from Concrete Floor in Building

The TechXtract technology was tested under the EPA's Superfund Innovative Technology Evaluation (SITE) Program in 1997 for removal of PCBs on concrete (U.S. Navy, 1997; EPA, 1998). The following paragraphs describe the test.

A field demonstration of TechXtract was performed under the SITE Program, in cooperation with the U.S. Navy's Pacific Division of the Naval Facilities Engineering Command (PACDIV) and the Pearl Harbor Public Works Center (PWC), at the Pearl Harbor Naval Complex on Oahu, Hawaii. A concrete floor, 124 square feet in area, was contaminated with PCBs and oils, including a 14 square foot area of high PCB concentrations and visible staining. The demonstration was performed during February and March, 1997.

Pretreatment wipe samples, of 100 cm² areas of the surface, showed PCB levels of 10,000 to 32,000 µg/100 cm². Pretreatment concrete core samples showed up to 3.5 percent subsurface PCBs, including as high as 2.5 percent at 2 to 4 inches below the concrete surface.

PWC staff performed the decontamination, after having been trained by EET staff. Twenty TechXtract 100 and twelve TechXtract 300/200 cycles were applied to the PCB contaminated concrete floor.

The significant ability of TechXtract to remove surface PCBs is indicated by the wipe sample data in Table 3.4-1. For the three most contaminated surface locations (where PCBs were 10,000 µg/100 cm² or greater), the contaminant removal efficiency was 99.5 to 99.8 percent. For the other thirteen surface locations with PCB levels below 1000 µg/100 cm², the removal efficiency was between 81 and 99.7 percent.

The subsurface decontamination effectiveness of TechXtract was variable, and the data show that the technology is not as effective as it is for surface contamination. Table 3.4-2 shows data indicating significant PCB removal at only one of five coring locations (C3). The other four sets of coring results (locations C1, C2, C4, and C5) indicate that subsurface contamination was unchanged or increased during the decontamination process.

Table 3.4-1. Surface PCB Removal Based on Wipe Samples

Location	Total PCBs (ug/100 cm ²)		Change
	Pre-Treatment	Post-Treatment	
W1	11	1.6	- 85%
W2	32,000	79	- 99.8%
W3	140	11	- 92%
W4	39	1.5	- 96%
W5	28	5.4	- 81%
W6	41	1.5	- 96%
W7	10,000	48	- 99.5%
W8	940	6.4	- 99.3%
W9	47	1.3	- 97%
W10	17	2.3	- 86%
W11	32	3.9	- 88%
W12	40	<1.0	- 98%
W13	35	<1.0	- 97%
W14	11,000	34	- 99.7%
W15	290	<1.0	- 99.7%
W16	85	12	- 86%

Table 3.4-2. PCB Removal at Depth Based on Corings

Location	Depth Below Surface (inches)	Total PCBs (ug/g)		Change
		Pre-Treatment	Post-Treatment	
C1	0 - 1	32,000	30,000	-6%
	1 - 2	22,000	19,000	-14%
	2 - 4	15,000	16,000	+6%
C2	0 - 1	35,000	27,000	-23%
	1 - 2	29,000	30,000	+3%
	2 - 4	25,000	21,000	-16%
C3	0 - 1	14,000	330	-98%
	1 - 2	33,000	39	-99.9%
	2 - 4	24,000	120	-99.5%
C4	0 - 1	3,400	29,000	+850%
	1 - 2	12,000	17,000	+140%
	2 - 4	13,000	13,000	0%
C5	0 - 1	4.80	26	540%
	1 - 2	0.11	9.1	830%
	2 - 4	0.48	6.2	130%

Figure 3.4-1 shows where the wipe and coring samples were collected. All of the coring samples were collected in or near the oil stained area, which is probably where the contamination was heaviest. Although EET did not analyze for oils other than PCBs, it is quite possible that the concrete was more organics saturated than the PCB data alone suggest. This would have made subsurface decontamination more difficult. The surface decontamination results are much more indicative of how TechXtract would perform in a building decontamination following a terrorist chemical attack.

The following section describes the use of TechXtract to decontaminate a large piece of equipment that had been contaminated with PCBs, polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs).

Removal of Dioxin Contamination for Gas Turbine Generator Set Repair

On October 6, 1997, an explosion and fire in Independence, Missouri at the Power and Light Department Gas Turbine and Electrical Substation No. 1 damaged and contaminated a large gas turbine generator. The generator needed to be repaired, but first it had to be decontaminated. One of two transformers at the substation had exploded, producing a fire that caused capacitors to rupture also. Wipe samples of the generator showed that it had been contaminated with PCBs, and with PCDDs and PCDFs that had been produced by the fire. Hexane wipe samples showed surface levels of PCDDs and PCDFs [in 2,3,7,8-tetrachloro-dibenzodioxin (TCDD) equivalents] in the range of 3.1 to 24,800 ng per m². The cleanup goal for the generator for PCDDs and PCDFs, so that it could be safely repaired, was 25 ng/m².

A contractor was hired to decontaminate the generator and, despite multiple passes with “widely recognized non-polar solvents,” the cleanup target was not achieved. Leach-back, which EET describes as the increase of contaminant levels over time after surface cleanup goals are reached, caused the concentrations to return to failing levels again. (Although the leach-back phenomenon might be expected in a porous material, Scott Fay of Active Environmental Technologies has indicated that the crystal boundaries of a metal can also hold contamination, leading to leach-back (SAIC, 2003).

EET was then contracted to perform the decontamination of the generator. EET recognized the significantly hydrophobic nature of PCDDs and PCDFs. To facilitate the water-based TechXtract decontamination process, an oxidation step was added to the cleanup process. The Fenton reaction, which produces strongly oxidizing hydroxyl radicals and ozone, was used to partly oxidize the PCDDs and PCDFs, making them more polar and more soluble.

Final concentrations of PCDDs/PCDFs are summarized in Table 3.4-3, which compares cleanup levels with initial contaminant levels. A minimum of 96 percent contaminant removal was achieved, and the cleanup goal was achieved.

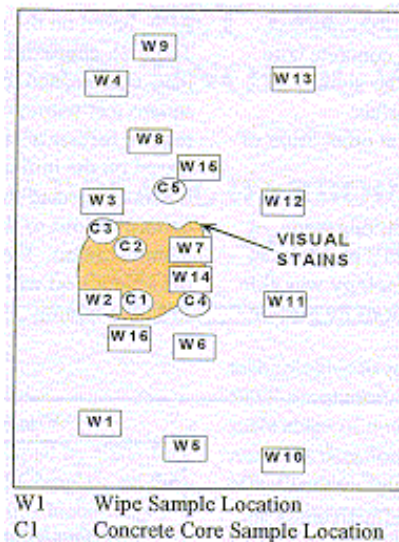


Figure 3.4-1. Locations of Wipe and Coring Samples

Table 3.4-3. Gas Turbine Generator PCDD/PCDF Wipe Samples Before and After

Sample Designation	Sample Name	Initial Concentration (ng/m ²)	Final Concentration (ng/m ²)	Change in Concentration
001TEWS	Turbine end plate, winding side	44.48	0.014	- 99.97%
002GEWS	Generator end plate, winding side	63.4	0.0053	- 99.99%
006LLT	Lead line tunnel	544.4	0.39	- 99.93%
007PAF	Plenum air flow	24,788.	0.067	- 99.9997%
009RRW	W side retaining ring	4769.	0.00	> - 99.9999%
010RRE	East side RR	3548.	0.00	> - 99.9999%
016LGE	Load gear, East	45.21	0.00	> - 99.99%
017LGT	Load gear, Top	21.35	0.00	> - 99.98%
018LGCE	Load gear coupling, East	35.02	0.00	> - 99.99%
023SPI-2	South end of pedestal inside wall	3.1	0.12	- 96%

3.4.5 Concerns for the User

Although TechXtract formulations can contain a variety of organic and inorganic acids, and organic solvents, EET claims that their spent solutions would not be RCRA characteristic hazardous waste. However, the spent solutions will take on the characteristics of the contaminant that is removed. These are some of the ingredients in TechXtract formulations that necessitate careful handling, based on EET's Material Safety Data Sheets:

- Sodium hydroxide, 1-5 percent
- Ammonium bifluoride, less than 1 percent
- Phosphoric acid, 1 percent
- Nitric acid, 1-5 percent
- Ethylene glycol monobutyl ether, 5-15 percent

When TechXtract formulations are handled, appropriate personal protective equipment (PPE) should be worn, including the following:

- Organic solvent resistant impermeable gloves
- Splash apron or rain gear
- Face shield
- Organic solvent resistant impermeable boots.

Other PPE may be required, for protection against the contaminants being removed based on a hazard assessment of site-specific conditions as documented in a Health and Safety plan.

Most TechXtract formulations are fairly stable on storage at ambient temperatures. Only the oxidizer-containing formulations are expected to have a limited life, because of the peroxide-forming compounds they contain. Their room temperature life expectancy (retaining 70 percent potency) is about 40 weeks to one year.

3.4.6. Availability of the technology for commercial applications

EET claims to have used TechXtract decontamination in over four hundred applications, with a 99 percent success rate (EET, 2004). It has been applied to removal of hydrophobic organics (PCBs, PCDDs, PCDFs) from concrete and steel surfaces, radionuclides from lead surfaces, organic lead from concrete and granite, inorganic lead and mercury from concrete, and tritium from concrete.

TechXtract Commercial Products and Services

EET provides decontamination services, and provides training to other companies who want to perform their own decontamination.

EET will also provide training on how to perform TechXtract decontaminations. They will sell TechXtract formulations, customized for a particular cleanup. The formulations sell for \$35 per gal in 55-gal quantities.

Decontamination services are provided by EET, including equipment, formulations, and trained staff (technicians and supervisor). EET's average cost for cleanup and disposal of PCBs (hydrophobic organics), for jobs over 5000 ft², is about \$4.50/ft².

For a PCB cleanup, with relatively uniform surface contamination of about 10,000 µg/100 cm², EET estimates the cleanup price to be \$5 to \$6/ft². This assumes seven to eight treatment cycles. Factors increasing the cost of cleanup include:

- Spalled (not smooth) concrete surfaces (about 10 percent increase)
- Walls and ceilings (about 25 percent increase compared to floors)
- Cold temperatures (40 °F cleanups cost about 20 to 30 percent more than 70 °F cleanups)
- More hydrophobic organics
- Higher contamination levels
- More stringent cleanup concentration goals
- Coated surfaces
- Deep contamination (up to 4 inches).

3.4.7 Advantages and Disadvantages

TechXtract has advantages and disadvantages for building decontamination. These are summarized in the following two sections.

Advantages of TechXtract

The TechXtract technology was designed with minimization of secondary wastes as a design criterion. The treatment formulations tend to be concentrated, and are applied by hand, minimizing their volume. Minimal amounts of rinse solutions are also used, and their removal is enhanced by wet vacuuming. EET often prices cleanups with the disposal of secondary waste included, giving EET an incentive to minimize the wastes requiring disposal.

Application of the TechXtract technology is relatively simple, and the techniques are not proprietary (though the formulations are). The technology is simple enough that EET will train a company's own staff to use it.

TechXtract can be used to clean solid matrices relatively deeply - up to 4 inches for concrete, for appropriate levels of contamination. This is a particularly innovative aspect of the technology. Most other competing in-place chemical decontamination technologies are only effective for surfaces.

TechXtract is applicable, with the appropriate formulations, to a wide variety of decontamination problems:

- Hydrophobic organics
- Heavy metals
- Organometallics
- Radionuclides
- Mixed waste (organics and radionuclides together).

Disadvantages of TechXtract

There are some disadvantages to the use of the TechXtract technology. The surfaces of treated matrices are abraded and dissolved away to some degree. Concrete surfaces that have been decontaminated with TechXtract are much more intact, however, than after spalling. Inorganic fluorides, which are relatively toxic at elevated levels, are used in some TechXtract formulations.

The TechXtract formulations are proprietary, so there is a cost that is greater than the raw materials might be. The selection of formulation ingredients is done by EET based on the specific application, the contaminants, and the matrix to be decontaminated.

TechXtract has not been tested for effectiveness in decontamination of CWAs from building surfaces or equipment. Its effectiveness can only be extrapolated from its performance in

extracting hydrophobic organics from building and equipment surfaces. These data, presented in section 3.4.4, suggest that TechXtract would be effective.

3.4.8 Potential Areas for Future Research

The application of the TechXtract technology to clean up building components contaminated with CWAs needs to be laboratory and field tested. VX, a hydrophobic organophosphate, or an analogous compound should be tested first. TechXtract has demonstrated its effectiveness for removal of other hydrophobic organics. Nest, mustard, and a G-agent such as GB, should be tested. These may be removed fairly readily; their degree of destruction by TechXtract formulations should also be measured. Thorough study of TechXtract effectiveness for CWAs would also include tests on both minimally porous surfaces like steel, on painted surfaces, and on porous surfaces such as concrete and wood.

Section 3.4 References

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4. FOAM AND GEL TECHNOLOGIES

4.1 Sandia Foam and Decon Green

4.1.1 Technology Description

Several peroxide-based systems are available for use in the decontamination of buildings, structures, and equipment. Two specific technologies are discussed in this section: “Sandia Foam” and “Decon Green.”

A common ingredient to these technologies is hydrogen peroxide (H₂O₂). Additional discussion of liquid hydrogen peroxide in non-foam applications is presented in Section 3.4 of this report. Most uses for hydrogen peroxide are based on its oxidizing properties and, as such, it becomes a candidate to consider for decontaminating chemical/biological agents.

Sandia Foam

Sandia Foam was developed by the Sandia National Laboratories and is manufactured by EnviroFoam Technologies, Inc. (EFT) under the trade name EasyDECON[®], and by Modec, Inc. under the trade name Modec Decon Formula (MDF) 200[®]. The Sandia Foam uses a combination of surfactants and oxidizers to inactivate both biological and chemical agents. These systems have been shown to be effective against chemical agents, easily applied, and environmentally friendly. Both Sandia and the West Desert Test Center at Dugway Proving Ground have reported 7-log (i.e., seven orders of magnitude) kills of *Bacillus anthracis* spores within one hour.

The “foam” is somewhat of a misnomer as the chemical can be supplied or created as a foam, liquid, or aerosol. How the foam kills spores—bacteria in a rugged, dormant state—still is not well understood. It is thought the surfactants perforate the spore's protein armor and allow the oxidizing agents to attack the genetic material inside.

Like a fire retardant, the foam could be sprayed from handheld canisters. When the foam is deployed, it expands to about 100 times its liquid volume through a special nozzle that draws air into the spray. The foam fills space and contacts chemical or biological agents in crevices and on open surfaces. In several hours it collapses back to its compact liquid state.

Decon Green

Edgewood Chemical Biological Center (ECBC), Aberdeen Proving Ground, Maryland, patented a similar peroxide-based system called Decon Green. This system has been demonstrated to be effective against all chemical agents, easily applied, and is considered to be environmentally friendly (hence, the name “green”).

This decontamination product is targeted to replace DS2 (Decontaminating Solution 2), the Army's non-aqueous decontamination standard.

Decon Green is a simple solution of hydrogen peroxide, potassium carbonate, potassium molybdate, propylene carbonate and Triton X-100® (a non-ionic surfactant) that affords the rapid, broad-spectrum decontamination of chemical warfare agents, even at low temperatures (-31 °C). The solution is non-corrosive to common surfaces of military interest and leaves no toxic residues, so it is considered environmentally friendly. In use, carbonate and molybdate catalytically activate the peroxide. Thus, the carbonate's basicity provides peroxy anion OOH- to effect the selective perhydrolysis of nerve agents VX and GD to non-toxic products, and both carbonate and molybdate generate peroxy species which afford oxidation of blister agent HD (e.g., mustard gas), initially, to the nonvesicant sulfoxide. Besides chemical agents, Decon Green also affords the destruction of anthrax spores to undetectable levels (as discussed below in Section 4.1.4). Decon Green and other common decontaminants were tested for efficacy of chemical agent decontamination of painted surfaces of military interest (Wagner, et al., 2002).

4.1.2 Technical Maturity

Sandia Foam

Vendor data suggest that the Sandia foam systems may be effective against both chemical and biological agents (see Section 4.1.4). Full scale application to buildings contaminated with anthrax was tried (see Section 4.1.3). However, testing by EPA using the AOAC Sporidical Activity Test on one of Envirofoam Technology's Products indicated that – contrary to claims on the product label – the formulation of this product tested at that time was not effective in decontaminating 6 logs of *B. subtilis* spores on a hard, non-porous surface at one hour contact time. As a result, the crisis exemption for EasyDECON and ModecDecon formula was withdrawn on March 29, 2002.

Decon Green

No detailed scale up information is available. Decon Green has been successfully sprayed using a standard military decontaminating apparatus (M13) and decontaminant pumper (M21) (ECBC, undated). It is not clear from the source materials if agent testing was conducted during this testing.

4.1.3 Applications of the Technology

Applications of Hydrogen Peroxide

Hydrogen peroxide releases oxygen readily, and acts both as a general oxidizing agent and as a convenient source of readily available active oxygen. Discussion regarding the applications of aqueous hydrogen peroxide is presented in Section 3.4 of this report. Compared to chlorine (or ozone, chlorine dioxide, or UV light), H₂O₂ is a rather poor disinfectant, and is not approved as a stand-alone treatment for microbial control in water systems.

Applications of Sandia Foam

The Sandia Decon Formulation was on hand for use during high-profile events such as the 2000 Democratic National Convention in Los Angeles, California, the 3rd Presidential Debate in St. Louis, Missouri (October 2000), and the 2002 Winter Olympics in Salt Lake City, Utah (Sandia, 2002).

Sandia Foam was used as one component in the decontamination of the Capitol Hill complex following the anthrax-containing letter that was received in Senator Daschle's suite in the Hart Senate Office Building (HSOB) in October 2001. In addition to the contamination in the Daschle suite, surface environmental sampling showed anthrax contamination in several other suites and common areas on several floors of the HSOB, as well as in filters within two heating, ventilation, and air conditioning systems that served the Daschle suite. Cross-contamination was also discovered in several other buildings and mail processing areas. The Daschle suite and the two ventilation systems serving it were fumigated with chlorine dioxide gas. The other areas within the HSOB where anthrax had been detected, and the other cross-contaminated buildings in the Capitol Complex, were cleaned using various surface treatment methodologies. The primary treatment of these other areas utilized chlorine dioxide liquid or hypochlorite bleach. Sandia Foam was used for some initial surface treatments, but was replaced by aqueous chlorine dioxide and bleach, which were easier to clean up. High-efficiency particulate air filter vacuuming was sometimes used as a preliminary source reduction step prior to other surface treatments. Extensive post-remediation environmental sampling at the Capitol Hill site was all negative for growth of anthrax spores, and on January 22, 2002, the Hart Building was cleared for re-occupancy (Whitman, 2002).

Although the overall decontamination of the HSOB was successful, the effectiveness of the Sandia Foam during this process was not specifically evaluated. There were no quantitative measurements of pre- and post-treatment contamination levels in areas treated solely by Sandia Foam.

Applications of Decon Green

Decon Green has not been applied outside of a test environment.

4.1.4 Evaluation of Available Data

Solutions of hydrogen peroxide, bicarbonate, and a suitable co-solvent for water-insoluble agents serve as the basis (activated hydrogen peroxide) for a broad decontamination application for G agents, VX and HD. More extensive discussion concerning the performance of aqueous hydrogen peroxide formulations in destroying chemical agents is presented in Section 3.4 of this report. In particular, Section 3.4 includes data regarding mixtures of hydrogen peroxide and one or more components of Decon Green (i.e., peroxide activators such as bicarbonate and molybdate), although no data on the aqueous version of Decon Green itself.

Sandia Decon Formulations

Tests conducted at Sandia showed that the foam destroyed simulants of VX, HD, Soman (GD), and anthrax (Modec, 2003a; Tucker et al., undated).

In October 2000, Sandia was funded by DOE to develop an enhanced version of their foam (originally called DF-100) to optimize performance for military and civilian first responders (Modec, 2003b). This resulted in the new decon formulation, DF-200 [Sandia, undated]. Based on test data, a 99.99999 percent kill of anthrax simulant was achieved after 30 minutes. This compares with a 99.99 percent kill for DF-100 for the same time period. Modec, Inc. has been licensed by Sandia to commercially produce DF-200. Modec sells this product as MDF-200. Commercial production began in December 2001.

Sandia reported the results of the original and improved formulations. Testing was conducted using chemical and biological agent simulants. The results are shown in Table 4.1-1.

Table 4.1-1. Summary Reaction Rates of Agent Simulant Testing – Versions of Sandia Foam

Formulation	1 minute	15 minutes	60 minutes
HD simulant (2-chloroethyl phenyl sulfide), % decontaminated			
DF-100 (pH 8)	18	42	81
DP-100 (pH 9.2)	16	38	83
DF-200	94	98	ND
VX simulant (O-ethyl S-ethyl phenylphosphonothioate,			
DF-100 (pH 10)	45	99	ND
DP-100 (pH 9.2)	33	71	93
DF-200	66	99	ND
G Agent Simulant (diphenyl chlorophosphate)			
DF-100A (pH 8)	53	ND	ND
DP-100A (pH 9.2)	ND	ND	ND
DF-200	ND	ND	ND
Anthrax simulant (<i>Bacillus globigii</i> spores)			
	30 minutes, % kill		60 minutes, % kill
DF-100A (pH 8)	99.99		99.99999
DP-100A (pH 9.2)	90		99.9
DF-200	99.99999		99.99999

Note: ND = below detection limit

Additional live agent testing was conducted at IIT Research Laboratories using test protocols and DF-200 product supplied by Sandia National Laboratories. The results are shown in Table 4.1-2.

Table 4.1-2. Live Agent Kill Rate Summary (testing conducted at IIT Research Institute)

Agent	1 minute, % kill	15 minutes, % kill	60 minutes, % kill
GD	99.98 +/- 0.01	99.97 +/- 0.01	99.98 +/- 0.01
+/- 0.01VX	91.20 +/- 8.56	99.80 +/- 0.08	99.88 +/- 0.04
HD	78.13 +/- 10.53	98.46 +/- 1.43	99.84 +/- 0.32
Ames RIID*	Not measured	99.99999	99.99999
ANR-1*	Nor measured	99.99999	99.99999

*Strain of *B. anthracis*

The Modec Decon Formulation (MDF-200) – a similar product also is marketed as EasyDECON 200 by Environfoam Technologies – is actually a three-part system. Part A, a biodegradable mixture of a cationic surfactant and a fatty alcohol, is formulated from benzyl C12-18 alkyl dimethyl quaternary ammonium compounds (the surfactant), isopropyl alcohol, and N,N,N,N',N'-pentamethyl-N' tallow-1,3-propan-diammonium dichloride. Part B is stabilized hydrogen peroxide (8%), and part C is glycol diacetate. The foam is composed of 90.7 percent water, 3.99 percent part B, 1.8 percent part C and the remainder part A.

The Sandia Decon Formulation was field tested at the U.S. Army Proving Grounds at Dugway, Utah (Sandia, 2003). The field test was designed to test the effectiveness of one formulation in killing anthrax spores. The anthrax simulant, *Bacillus globigii* was sprayed onto various panels (2' x 2') of materials which would commonly be found in a typical office building. Since the area to be decontaminated was relatively small, and to show versatility, the formulation was deployed onto the panels as an aqueous spray (using a standard paint sprayer) rather than as a foam. After 20 hours exposure to the formulation, Dugway personnel tested the panels for surviving spores. The tests were repeated on four consecutive days, and the results for the Sandia Decon Formulation indicated the spores were eliminated (see Table 4.1-3). The 20 hour exposure exceeds the one hour contact time identified on the label direction and used by EPA in assessing the effectiveness of the product for crisis exemption purposes.

Table 4.1-3. *B. globigii* (Anthrax Simulant) Spore Kill During Dugway Filed Tests

Surface	Contaminated (Surface average in CFU*/in. ²)	Decontaminated (ND = not detected)
Floor (painted concrete)	7.67 x 10 ⁷	ND
Floor (tile)	1.31 x 10 ⁷	ND
Floor (carpet)	1.23 x 10 ⁷	ND
Floor (wood)	7.30 x 10 ⁶	ND
Window (glass)	5.32 x 10 ⁴	ND
Painted wall below window	8.16 x 10 ⁴	ND
Left hand wall panels	4.70 x 10 ⁴	ND
Wall (stucco)	2.80 x 10 ⁵	ND
Painted wall above carpet	4.56 x 10 ⁴	ND
Carpeted wall	1.08 x 10 ⁶	ND
Door	3.13 x 10 ⁴	ND
Ceiling	8.49 x 10 ²	ND

*CFU = colony-forming units

The MDF-200 has also been demonstrated to be effective against chemical agents. Testing was conducted at ECBC, Aberdeen Proving Ground, MD. The decontamination effectiveness is compared to DS2 (the Army's non-aqueous decontamination standard). Sandia reports that after 1 hour of contact, 100 percent of the chemical agent was decontaminated (see Table 4.1-4).

Table 4.1-4. Percent Decontamination in Live Agent Testes at ECBC

Decontaminant	HD		GD		VX	
	10 min	1 hour	10 min	1 hour	10 min	1 hour
DS2	100	100	100	100	100	100
Sandia Foam (MDF 200)	47	100	>99	100	100	100

Sandia has also reported results using the Modec foam against selected Toxic Industrial Chemicals (TICs). Results are reported in percent decontamination of the TIC (see Table 4.1-5).

Table 4.1-5. Modec Decon Foam against Toxic Industrial Chemicals

TIC	% Decontamination		
	1 minute	15 minutes	60 minutes
Malathion (liquid)	89	95	BDL
Hydrogen Cyanide (gas)	>99	>99	>99
Sodium Cyanide (solid)	93	98	>99
Butyl Isocyanate (liquid)	99	BDL	BDL
Carbon Disulfide (liquid)	>99	>99	BDL
Phosgene (gas)	98	>99	>99
Anhydrous Ammonia (gas)	>99	>99	>99

Note: BDL = below detection limit

The above results of testing with the Sandia Foam formulation – representing information made available primarily from Sandia National Laboratory, Modec, Inc., and EnviroFoam Technologies, Inc. web sites – appear to indicate that the decontamination formulation is effective against chemical and biological agents. It must be noted that no analytical method detection limits, analytical method description, quality control data, nor test conditions were available to validate the results as presented. Therefore, no critical review of the results as presented is possible.

EPA’s testing of Sandia Foam products using the AOAC protocol appears to disagree with the above results. EPA’s tests were conducted on EasyDECON 4215 (Envirofoam) using *Bacillus subtilis* as the test organism. Two media were tested: (1) a porcelain carrier inoculated with 9.2×10^5 spores; and (2) suture loops inoculated with 2.0×10^6 spores. The carriers were exposed to EasyDECON 4215 for 60 minutes. The results are shown in Figure 4.1.1.

Since Sandia Foam has an aqueous base, paper products will wrinkle after the solution is applied and allowed to dry. EasyDECON 200 solution has been tested on a variety of surfaces. Concrete, asphalt, wood, ceramic, carpet, fabric, leather, steel and aluminum are just a few of the many surfaces tested. Bare, steel objects are susceptible to surface rust after application.

Suture Loops ^a:

Contact Time with Suture Loops	<u>Neutralizer-Primary Cultures</u> ^b # Positive	<u>Secondary Cultures</u> ^c # Positive	Total # Carriers (Sets) ^d Positive
60 minutes	9/60	0/60	9/60
Conclusions: Product not effective at 60 minutes.			

^a Apparatus was used to hold suture loops in product during contact period.^b Tubes contain broth (FTM) plus neutralizers. Notation (e.g., 9/60) indicates 9 positive cultures out of 60 samples tested.^c Secondary tubes (FTM) contain only broth with the carrier.^d One carrier set consists of one primary tube and corresponding secondary tube.**Suture Loops ^a:**

Contact Time with Suture Loops	<u>Neutralizer-Primary Cultures</u> ^a # Positive	<u>Secondary Cultures</u> ^b # Positive	Total # Carriers (Sets) ^c Positive
60 minutes	59/60	0/60	59/60
Conclusions: Product not effective at 60 minutes.			

^a Suture loops floated to the surface of the product during contact period.^b Tubes contain broth (FTM) plus neutralizers (10 uL of a 10% catalase solution added instead of 10 uL of a 1% catalase solution).^c Secondary tubes (FTM) contain only broth with the carrier.^d One carrier set consists of one neutralizer-primary tube and corresponding secondary tube.**Porcelain Carriers:**

Contact Time with Porcelain Carriers	<u>Neutralizer-Primary Cultures</u> ^a # Positive	<u>Secondary Cultures</u> ^b # Positive	Total # Carriers (Sets) ^c Positive
60 minutes	52/60	42/60	52/60
Conclusions: Product not effective at 60 minutes			

^a Tubes contain broth (FTM) plus neutralizers.^b Secondary tubes (FTM) contain only broth with the carrier.^c One carrier set consists of one primary tube and corresponding secondary tube.**Porcelain Carriers:**

Contact Time with Porcelain Carriers	<u>Neutralizer-Primary Cultures</u> ^a # Positive	<u>Secondary Cultures</u> ^b # Positive	Total # Carriers (Sets) Positive ^c
60 minutes	33/60	3/60	33/60
Conclusions: Product not effective at 60 minutes			

^a Tubes contain broth (FTM) plus neutralizers (10 uL of a 10% catalase solution added instead of 10 uL of a 1% catalase solution).^b Secondary tubes (FTM) contain only broth with the carrier.^c One carrier set consists of one primary tube and corresponding secondary tube.**Figure 4.1-1. EPA Test Data for EasyDECON 4215**

Decon Green

Over four years of R&D testing at the ECBC has been devoted to Decon Green, a hydrogen peroxide-based decontaminant. This universal decontaminating solution for chemical warfare agents was patented by George Wagner and Yu-Chu Yang (U.S. Patent No. 6,245,957). The major components include 35 percent hydrogen peroxide solution (30 percent by volume), propylene carbonate (60 percent by volume), and Triton X-100 (10 percent), a non-ionic surfactant.

Data show that the perhydrolysis of VX avoids creation of the toxic byproduct EA2192, formed in generic hydrolysis. Decon Green performed 12 percent better than DS2 when decontaminating VX on chemical agent resistant coating (CARC) panels. Data also indicate that Decon Green is more effective in decontaminating painted panels exposed to GB or HD than VX (Wagner et al. 2002; ECBC, undated). (See Table 4.1-6.) Surface decontamination in 15 minutes was demonstrated to be greater than 99.98 percent using filter paper. Tests have demonstrated that the solution can decontaminate surfaces contaminated with up to 2.5×10^8 *B. anthracis* spores after a 15-minute contact time.

Table 4.1-6. Decontamination of CARC Panels^a

Decontaminant	VX	GD	HD
DS2	72.1%	96.4%	86.7%
Decon Green ^b	86.5%	98.0%	90.0%

Notes:

a. 10g/m² agent challenge; 30 minute neutralization; CARC=chemical agent resistant coating

b. Decon Green formulated with 50% H2O2

Laboratory data reported by Wagner and Yang (2002) show how the effectiveness of hydrogen peroxide against the decontamination of chemical agents is enhanced by the addition of bicarbonates, carbonates and molybdates. The use of “activated hydrogen peroxide” can be formulated from food grade materials, formulated for low temperature application and is a fast, effective decontaminant.

Data regarding the efficacy of Decon Green for *B. anthracis* is presented by Wagner et al. (2002). Spore count was reduced from 7×10^7 to less than 10 in a 10 minute test, resulting in a greater than 7 log kill. The Decon Green used in the test was formulated at 35 percent hydrogen peroxide. Testing protocol (e.g., solution versus surface) was not described.

Decon Green is not currently commercially available. It was designed specifically to meet military needs. Decon Green is based on relatively non-toxic, environmentally acceptable materials such as baking soda, hydrogen peroxide, and a co-solvent. The product consists of two solutions plus a catalyst that can be easily mixed using multi-component mixing and storage system. The decontaminant can be used with fielded decon equipment or commercial off-the-shelf high pressure sprayers.

4.1.5 Concerns for the User

Typical precautions for hydrogen peroxide should be observed. Material Safety Data Sheets (MSDSs) for hydrogen peroxide and MDF-200 are available on the web.

Sandia Foam

Sandia claims that the foam represents no hazard, and the foam's MSDS indicates no reported significant toxic effects. Respiratory protection may be required if workplace exposure limits are exceeded. The manufacturer claims that the foam reduces environmental hazards to the point where the effluent may be disposed of "down the drain." The foam is non-flammable and advertised as a dual-use fire-fighting foam and CB decontaminant. [For reference, it is noted that the commercially available high-expansion Aqueous Film-Forming Foam (AFFF)—a fire-fighting foam—must be stored and treated as hazardous material.]

Decon Green

This decontaminant is targeted to replace DS2. The current design requires three separate containers to be mixed prior to use. The Decon Green solution is reported to be non-corrosive to common surfaces.

4.1.6 Availability of the Technology for Commercial Applications

Sandia Foam

The Sandia Decon formulations can be purchased from the following vendors:

Modec, Inc.
4725 Oakland St
Denver, CO 80239
Toll-free: (800) 967-7887
Phone: (303) 373-2696
Fax: (303) 373-2699
Web: <http://www.deconsolutions.com>

Envirofoam Technologies, Inc.
2903 Wall Triana Hwy
Huntsville, AL 35824
Toll-free: (800) 542-4665
Phone: (256) 319-0137
Fax: (256) 461-8136
Web: <http://www.envirofoam.com>

The Modec Decon formula MDF-200 is available in a variety of configurations, as summarized below:

- “Twin-Pak”: boxed set of 5 gallons
- “Quik-Set”: 10 gallon single container
- Single 55 gallon barrel
- Two-55 gallon barrels
- Two-250 gallon Intermediate Bulk Container or tote (IBC)
- Two-350 gallon IBC.

EasyDECON 200 decontamination solution is packaged in several convenient ready to mix containers. Each container comes ready to use consisting of pre-measured components. According to the manufacturer, preparing EasyDECON 200 decontamination solution is fast and easy and is ready for use within minutes. EasyDECON 200 decontamination solution is available in various sizes and amounts and is capable of remediating both chemical and biological contamination.

EasyDECON 200 solution is sold in a variety of sizes and packages. EasyDECON 200 solution can be purchased in 2.5 gallon containers up to a 250 gallon tote.

EnviroFoam Technologies offers a variety of EasyDECON application equipment including:

- Fogging systems
 - Apply decontamination solution to small enclosed areas
 - Adjustable droplet mist
- Handheld pump sprayers
 - Apply as a liquid rather than a foam
 - Small area decontamination
- MACAW[®] Backpack compressed Air Foam System
 - Manufactured by Intelagard
 - Portable self contained compressed air foam system
 - 5 gallon capacity
 - 35 foot stand-off distance
- Merlin[®] Handcart Compressed Air Foam (CAF) System
 - Manufactured by Intelagard
 - Handcart mounted CAF system
 - 15 gallon capacity
- EASYCAFS[®] Foam Delivery Vehicle (FDV)
 - Compressed air foam system
 - Mounted on a 6x6 Polaris Ranger[®] all terrain vehicle
 - 75 gallon capacity
- Vehicle Mounted EASYCAFS Model 25 Low Profile Slip-in System
 - Self contained for truck transportability
 - Powered by 19HP air-cooled diesel

Decon Green

Developmental stages are complete and ECBC anticipates that Decon Green will be commercially available in the near future and available to the military soon after that.

4.1.7 Advantages and Disadvantages

No specific information was found on how the Sandia foam systems were field tested. It is apparent that the foams can be used in small areas, single rooms, on office fixtures and equipment. The technologies do not appear to be applicable to HVAC systems.

Sandia Foam

The Sandia Foam decontamination technologies are claimed to have the following advantages:

- Claimed to decontaminate chemical agents
- Claimed to be a general disinfectant for vegetative bacteria and viruses, although EPA's AOAC data raise questions regarding its efficacy
- Leaves no persistent toxic residues or toxic by products
- Non-corrosive
- Easy application (no special equipment required)
- Apply as foam, liquid spray or fog
- Relatively rapid reactions – works quickly
- Applicable to various surfaces (though may be a problem for some, such as paper)
- Stable over a wide temperature range including freezing temperatures and hot surfaces
- Variable shelf life claimed for various formulations; 10-year shelf life claimed for EasyDECON.

Issues associated with the use of the Sandia Foam decontamination technologies include the following:

- Efficacy has not been independently verified
- Detailed analytical data need to be reviewed (non-detect value not related to method detection limits); analytical methodology not available for review
- No detailed scale up information available
- Public safety issues need to be assessed when applied in the field
- Full scale demonstration: efficacy of application to equipment and structures is uncertain
- Bare, steel objects are susceptible to surface rust after application; paper will wrinkle
- Potential removal challenges following treatments in civilian settings

Decon Green

The Decon Green decontamination technology is claimed to have the following advantages:

- Leaves no persistent toxic residues
- Non-corrosive
- Easy preparation, no water required
- Easy application (no special equipment required)
- Rapid reactions
- Compatible with cold weather
- Stable over a wide temperature range including freezing temperatures and hot surfaces.

Issues associated with the use of the Decon Green decontamination technologies include the following:

- Efficacy has not been independently verified
- Detailed analytical data need to be reviewed
- No detailed scale up information available (used successfully with M13 decontaminating apparatus and M21 decontaminant pumper).
- Designed for military applications; practicality for building applications needs further demonstration.
- Public safety issues need to be assessed when applied in the field

4.1.8 Potential Areas for Future Research

Data generated under laboratory controlled conditions show that the Sandia Foam and Decon Green are effective to some degree in decontaminating chemical and biological agents, but substantiating data have not been reviewed by EPA. The solutions, therefore, are promising candidates for additional test and development. Under some conditions, field trials were conducted with good results.

It is not clear how well the decontamination solution will withstand excessive temperatures and “dirty” surfaces such as asphalt and concrete. The stability of hydrogen peroxide is understood from the literature, but actual field test data were not available for evaluation. It is suggested that a test program be designed to better evaluate the “real world” parameters and effectiveness of these decontamination systems.

4.1.9 References for Section 4.1

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Modec, 2003a. *Modec Decon Foam – Results Against Selected Toxic Industrial Chemicals*. Modec, Inc. <http://www.deconsolutions.com/TIMS.htm>. Accessed November 2004.

Modec, 2003b. *Performance of the Modec Decon Formulation (MDF-200)*. Modec, Inc. http://www.deconsolutions.com/Formulation_accelerated.htm. Accessed November 2004.

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Tucker et al., undated. Tucker, M.D.; Williams, C.V.; Tadros, M.E.; Baca, P.M.; Betty, R.; and Paul, J. *Aqueous Foam for the Decontamination and Mitigation of Chemical and Biological Warfare Agents*. Sandia National Laboratories, Albuquerque Staff Augmentation Providers, and Orion International Technologies.

Wagner et al., 2002. Wagner, G.W.; Procell, L.R.; Henderson, V.D.; Sorrick, D.C.; and Yang, Y.-C. "Decon Green". Presented at the 23rd Army Science Conference, Orlando, Florida. 2002.

Wagner and Yang, 2002. Wagner, G. W.; and Yang, Y.-C. "Rapid Nucleophilic/Oxidative Decontamination of Chemical Warfare Agents," *Industrial Engineering and Chemistry Research*, **41** (8): 1925-1928 (2002).

Whitman, Christine Todd. Statement before the Committee on Environment and Public Works, September 24, 2002. U.S. Environmental Protection Agency.

4.2 Canadian Aqueous System for Chemical-Biological Agent Decontamination (CASCAD®)

The Canadian Aqueous System for Chemical-Biological Agent Decontamination (CASCAD) was developed in the late 1980s as a classified program under Defence Research and Establishment Suffield (DRES). In the 1990s the concept was shared outside of the defense community. The system was originally designed for the decontamination of military equipment exposed to chemical or biological warfare agents. The formulation was designed to have minimal effect on materials while inactivating biological and chemical agents. Additional considerations were to minimize toxicity, maintain compatibility with existing chemical and biological agent detectors, and to make the formulation a stable foam to enable coatings of contaminated surfaces for extended periods of time. CASCAD is one of the original eight decontaminants identified by a study under the Joint Fixed Site Decontamination program by the U.S. Government.

4.2.1 Technology Description

CASCAD contains several surfactants in a proprietary mixture in combination with chlorinating agents. It is a well-published decontamination system that contains Fichlor (sodium dichlorisocyanurate) as an active ingredient. The mixtures are supplied as a powder and liquid, packaged separately. The powder is the time-release chlorinating agent that is responsible for most of the effectiveness of the material. When combined, a foam is generated that is sprayed on the equipment to be decontaminated. The rigidity of the foam allows for a longer contact time than pure liquids resulting in improved inactivation of biological and chemical agents.

The system is extremely scalable, is available in a 20-liter backpack module, and can also be connected to a fire hose for coverage up to 2,500 square meters per hour. The backpack version is self-contained and uses air pressure to create the CASCAD foam. In larger applications, water is added to create the foam. Figure 4.2-1 shows large scale application of the foam.

A unique feature of this technology is the ability to use water from a variety of sources. The foam is equally active using distilled water, tap water, non-potable water, and even seawater. This degree of versatility minimizes the logistical burden of system implementation. This factor is also attractive for building remediation because the water supply for the building can be used for the generation of the foam. Clean up is conducted using a wet-dry vacuum system.

The patented chemical formulations used by NBC Team Ltd. are designed for both blast mitigation as well as the decontamination of chemical, biological, and radiological compounds. The different applications require different formulations. The blast mitigation foam is a much more dense foam while the radiological formulation is designed to wash off particles and is much less dense. The formulation for decontamination of chemical and biological agents is more dense than the radiological, but less dense than the blast mitigation foam. In addition to the alterations in foam densities, the amount and formulation of the active ingredients are also tailored to specific applications.



Figure 4.2-1. Demonstration of the Foam Application on a Tank Vehicle

4.2.2 Technical Maturity

The CASCAD system is completely mature and ready for operations. The Canadian Defence Research Establishment originally funded the technology and have transferred the technology for commercialization. The commercialization team consists of the Defence Research Establishment Suffield (DRES), The Royal Canadian Mounted Police (RCMP), the National Research Council (NRC), the U.S. Department of Defense (DoD), George Cowan Enterprises, O'Dell Engineering Ltd., and NBC Team Ltd. O'Dell Engineering Ltd. was founded in 1995 to develop and market unique Chemical and Biological weapon decontamination products worldwide. NBC Team Ltd. is the authorized distributor of products. Their address is:

P.O. Box 11040
921 Barton St.
Stoney Creek Ontario, Canada L8E 5P9
Telephone: 905-643-8801
Fax: 905-643-8824
Email: info@nbcteam.com
Web site: www.nbcteam.com

4.2.3 Applications of the Technology

Fichlor is a chemical that is effective in decontaminating chemical and biological agents. Chloroisocyanurates are used as disinfectants in general sanitizers, scouring powders, household bleaches, institutional and industrial cleaners, and swimming pool/ hot tub disinfectants (Kirk Othmer, 1993). Chloroisocyanurates (sold in granular or tablet forms) are among the leading swimming pool sanitizing agents in the U.S., with 1992 use of approximately 50,000 tons (Kirk Othmer, 1998).

4.2.4 Evaluation of Available Data

Chemical agent decontamination

Comparative information regarding the effectiveness of the CASCAD system versus well known decontamination formulations is shown in Table 4.2-1 (published by NBC Team Ltd.). Decontaminating Solution 2 (DS2) is 70 percent diethylenetriamine, 28 percent 2-methoxyethanol, and two percent sodium hydroxide (NaOH). C8, also called the German emulsion, is 15 percent tetrachloroethylene, 76 percent water, one percent anionic surfactant, and eight percent calcium hypochlorite, Ca(OCl)₂ (National Institute of Justice, 2001). No analytical data were available for a technical assessment of the decontamination effectiveness.

Table 4.2-1. Comparison of CASCAD to DS2 and C8

Feature	DS2	C8	CASCAD
Form as applied	Clear liquid	Cloudy liquid	White Foam
Form as delivered	Clear liquid in quart containers	Multi-part liquid & powder requiring emulsifying	Powder and liquid
Additional ingredients	None	Water	Water (fresh, salt, grey)
Destroys agents on surface			
Nerve - G, V	Yes	Yes	Yes
Vesicants - H, L	Yes	Yes	Yes
Biological Agents	Yes	Yes	Yes
Destroys CW agents in paint	Not suitable	Not suitable	Yes
Toxicity of residue	Highly toxic	Highly toxic	Non-toxic
Effect on typical:			
Paint	Removes	Removes some	None
Rubber	Softens/breakdown	Softens	None
Aluminum	Pitting	Minor	None
Tested for removal and control of radioactive contamination	Not tested	Not tested	Best tested
Typical Application Method	20 litre spray	500 gal mixer requires approx. 30 minutes	Continuous injection system reloadable without shutdown. Draw from any available water source

a. Based on Canadian Forces testing and publications. CW agents which contain arsenic will retain less toxic arsenic compounds in the residual material.

b. Liquid nature of DS2 and C8 makes it difficult to remain in contact with surfaces and effectively remove agent without destroying surface finishes.

c. Canadian Forces and French Government test results.

Source: NBC Team Ltd. (Vanguard Response Systems, Inc.) http://www.nbcteam.com/products_decon_index.shtml

Table 4.2-2, published by NBC Team Ltd. (now Vanguard Response Systems, Inc.), reports the effectiveness of CASCAD against standard chemical warfare agents. The amount of chemical agent used at the start of the experiment is not reported. This makes the evaluation of the data very difficult.

Table 4.2-2. CASCAD Effectiveness Against Chemical Warfare Agents

Agent	Time (minutes)	Percentage of agent remaining
Nerve Agent GA	1	<0.56
	3	0
Nerve Agent GB	1	<0.56
	3	0
Nerve Agent GD	1	Trace
	3	0
	5	0
	10	0
Nerve Agent VX	6	-
	7	0
	11	0
Blister Agent HD	3	<0.05
	5	-
	19	-

Source: Vanguard Response Systems, Inc.

The company states that all tests were conducted at unspecified independent government laboratories. While that is certainly accepted, the data presented in this fashion without specific experimental details have limited utility.

Biological Agent Decontamination

A series of experiments were conducted by the Canadian government to determine the effectiveness of CASCAD for the killing of *Bacillus anthracis* (Anthrax) spores. Ames strain of *B. anthracis* was prepared by culture on blood agar plates followed by transfer of the bacteria into a buffer solution. The suspension was heated to 60 degrees Celsius for one hour to kill all vegetative organisms. A suspension of spores was distributed onto a metal plate and allowed to dry overnight. Plates were covered either with a control foam or the CASCAD formulation and incubated for thirty minutes at room temperature. Plates were rinsed and then the spores removed by wiping with a sterile cotton swab. Spores were dispersed in growth medium and aliquots were streaked onto blood agar plates for subsequent colony counts. A four log reduction in spore viability was demonstrated after a thirty minute contact time.

These experiments compared the effects of CASCAD with control foam containing no active ingredients. It is not known what the effect of the control foam was on the bacterial spores. Although this experiment did not control for spores washing off the plate during incubation and subsequent rinsing, since both populations of plates were treated similarly, these errors most likely canceled out during the experimentation process (Kourmikakis, Purdon and Chenier, 2000).

Compared with the control foam, the CASCAD product demonstrated a four-log (99.99 percent) killing of the *Bacillus anthracis* spores. Although this does not meet the U.S. EPA's Federal

Insecticide, Fungicide, and Rodenticide Act (FIFRA) sterility requirement, it does meet the North Atlantic Treaty Organization (NATO) decontamination requirement.

In a separate publication from DRES, the effect of CASCAD on *Bacillus globigii* spores was evaluated. The authors concluded that CASCAD was a very effective decontaminant (Spence, undated). While the conclusion appears to be supported by the data, the data are qualitative and not quantitative. Therefore one can not calculate a log reduction factor from these results.

Table 4.2-3 presents product information published by the commercial vendor of CASCAD indicating effectiveness against biological material. No tests have been reported against any toxins or toxic industrial compounds.

Table 4.2-3. Effectiveness of CASCAD Treatment

Agent	Time of exposure (minutes)	Percentage of agent remaining viable
<i>Bacillus globigii</i> spores	5	0.0001%
"	60	0.000001%
<i>Erwinia</i>	5	0.000001%
<i>Bacillus anthracis</i> spores	30	0.001%
"	30	0.011%

Source: Vanguard Response Systems, Inc.

Evaluation of “Rapid Lightning Report”

Rapid Lightning was a biological warfare simulant sampling and decontamination exercise funded by the Defense Threat Reduction Agency in August of 1999. CASCAD killing efficiency was evaluated for the BW simulants *Bacillus globigii* (Bg) spores, and *Erwinia herbicola* (Eh) vegetative bacteria. This exercise represented the first evaluation of CASCAD in the U.S. These laboratory trials were a series of experiments that varied the mix of CASCAD to simulant in ratios from 10:1 to 0.5:1, with contact times ranging from five to 60 minutes. No comparisons were conducted against any other decontamination technology with the exception of 5 percent bleach. CASCAD effectiveness was determined by measuring the number of colony forming units (cfu) in the presence and absence of CASCAD. A six log reduction was considered effective decontamination.

The data presented support the use and further evaluation of CASCAD as a decontamination protocol for spore remediation. The data presented in the Rapid Lightning report do not provide standard error measurements. This degree of resolution is essential because of the apparent variability of the protocol. In the Rapid Lightning study, CASCAD at a 1:1 ratio for a 60 minute exposure demonstrates an eight log reduction of Bg spores, while the same experimental conditions yielded only a 2.5 log reduction. The authors proposed this variability was due to different spore preparations. However, it is unlikely that spore preparation could adequately explain such a divergence in results. Accordingly, additional experimentation is required to determine the actual effectiveness against a spore population.

Experiments with the vegetative bacteria, *Erwinia herbicola*, demonstrated a seven log reduction at a 1:1 volume ratio even after only five minutes contact time. These data are consistent with

the accepted fact that vegetative bacteria are much more susceptible to destruction than the bacterial spore.

4.2.5 Concerns for the User

According to results published by the Canadian Government, the residue from CASCAD is non-toxic. Unlike some of the harsher decontaminants like DS2, CASCAD is reported not to harm paint, rubber, or aluminum surfaces. While the material in the formulation of the foam does not appear to be toxic to users, one must recognize that the target of the remediation is harmful to the user. Therefore, the user should employ personal protective equipment while using this product. A user should consult the MSDS for the active ingredient in CASCAD, MILCON-T.

4.2.6 Costs

CASCAD products are available commercially. The fully integrated system that can be hooked up to a fire truck or other water source retails for \$85,000. Intermediate sized systems are also available. A portable backpack sprayer is \$2,500. Coverage areas as a function of deployment system are not mentioned. However decontamination for 10 square feet of surface requires one liter of CASCAD. Operational costs range from \$0.30 to \$0.60 per square foot depending on quantity ordered. These operational costs are for outside equipment decontamination. Use within a building could have significantly greater operational costs, based on recent experience in decontaminating some buildings impacted by the 2001 anthrax mail incident.

4.2.7 Advantages and Disadvantages

CASCAD is a demonstrated technology for remediation of chemical and biological warfare agents. The product was designed for the military for use in battlefield environments. Demonstrations have been on the exteriors of tanks, ships, and aircraft. In these situations the product performs as stated. This product was not developed as a building interior remediation alternative.

With the recent terrorist attacks with *Bacillus anthracis* spores in envelopes, the CASCAD vendor has claimed value for this product in such applications. The value claimed is two-fold. The first is in limiting the spread of the biological or chemical agent. The foam acts as an insulator to prevent further dissemination. The second effect is the decontamination. While this may be a useful approach for rapid isolation, it is much more invasive and destructive than fumigation due to the wet nature of the product and the need to remove after application. These are vendor claims that have not been evaluated by the EPA.

CASCAD, as well as other foam based decontamination alternatives, is very labor intensive when applied to building interiors. Sandia Foam was used for remediation of the Dirksen and Ford Office Building mailrooms in the fall of 2001; a material expected to have a consistency similar to CASCAD. Not only was the foam not fully effective, the clean up operations were extensive and time consuming (personal communication with the Coast Guard personnel conducting remediation operations).

The most significant advantage to a system of this type is immediate isolation and containment of the exposed area. Application of this type of technology could have significant impact on spread of the contamination.

4.2.8 Potential Areas for Future Research

The CASCAD formulation is mature for chemical and biological decontamination operations. Additional documentation by independent researchers would validate the vendor's claims. The concept for utilization of this type of a product for initial isolation is quite promising, but not validated by experimentation. The data presented in this report are very suggestive of efficacy, but more rigorous experimental conditions are required.

4.2.9 References for Section 4.2

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Kirk-Othmer, 1993. *Encyclopedia of Chemical Technology, Fourth Edition, Volume 7*, "Cyanuric and Isocyanuric Acids."

Kourmikakis et al., 2000. Kourmikakis, B; Purdon, J.G; and Chenier, C.L. *Verification of CASCAD in the Decontamination of Bacillus anthracis Spores*. Report ECR-2000-141. Defense Research Establishment, Suffield. 2000.

National Institute of Justice, 2001. *Guide for the Selection of Chemical and Biological Decontamination Equipment for Emergency First Responders: Volume I*. NIJ Guide 103-00, Volume I, U.S. Department of Justice. October 2001.

Spence, undated. Spence, M.; Ho, J.; and Ogston, J. *Decontamination of Vehicle Using CASCAD After Exposure to Biological Aerosol Hazards*.

4.3 L-Gel

L-Gel is a spray-on decontamination gel that has been found effective to some degree against both toxic chemicals and biological agents. The following sections describe how it works, laboratory and field test results, and practical considerations for its use.

4.3.1 Description of the Technology Alternative

L-Gel is a decontamination technology developed at Lawrence Livermore National Laboratory (LLNL) with three important characteristics:

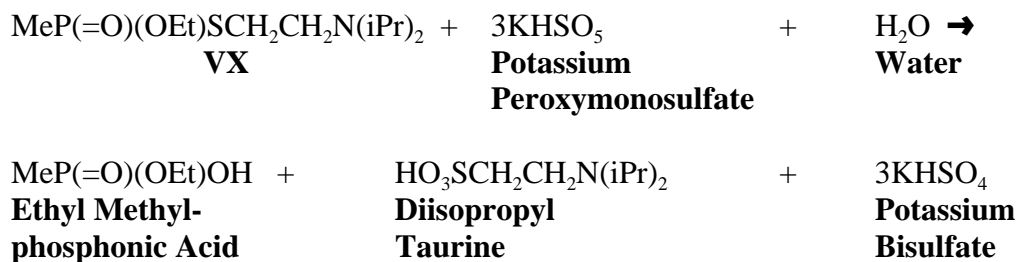
- It oxidizes chemical warfare agents (CWAs)
- It kills bacterial spores used as biological warfare agents (BWAs)
- It sticks to vertical and overhead surfaces.

Raber and McGuire, of the Environment Protection Department at LLNL, have reported on the development and testing of L-Gel (Raber and McGuire, 2002; LLNL, 2002; Raber and McGuire, undated). It is non-toxic, non-corrosive, easy to manufacture (and therefore relatively inexpensive), and easy to deploy (LLNL, 2002). The oxidizing agent in L-Gel is Oxone[®], a Dupont Corporation patented triple salt with the following formula (DuPont 1998a):



The active ingredient in Oxone is the first component of the triple salt, and is called potassium peroxymonosulfate. The peroxymonosulfate anion is a moderate strength oxidizer, strong enough to oxidize a halide anion to a halogen (neutral) or a hypohalite anion, a ferrous cation to ferric, and a manganous cation to manganic (DuPont 1998a).

Oxone has been shown in laboratory studies to oxidize VX to ethyl methylphosphonic acid (EMPA) and diisopropyl taurine (Yang, Baker, and Ward, 1992):



where Me = methyl, Et = ethyl, iPr = isopropyl.

The sulfur in the thiol ester link in VX is oxidized to a sulfonic acid functional group, producing the two products from VX that are much less toxic than VX. Potassium bisulfate is a neutral salt with very low toxicity.

The gelling agent in L-Gel is Cab-O-Sil® EH-5, a synthetic amorphous colloidal silica (silicon dioxide) made by Cabot Corporation (LLNL, 2002). Cab-O-Sil EH-5 has an average particle length of just 0.2-0.3 μm (Cabot, 2002). When Cab-O-Sil EH-5 is added (15 percent) to an aqueous solution of Oxone, a gel is formed that can be applied to surfaces using paint spraying equipment. After application, it begins to dry and thicken, so that it adheres well to walls and ceilings.

L-Gel is packaged as a high-viscosity, gelatin-like semi-solid, as shown in Figure 4.3-1, that is liquified by shaking or stirring. The liquified product can be applied using paint spraying equipment that is commercially available (Raber, 2002). The researchers note that due to L-



Figure 4.3-1. L-Gel, Delivered as Semisolid, is Liquified for Use

Source: LLNL, 2002.

Gel's acidic properties, stainless steel spray nozzles must be used (Raber and Maguire, 2002).

Decontamination with L-Gel takes about 30 minutes after application. L-Gel eventually dries out completely, in about one to six hours, to a residue that can be removed by vacuuming.

4.3.2 Technical Maturity

L-Gel has been tested for decontamination of BWAs and CWAs, in the laboratory and in the field (see Section 4.3.4). It is not yet commercially available. It has been developed in three different forms:

- L-Gel 115 was the first decontamination gel developed by LLNL
- L-Gel 200, an improved version of L-Gel 115, is being developed to have the ability to penetrate coatings of paint or varnish
- An aerosol version of L-Gel is being developed for decontamination of the interior of ventilation systems.

LLNL is negotiating with several companies to license the manufacturing and marketing of L-Gel.

The cost for L-Gel is estimated at about \$1 to cover 1 m², which is about 11 ft² (LLNL, 2002). Labor, equipment, and mobilization will be additional costs.

4.3.3 Applications of the Technology

The active ingredient in L-Gel is Oxone, a commercial product of Dupont used for oxidation of organics. Dupont literature cites the use of Oxone in numerous applications (DuPont, 1998b), including:

- Denture cleaners contain at least 25 percent Oxone, which provides stain removal.
- Pool and spa shock treatments in which Oxone is used as an auxiliary oxidant. In this application, Oxone is not a disinfectant.
- Pool and spa disinfectants, when used in a two-part combination with sodium bromide. A mixture of 80 percent Oxone to 20 percent sodium carbonate for the first step is recommended as a means to control the pH. This application is registered under FIFRA.
- Repulping recycled papers, which uses Oxone as an alternative to chlorine-containing repulping agents.
- Printed circuit board etching, which uses Oxone in combination with acid and temperature controls to achieve etch rates of 0.25 to 2.5 μm/min (10 to 100 μ in/min).
- Wool shrinkproofing as a replacement to chlorine applications.
- Laundry bleach as an alternative to hypochlorite provided the concentration of Oxone in the water is at least 25 ppm.
- Treatment of reduced sulfur or cyanides in waste streams.

On March 5, 2001, DuPont announced that it planned to increase the supply of Oxone to meet demand from its customer, Antec International (DuPont, 2001). Antec manufactures Virkon[®] S, a disinfectant used to prevent the spread of foot and mouth disease in the United Kingdom.

4.3.4 Evaluation of Available Data

Oxone Test Results

Oxone, the oxidizing agent in L-Gel, was tested by LLNL for its effectiveness in decontaminating surrogates for three types of BWA:

- *Bacillus subtilis* (for anthrax and other spore-forming pathogens)
- *Pantoea hericola* (for plague)
- *Ovalbumin* (for botulinum toxin).

Oxone was more than 99 percent effective in oxidizing the surrogates, which had been applied to common building materials such as carpet, wood, and stainless steel (LLNL, 2002).

In similar tests, Oxone was equally effective at treating surrogates for three CWAs:

- Amiton, or S-[2-(diethylamino)ethyl] O,O'-diethylphosphorothioate (for VX)
- Diphenyl chlorophosphate (for sarin, GB)
- Chloroethyl ethyl sulfide (for sulfur mustard, HD).

The HD surrogate was 100 percent oxidized in 10 min by double the molar amount of Oxone. The VX surrogate was 93 percent oxidized in 30 min, and more than 99 percent oxidized in 40 min. Based on the work with Oxone for oxidation of HD and VX performed by Yang, Baker, and Ward (1992), the effectiveness of Oxone in oxidizing the LLNL surrogates was expected. The same researchers, however, showed that G agents are only slowly hydrolyzed by Oxone solutions, and not oxidized at all. LLNL found diphenyl chlorophosphate to be 100 percent destroyed in the time allotted. (The amount of time was not given. Destruction was probably through acid catalyzed hydrolysis, since Oxone solutions are strongly acidic.)

Battelle (1999) reports that the active ingredient in Oxone, potassium peroxydisulfate, rapidly oxidizes VX and does not form EA2192 as a by-product like VX hydrolysis does. Also, HD is oxidized to the sulfoxide immediately, and then to the sulfone within an hour. These are less toxic products. Battelle reports that Oxone can only decontaminate or detoxify the G agents by slowly hydrolyzing them by acid catalysis. Battelle is citing the results reported by Yang, Baker, and Ward (1992) that showed hydrolysis half-lives of about 50 and 80 min for 0.03 M GB and 0.02 M GD, respectively, in 0.1 M Oxone at pH 2. (Note that it takes seven half-lives to reduce a starting material by 99 percent, and ten half lives to reduce starting material by 99.9 percent.)

L-Gel Laboratory Tests with CWAs

The final design formulation of L-Gel, called L-Gel 115, was tested at LLNL against CWA surrogates on materials commonly found in buildings: varnished wood, painted steel, glass, fiberglass, and carpet (LLNL, 2002). (Presumably, the same surrogates were used as those described above for LLNL's testing of Oxone alone.) The L-Gel was applied to each agent-contaminated test surface, allowed to dry for 30 min to several hours, and then surrogate residual levels were determined. L-Gel 115 was found to be more than 99 percent effective for all agents on all surfaces.

L-Gel was laboratory tested by two other organizations against real CWAs during the period from October to November, 1999:

- Edgewood Chemical and Biological Forensic Analytical Center, Maryland, US
- Defense Evaluation and Research Agency (DERA), Porton Down, United Kingdom (UK).

At Edgewood, L-Gel's decontamination effectiveness was tested on acrylic-painted metal, polyurethane-coated oak flooring, and indoor-outdoor carpet surfaces. The tests showed that L-Gel was more effective for decontamination of 2.5 μ l samples of VX (2.53 μ g), GD (soman; 2.52 μ g), and HD (3.18 μ g) than calcium hypochlorite, a CWA decontaminating agent

commonly used by the US military. The CWAs were placed on the substrates for 15 min, then L-Gel was applied and allowed to dry for 24 hr. Samples were collected, extracted with 10 mL of dichloromethane, and the extracts were analyzed. Agent decontamination was complete in all but the GD tests on acrylic- and polyurethane-coated surfaces. All VX and HD was treated, with detection limits of 0.1 µg/mL for VX and GD, and 1.0 µg/mL for HD. (If it is assumed that the extracts were concentrated to 1 mL before analysis, the treatment effectiveness for “complete” decontamination can be calculated by the reader to be at least 96 percent for VX and GD, and 69 percent for HD.)

At Porton Down in the UK, L-Gel was laboratory tested for its decontamination effectiveness on thickened GD (TGD) and thickened HD (THD) applied to about 3 by 5 inch metal plates painted with either alkyd or polyurethane paint. The thickened CWAs were applied to the test surfaces 1 hr before decontamination. L-Gel 115 was then applied to the metal plates in a vertical position with a commercial compressed air paint sprayer. After 30 min, the sample plates were sprayed with ambient temperature high pressure water, then soaked in isopropanol for 2 hr, and the extracts were analyzed. (One would assume that the untreated control plates were also sprayed with high pressure water, and that the analyses represented only the agent remaining that had diffused into the paint.) L-Gel 115 decontaminated 35 percent of the TGD and 50 percent of the THD in the alkyd paint, and 64 and 66 percent in the polyurethane paint, respectively.

To be effective, a technology must not only clean the contaminated surface but also reach below the polymeric paint to treat CWA that penetrated the surface during the attack or as a result of surface cleaning. The Porton Down test required L-Gel to demonstrate effective treatment of the thickened agents on the surface as well as treatment of contaminants below the surface of the polymeric paints within 30 minutes. The 30-minute period allowed in the Porton Down test is not adequate time and seems to be an impractical test. Complete removal of the paint layer would seem to be more appropriate if rapid decontamination is important. Alternatively, multiple applications of L-Gel, with gentle heating of the paint layer to enhance diffusion, might be considered. (See section 3.2, in which TechXtractis applied many times for difficult decontaminations.) This is the only test conducted with L-Gel that specifically required subsurface decontamination. The solution suggested by the developers of L-Gel, for further development, was incorporation of a co-solvent. They said that this might “eliminate the problem with gelled chemical agents.” The problem may also exist on any painted horizontal surface, with any agent persistent for at least 1 hour. Interestingly, the Porton Down study data did not include results for any other decontamination method for comparison.

L-Gel Laboratory Tests with BWAs

L-Gel 115 was also tested at LLNL against BWA surrogates on varnished wood, painted steel, glass, fiberglass, and carpet, as with CWA surrogate tests (Raber and McGuire, 2002; LLNL, 2002). The L-Gel was applied to each agent-contaminated test surface, allowed to dry for 30 min to several hours, and then surrogate residual levels were determined. L-Gel 115 was found to be more than 99 percent effective for all agents on all surfaces.

LLNL also performed *in vitro* tests of two safe (nonvirulent) strains of the biological warfare agents (BWAs) *Bacillus anthracis* (spore form) and *Yersinia pestis* (bacteria): Sterne and Strain D27, respectively. The agar plate resistance test is a standard test for measuring the efficacy of antibiotics. L-Gel was more than 99.9 percent effective in killing the spores and bacteria (LLNL, 2002).

L-Gel Field Tests with CWAs

L-Gel was field tested by the Military Institute of Protection in Brno, Czech Republic against real CWAs during October, 1998. L-Gel 115 was tested outdoors on aged (more than 20 years old) concrete, new concrete, aged asphalt, and new asphalt. The performance of L-Gel was compared with a standard water solution of high test hypochlorite (HTH), for treatment of GD and VX (the latter on new substrates only). Agent was deposited on a circular area of about 20 m² using a hand sprayer, at a density of about 15 g/m². After 2 hr, untreated agent samples were collected. The decontaminant was then sprayed on about 5 m², allowed to remain in contact for 30 min, then 25 cm² samples were collected and analyzed. L-Gel showed 98, 98, and 70 percent agent destruction for GD on new and old asphalt and for VX on new asphalt, respectively; HTH showed 80, 95, and 72 percent destruction for the same agent-substrate combinations. L-Gel showed 100, 98, and 99 percent agent destruction for GD on new and old concrete and for VX on new concrete, respectively; HTH showed 100, 95, and 95 percent destruction for the same agent-substrate combinations. In summary, L-Gel was slightly more effective than the standard HTH decontamination solution in four tests; equal in one test; and slightly less effective in one test.

L-Gel Field Tests with BWAs

In December, 1999, L-Gel was field tested on surrogate bacterial spores at the U.S. Army Soldier Biological and Chemical Command (SBCCOM) facility at Dugway Proving Ground in Utah. Initial surrogate organism counts on 40 cm² panels of acoustic ceiling tile, tightly woven fabric, fabric-covered office partition, painted wallboard, concrete slab, and painted metal were about 10⁷ spores/10 cm². L-Gel was applied, and allowed to stand for 24 hours. Swabs samples of the panels were collected, and live spore counts were reduced by an average of 99.988 percent, and a minimum of about 99.96 percent (LLNL, 2002) (See Table 4.3-1).

Table 4.3-1. Surrogate Spore Counts Before and After L-Gel Treatment*

Test Panel Material	Spore Count Before	Spore Count After	Reduction
Cement	2 x 10 ⁶	5 x 10 ²	99.98 %
Ceiling	1.5 x 10 ⁶	6 x 10 ²	99.96 %
Panel fabric	4 x 10 ⁶	5 x 10 ²	99.99 %
Painted metal	4 x 10 ⁶	1 x 10 ²	99.998 %
Painted wallboard	6 x 10 ⁶	4 x 10 ²	99.993 %
Carpet	3 x 10 ⁶	1 x 10 ²	99.997 %

* Level of detection was 1 x 10² spores. Counts were averages of five trials, for areas of 10 cm². Before and After counts were estimated for this table from a logarithmic-scaled graph of results (LLNL, 2002).

In October, 2000, LLNL staff took part in another surrogate BWA test at Dugway in which a full-scale mock office with different floor and wall materials was contaminated and decontaminated. The floor materials were carpet, vinyl tile, varnished oak, and painted concrete. Wall materials included stucco, wood paneling, plasterboard, and carpet. The ceiling was suspended ceiling tile.

The office was contaminated with 4 g of *Bacillus subtilis* spores by a simulated explosion using a disseminator; then the spores were further spread by an oscillating fan. L-Gel was used to treat the room, then 400 swab samples were collected from throughout the office. Swabs were quenched in sterile, buffered sodium thiosulfate solution. (This would use up any remaining oxidizing capacity of the L-Gel. With this care in controlling the period of treatment, it is surprising that no treatment time data were provided.) Quenched samples were plated and live colonies were counted. The detection limit was 100 colony-forming units (cfu) per 4 in² (4 cfu/cm²). L-Gel reduced the spore counts by about five orders of magnitude and did not damage office surfaces, except that it created some surface rust on ceiling supports. In comparison, paraformaldehyde was similarly effective at reducing the live spore counts (Raber and McGuire, 2002; LLNL, 2002).

Research indicates that L-Gel does not harm carpets or painted surfaces (LLNL, 2002), however as noted earlier, L-Gel does have acidic properties that require the application of the material with a stainless steel sprayer nozzle.

4.3.5 Concerns for the User

The pH of L-Gel is approximately 4 (LLNL, 2002). Like other decontamination technologies discussed in this publication, appropriate caution should be taken to avoid exposure to both the treatment chemical and the target chemical/biological agent. Users should ensure that all appropriate personal protective equipment are used.

Oxone is an acidic oxidizer that is corrosive to the eyes, skin, nose, and throat. DuPont states that they observe a 1mg/m³, 8-hour time-weighted average airborne exposure to Oxone (DuPont, 1998a). Oxone is incompatible with halide or active halogen compounds, cyanides, transition heavy metals, and oxidizable organics (DuPont 1998a).

4.3.6 Availability of the Technology for Commercial Applications

L-Gel is not commercially available. Licensing discussions are underway between Lawrence Livermore National Laboratory and potential vendors.

4.3.7 Advantages and Disadvantages

L-Gel has a number of advantages over other decontamination technologies. It can be used for both CWA and BWA decontamination. As a general purpose oxidizer of organic compounds, it can be expected to be effective against a wide variety of hazardous industrial chemicals as well.

It has the advantage over decontamination solutions that it is in gel form, so that it will adhere to vertical and overhead surfaces like walls and ceilings. The oxidizing power of Oxone tends to reduce hazardous compounds to less toxic oxidation products, but this must be ascertained on a chemical-by-chemical basis.

L-Gel 200 has the ability to penetrate into polymeric coatings like paints and varnishes, an important capability for decontaminating persistent CWAs that have soaked into surface coatings. Without this ability, decontaminated surfaces will continue to become re-contaminated as subsurface agents gradually diffuse back to the surface. This phenomenon has been referred to as “leach-back” (see section 3.2.4), and is a potential problem for decontamination of most surfaces, including coated or porous surfaces, and even steel.

Application of L-Gel to decontaminate a surface is relatively simple: commercially-available spray painting equipment can be used. L-Gel’s estimated cost of \$1 (materials only) to treat an area of 1m² (11 ft²; LLNL, 2002) is quite reasonable. Applying L-Gel is simple, so labor costs will not be high.

The disadvantages of L-Gel include: (1) It is not available commercially; (2) The residual salts and silica significantly increase the mass of the waste produced, which may have hazardous properties, depending on what products are formed in the oxidation by Oxone; (3) The efficacy of the product against anthrax spores needs to be tested further to determine whether it meets EPA’s pesticide registration requirements.

4.3.8 Potential Areas for Future Research

L-Gel is being developed along two lines: (1) Penetration into surface coatings to prevent leach-back (L-Gel 200); and (2) Making L-Gel available as an aerosol for decontamination of the interior of ventilation systems. These improvements will be significant advantages for the L-Gel technology.

Minimizing the mass of amorphous silica used to form the gel would be another area with potential benefit for commercializing L-Gel. Research into the ability of L-Gel decontamination wastes to be solidified, such as by silicate or Portland cement stabilization, would be useful for controlling the costs of waste disposal, an important component of the overall cost of the technology.

4.3.9 References for Section 4.3

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5. GAS AND VAPOR TECHNOLOGIES

5.1 Chlorine Dioxide Gas

As a biological sterilizer, chlorine dioxide (ClO_2) reacts as an oxidizing agent. The predominant target of its oxidizing action is thought to be the protein of the bacteria or virus. Oxidation of the protein molecules is thought to lead to functional disruption. Although the exact mechanism of this process is not fully characterized, data exist demonstrating the antimicrobial effects of ClO_2 on many common surfaces. ClO_2 is a relatively unique oxidizing agent in that it functions by single-electron transfer. Unlike chlorine, it does not react with organics to form harmful chlorinated products such as trihalomethane (THM) and chloramines.

Although its name and chemical formulation suggest a close relationship with chlorine gas (Cl_2), this is not the case. ClO_2 gas is not stable under high pressures, and therefore cannot be stored in high-pressure cylinders as most gases are. ClO_2 is readily soluble in water, and is stable for extended periods of time in this form. Unlike chlorine, ClO_2 remains a true gas in solution. This lack of significant interaction with water molecules is partly responsible for the effectiveness of ClO_2 over a wide pH range.

5.1.1 Description of the Technology

Chlorine dioxide gas is generated at the decontamination site (as discussed below), and injected into sealed building areas. It is allowed to remain in place for the required period of time, typically on the order of 12 hours. When treatment is complete, the chlorine dioxide is neutralized, for example, by circulating the building air through a sodium sulfite/bisulfite solution.

Chlorine dioxide gas has been registered as a sterilant under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) since 1988. However, it is not registered for use against anthrax in building applications. Accordingly, EPA needed to grant crisis exemptions for its use in response to the 2001 anthrax events. Site-specific crisis exemptions were issued for each of the four sites that were fumigated with ClO_2 gas – the Hart Senate Office Building (HSOB); the U.S. Postal Service’s mail processing and distribution centers in Washington, DC (“Brentwood”) and Trenton, NJ (“Hamilton”); and the Boca Building in Boca Raton, Florida. Prior to issuance of the first exemption, conditions for chlorine dioxide fumigation were established using a trailer test facility at Brentwood. Based upon the trailer tests and the experience with the initial fumigations, the conditions specified on EPA’s web site (EPA, 2004) for ClO_2 fumigation of a building to treat for anthrax are:

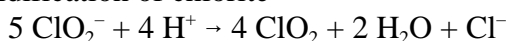
- Target ClO_2 concentration and exposure time: 750 ppm for 12 hours, for a total concentration times time multiple (CT) of 9,000 ppm-hours;
- Minimum temperature: 70 °F (the most recent crisis exemption, for the Trenton facility, specified 75 °F)
- Minimum relative humidity (RH): 65 percent (the most recent exemption specified 75%).

Although the three ClO₂ fumigations indicated above utilized one particular ClO₂ generation technology, the gas could potentially be generated on-site by one of several technologies. Commercial ClO₂ gas generators are available in a range of sizes, although most have not been demonstrated at the scale required to treat a large building. Many of the alternative chemical reactions that are utilized by different vendors to generate ClO₂ gas are illustrated in Section 5.1.2 below (ERCO, 2004).

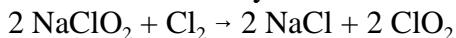
5.1.2 Methods for the Generation of Chlorine Dioxide

ClO₂ from Sodium Chlorite:

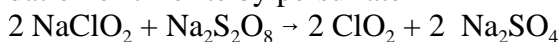
1. Acidification of chlorite



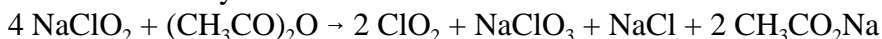
2. Oxidation of chlorite by chlorine



3. Oxidation of chlorite by persulfate



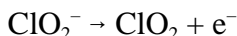
4. Action of acetic anhydride on chlorite



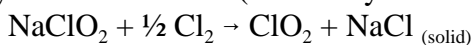
5. Reaction of sodium hypochlorite and sodium chlorite (Sabre Technologies)



6. Electrochemical oxidation of chlorite

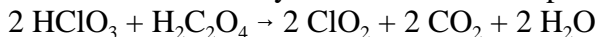


7. Dry chlorine/chlorite (laboratory method)



ClO₂ from Sodium Chlorate:

8. Reduction of chlorates by acidification in the presence of oxalic acid



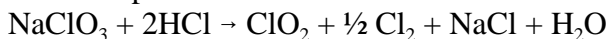
9. Reduction of chlorates by sulfur dioxide (Mathieson Process)



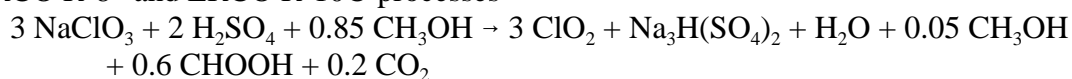
10. ERCO R-2[®] and ERCO R-3[®] processes



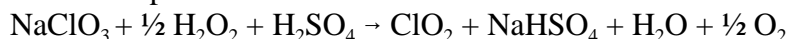
11. ERCO R-5[®] process



12. ERCO R-8[®] and ERCO R-10[®] processes



13. ERCO R-11[®] process



In all of the above reactions ClO_2 gas is one of the products generated from one of the two parent compounds, chlorite (ClO_2^-) or chlorate (ClO_3^-). The selection of a particular process is determined by what materials are available, what side products are useful to the specific industry, and the need for efficiency of the process. Individual manufacturers also have their favorite processes and will adapt them to the situational need.

There are two basic concerns when choosing a synthesis method for chlorine dioxide. These are the amount of gas needed and the safety concerns of the precursors and byproducts. The electrochemical generation of chlorine dioxide from a ClO_2^- salt (Equation 6 above) presents the fewest safety concerns. Systems are commercially available that can generate from two to fifty pounds of gas per day.

Larger quantities can be generated by both “wet” and “dry” processes. The dry process passes chlorine gas through a solid bed of NaClO_2 , thereby generating pure chlorine dioxide gas. There are two concerns with this process. The first is the transportation and storage of chlorine gas. Some manufacturers dilute the chlorine in nitrogen for safety reasons. The second concern is the possible “channeling” of chlorine gas through the solid bed resulting in the release of chlorine gas.

The wet process used for the HSOB, Brentwood, and Hamilton reacted hydrochloric acid and sodium hypochlorite to generate chlorine gas, followed immediately by reaction of the chlorine gas with a solution of sodium chlorite to produce ClO_2 (effectively, Equation 5 above).

The last two processes are frequently used in commercial applications. The chemical reactions between the chlorine and chlorite in the two processes are chemically identical. The “gas:solid” process (as termed by CDG technologies) – Equation 7 above – does not use liquids. The Sabre Technologies approach employs a two-step process within a single reactor (Equation 5), using the chemicals in water. These reactions are presented in more detail in Table 5.1-2 later in this report.

All three of the above processes, when operated properly, are claimed by the vendor to generate pure chlorine dioxide gas without contaminating chlorine gas. The systems are all designed not to have impurities in the product, allowing for accurate comparisons of the different usages of the gas produced. By-products of the reactions remain in either the solid or liquid phases of the reaction.

5.1.3 Applications for Chlorine Dioxide

Chlorine dioxide was first discovered in the early 1800s by Sir Humphrey Davy, who reported the reaction of sulfuric acid with potassium chlorate (Davy, 1811). The gas exists in air as a yellow-green gas with a molecular weight of 67.5.

The vast majority of applications of chlorine dioxide utilize the gas dissolved in water. Wood pulp bleaching is the largest use of chlorine dioxide, accounting for an estimated 95 percent of the chemical's production. ClO_2 was used for water odor problems at Niagara Falls in the 1940s (McCarthy, 1945). This first successful application led to its use in other water treatment facilities. The widespread use of ClO_2 for water purification developed later as a result of studies in the 1970s that linked chlorine, the preferred disinfectant of the time, with cancer (Alavanja et al., 1980; Cantor, 1997; Page et al., 1976). The cancer causing effect of chlorine was linked to the formation of THM as a disinfection by-product (Roe, 1976). Researchers had previously conducted comparisons between ClO_2 and chlorine, and determined ClO_2 to be quite effective for water purification without the generation of harmful by-products found with chlorine (Synan et al., 1975; Bernard et al., 1976a and 1976b; Ridenour and Armbruster, 1949).

Chlorine dioxide is used to treat drinking water in approximately 5 percent of the water treatment facilities in the United States serving more than 100,000 people (ASTDR, 2004). However, throughout Europe, chlorine dioxide is commonly used as a disinfectant in distribution systems (ERCO, 2004). In drinking water supplies, chlorine dioxide is utilized as a primary or secondary disinfectant, for taste and odor control, total trihalomethane/ haloacetic acid (TTHM/HAA) reduction, iron and manganese control, color removal, sulfide and phenol destruction, and Zebra mussel control. Aqueous solutions of chlorine dioxide will release gaseous chlorine dioxide into the atmosphere above the solution. Some newer generators produce a continuous supply of dilute gaseous chlorine dioxide in the range of 100 to 1,000 mm Hg (abs) instead of using an aqueous solution. Aqueous solutions in the range of 0.1– 0.5 percent are common in a number of current generation technologies used in potable water treatment processes (EPA, 1999). As in the pulp and paper industry, chlorine dioxide is preferred over chlorine in some instances due to a reduced formation of chlorinated organic compounds. These results led to the EPA's suggestion in 1983 to use ClO_2 as an effective disinfectant. Partially as a result of these actions, the number of applications to use ClO_2 for water purification grew to 200-300 in the U.S. and thousands in Europe (Aieta and Berg, 1986).

While the initial commercial use for ClO_2 was water purification, the utility of this gas expanded. ClO_2 is now used in the paper processing industry (Balcer, 1981), fruit and vegetable processing industries (Anon, 1977; Costilow et al., 1984), and the dairy (Oliver et al., 1989), poultry (Baran et al., 1973; Lillard, 1979; Thiessen et al., 1984), and beef (Emsweiler et al., 1976) industries. ClO_2 is not as reactive as chlorine and therefore is more stable in wastewater environments because it has fewer reactive targets in solution. As a result, it is also used in industrial waste processing facilities (EPA, 1979; Rauh, 1979; Freymark and Rauh, 1978).

The gaseous form of chlorine dioxide is the form most frequently employed as a fumigant. Chlorine dioxide gas was registered by the EPA as an antimicrobial sterilant in the 1980s. It is

registered for sterilizing manufacturing and laboratory equipment, environmental surfaces, tools, and clean rooms. It is also used in pharmaceutical research and production. Another use of chlorine dioxide gas is in the washing of fruit and vegetables. Published research studies indicate that chlorine dioxide gas can effectively kill *Listeria monocytogenes* cells on apple skins and reduce bacteria in the stem cavity and in the calyx (Du et al., 2002). Liquid chlorine dioxide formulations were registered in the 1960's as a disinfectant. It is used in this manner on pets and farm animals, in bottling plants, and in food processing, handling and storage plants. Other industrial uses of chlorine dioxide gas and liquid formulations include: bleaching textiles, disinfecting flume water, disinfecting meat and poultry, disinfecting food processing equipment, sanitizing water, controlling odors, and treating medicinal wastes.

Whether aqueous or gaseous in form, chlorine dioxide is produced at the point of application. Due to its instability, chlorine dioxide is not transported in pure form as a compressed gas. Instead, it is generated from sodium chlorite or sodium chlorate (solid or aqueous materials that are easily transported and stored), according to one of the reactions in Section 5.1.2 above. Gaseous chlorine dioxide is explosive at concentrations above 10% by volume in air (10 kPa, or 76 mm Hg, partial pressure at 1 atmosphere total pressure). Chlorine dioxide solutions are normally stored cold at concentrations of less than 10g/L in order to keep the concentration of gaseous chlorine dioxide above the aqueous solutions below the explosive limit. These solutions are corrosive to the skin and eyes, and must be handled with adequate ventilation. Protective equipment required for the handling and application of chlorine dioxide include impervious clothing, neoprene gloves and boots, gas-tight chemical splash goggles and face shields, and other appropriate clothing to prevent the contact of skin with aqueous solutions or vapor. NIOSH/OHSA-approved respiratory protection is required for chlorine dioxide concentrations above 0.1 ppm. Self-contained breathing apparatus is required for entry and escape, and in firefighting, when ClO₂ concentrations are above 10 ppm or are unknown (Kirk-Othmer, 1993).

The application of gaseous chlorine dioxide for building contamination was demonstrated in the remediation of the Hart Senate Office Building (HSOB), the Brentwood Mail Processing and Distribution Center (P&DC), and the Trenton P&DC following the 2001 release of anthrax spores through the mail.

5.1.4 Evaluation of Available Data

5.1.4.1 Data from laboratory and trailer testing

Testing by the pharmaceutical industry

Prior to the 2001 anthrax mail attacks, the pharmaceutical industry conducted extensive testing of ClO₂ for its toxic effect on bacteria, viruses and spores in pharmaceutical sterilization applications.

In one such test program, the Sterilization Science and Technology section of Johnson & Johnson tested the efficiency of ClO₂ for the destruction of bacterial spores. These experiments were conducted under controlled laboratory conditions using a 316-liter research sterilizer. The

results presented in Table 5.1-1 were conducted using inlet gas pre-humidified to 70-85 percent RH and an operating temperature of 30-32 °C, with the targets for decontamination being spore strips containing 10⁶ spores of *B. subtilis*.

Table 5.1-1. Effect of ClO₂ Gas Concentration on the Rate of Inactivation of 10⁶ *B. subtilis* Spores on Paper Strips^a

Exposure Time (Minutes)	Fraction Nonsterile ^b		
	10 mg/L (3,000 ppm)	20 mg/L (6,000 ppm)	40 mg/L (12,000 ppm)
0	NT	20/20	19/20
15	NT	19/20	1/20
30	20/20	4/20	0/20
60	9/20	0/60	0/20
90	3/60	NT	NT
180	0/20	NT	NT
240	0/20	0/20	NT

^a The paper spore strips were placed next to the foil suture package and then overwrapped with Tyvek/Mylar.

^b NT = not tested

Based upon these data, the following were the minimal concentration-time (CT) values determined to be required for complete sterilization of the spore strips at three ClO₂ concentrations, where CT is the concentration of ClO₂ gas in ppm multiplied by the duration of exposure in hours.

- 3 hours x 3,000 ppm = CT value of 9,000;
- 1 hour x 6,000 ppm = CT value of 6,000; and
- 0.5 hours x 12,000 ppm = CT value of 6,000.

Following these initial experiments, the Johnson & Johnson scientists postulated that the same gas could be employed utilizing a flexible-wall barrier isolation system. The scientists conducted geometry testing using indicator strips located at various regions within the chamber and concluded that within “reasonable limits”, a ClO₂ gas generation system is unaffected by the size or location of targets within the structure.

The Johnson & Johnson researchers also concluded that ClO₂ did not appear to leave a residue on the sterilized surface, as is observed with some other gaseous sterilants. Not only is the residue non-observable, but the gas itself breaks down very rapidly. Beginning with a concentration of 3,000 ppm at start, there was only 2 ppm remaining at 15 minutes and less than 0.5 ppm after 30 minutes. While this is a benefit for removal of ClO₂ from a system after sterilization is completed, it also clearly points to the need for a robust system that can generate the gas at the required amounts for the required time during the sterilization process. This effect becomes increasingly more important as larger structures are used.

EPA-Sponsored Evaluations of ClO₂ for Anthrax Decontamination – Testing at Dugway

Chlorine dioxide fumigation was one of the remediation steps selected to decontaminate some of the buildings impacted by the anthrax-containing letters that were introduced into the U.S. mail system in October 2001. To help determine the appropriate ClO₂ fumigation conditions for treating treat *B. anthracis*, to be incorporated into the crisis exemptions for treatment of these facilities, EPA's Regional Office in Denver, Colorado – in cooperation with EPA's Office of Pesticide Programs (which is responsible for issuing the crisis exemption) – contracted the West Desert Test Facility at Dugway Proving Ground to test the effects of ClO₂ on a variety of dried *Bacillus* spores:

- BAA – *Bacillus anthracis* var. *ames*,
- BAV – *Bacillus anthracis* var. *vollum*,
- BAS – *Bacillus anthracis* var. *sterne*,
- BGN – *Bacillus subtilis* var. *niger*,
- BT – *Bacillus thuringiensis*, and
- BST – *Bacillus stearothermophilus*.

The data discussed and illustrated below were excerpted from West Dugway Test Center, 2002.

For these tests, spores from three strains of *Bacillus anthracis* (BA) and three BA simulants were dried on either glass slides or porous filter paper and exposed to chlorine dioxide gas for 1, 2, 4, 6, 8, and 12 hours at different relative humidities (30 to 92 percent). Temperature was not specifically controlled; discussions with the Dugway team indicated that they operated at ambient temperatures (70-75 °F).

Spore preparations were cultured and a liquid slurry was applied to either porous filter paper or glass slides and dried. Triplicate slides or filter paper were removed from the sterilization chamber at specific intervals and cultured to determine presence of viable spores. Experiments were conducted at various chlorine dioxide concentrations as well as various relative humidity values.

The Dugway team noted that – at ClO₂ concentrations between 125 and 1,050 ppm – the relative humidity is very important for killing all three strains of BA spores. The authors recommend a relative humidity of greater than 70 percent for effective spore killing activity.

The authors stated that the spores dried on the glass slides were more resistant to the remediation. This is understandable, since the spores are known to clump when wet and most likely provided a level of insulation for spores farther away from the air interface. The spore preparations on the filter papers were not subjected to analysis because the majority demonstrated a six-log kill after only one hour under most conditions. It is important to note that the filter paper preparations were most like the conditions at the HSOB. The spore preparation in the envelope received at HSOB was reported to be very dry. It is possible that some spore clumping occurred in regions where sampling was conducted, but this was likely minimal.

Another interesting finding from the Dugway report is that their data using spores of *Bacillus subtilis* var. *niger* were sufficiently variable such that these data could not be included in the analysis. *B. subtilis* v. *niger* is the same strain often used on the spore strips that are utilized in the field to validate the chlorine dioxide remediation.

Figure 5.1-1 presents Trial 11 of the Dugway testing. This figure indicates that, at 30 percent RH, a modest concentration of ClO₂ has no measurable effect on viability of any spore type tested. Figure 5.1-2 presents Trial 9 – also at 30 percent RH, but at a much higher concentration of ClO₂ (1,050 ppm) – there is still no significant loss of viability over time for any of the organisms, *except* for the BGN spores. These data support the authors’ conclusion that BGN may be the most susceptible spore tested against ClO₂. However, the Dugway tests were only a range-finding study, using only three spore strips or carriers per run. As a result, this analysis of BGN’s relative susceptibility is not statistically definitive.

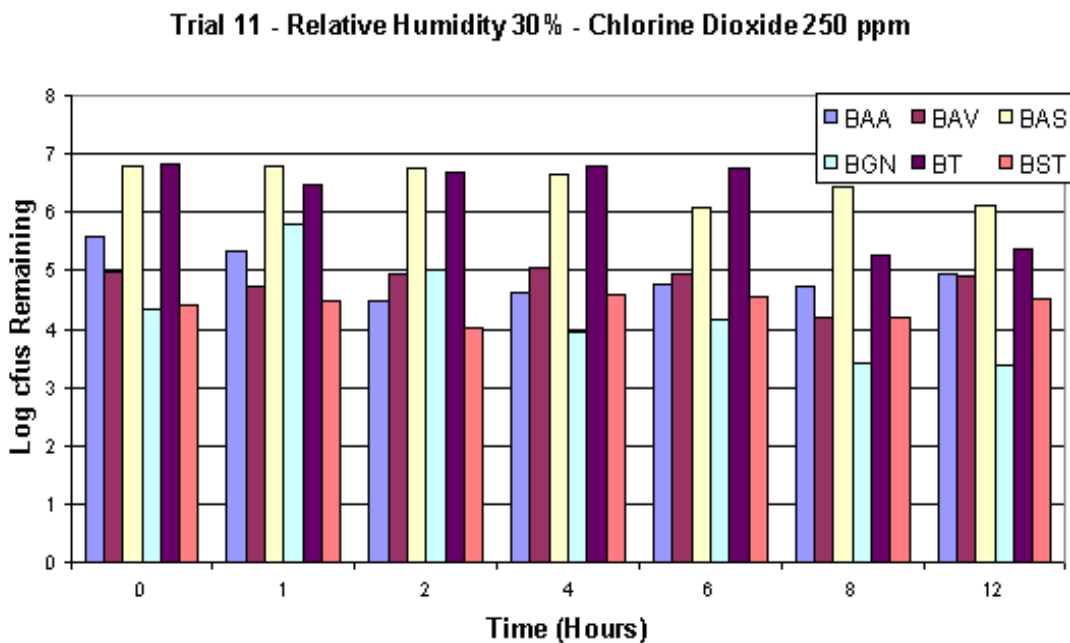


Figure 5.1-1. Log of Colony Forming Units (cfus) Remaining at Each Time Point for Trial 11; Laboratory Validation of Chlorine Dioxide Decontamination

NOTE: BAA – *Bacillus anthracis* var. *ames*, BAV – *Bacillus anthracis* var. *vollum*, BAS – *Bacillus anthracis* var. *sterne*, BGN – *Bacillus subtilis* var. *niger*, BT – *Bacillus thuringiensis*, BST – *Bacillus stearothermophilus*.

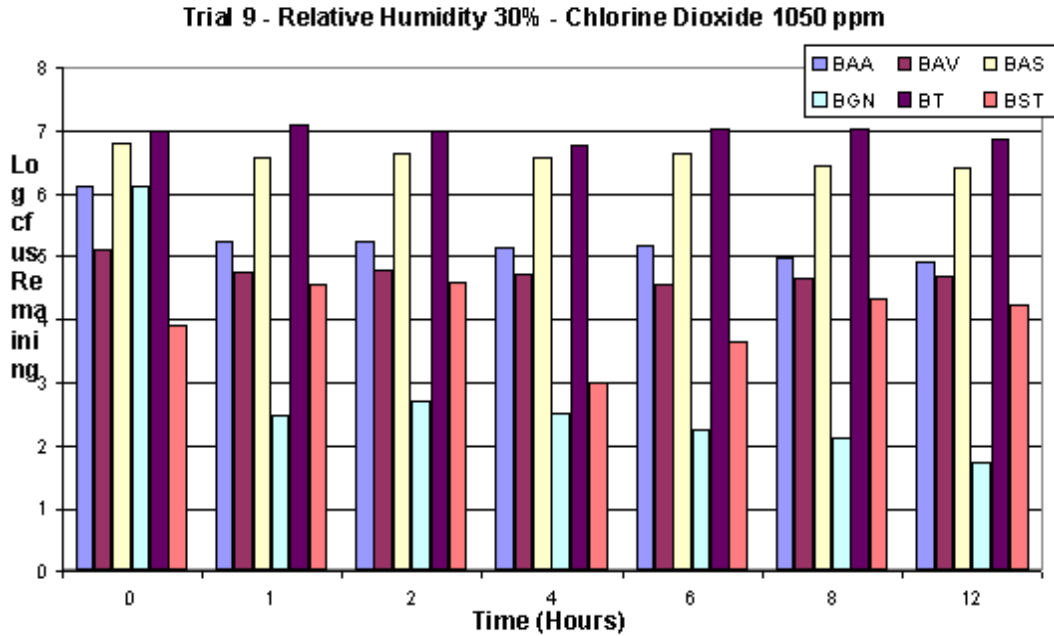


Figure 5.1-2. Log of Colony Forming Units (cfus) Remaining at Each Time Point for Trial 9; Laboratory Validation of Chlorine Dioxide Decontamination

NOTE: BAA – *Bacillus anthracis* var. *ames*, BAV – *Bacillus anthracis* var. *vollum*, BAS – *Bacillus anthracis* var. *sterne*, BGN – *Bacillus subtilis* var. *niger*, BT – *Bacillus thuringiensis*, BST – *Bacillus stearothermophilus*.

Figure 5.1-3 presents Trial 5, which utilized an intermediate concentration of ClO₂, 613 ppm, at 60 percent RH. Even at this higher RH value and at a moderate concentration of ClO₂, still only BGN was susceptible to the gas. These data support the conclusion that an RH above 60% is needed for ClO₂ to be effective in this application.

Figure 5.1-4 presents Trial 1, which utilized an intermediate concentration of ClO₂, 650 ppm, at a still higher RH of 75 percent. Under these conditions, the BGN was again most susceptible, although the other organisms are now also showing clear susceptibility. No viable spores were observed of any organism after 12-hour incubation. These conditions correlate to a CT value of 7,500 ppm-hr.

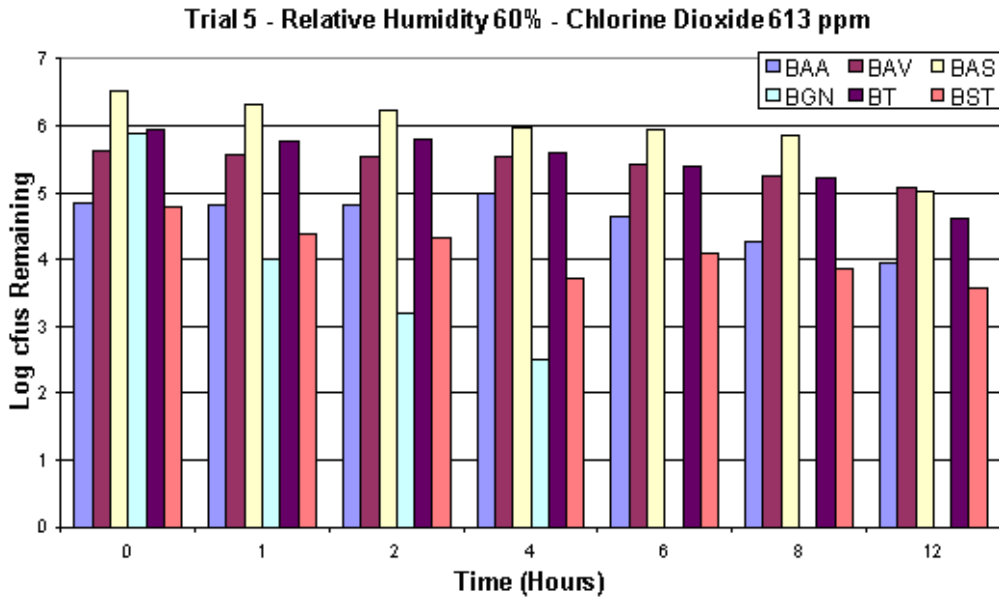


Figure 5.1-3. Log of Colony Forming Units (cfus) Remaining at Each Time Point for Trial 5; Laboratory Validation of Chlorine Dioxide Decontamination

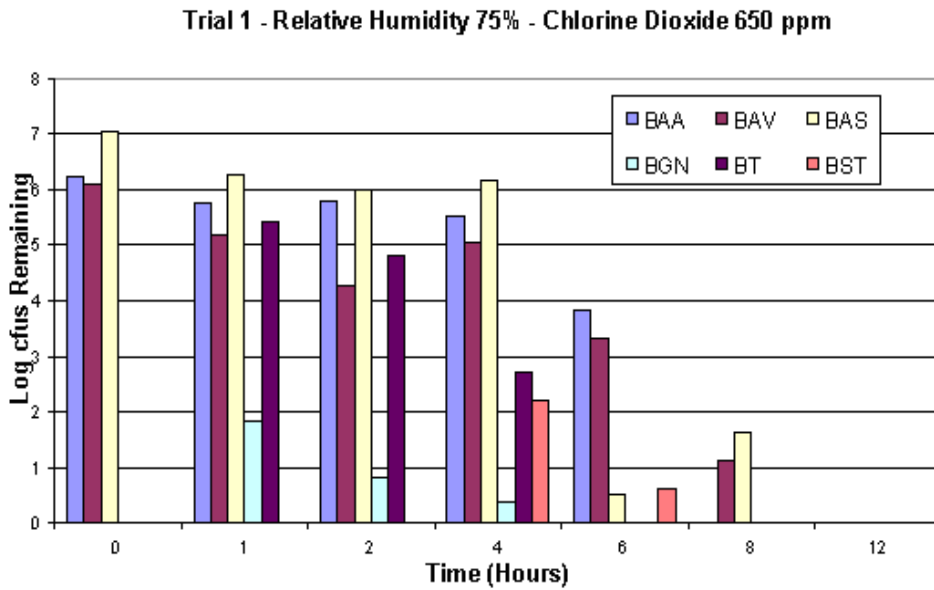


Figure 5.1-4. Log of Colony Forming Units (cfus) Remaining at Each Time Point for Trial 1; Laboratory Validation of Chlorine Dioxide Decontamination

NOTE: BAA – *Bacillus anthracis* var. *ames*, BAV – *Bacillus anthracis* var. *vollum*, BAS – *Bacillus anthracis* var. *sterne*, BGN – *Bacillus subtilis* var. *niger*, BT – *Bacillus thuringiensis*, BST – *Bacillus stearothermophilus*.

Figure 5.1-5 clearly identifies relative humidity as the most critical parameter for the ability of ClO₂ to kill *Bacillus* spores. At a relatively low concentration of ClO₂, 250 ppm, and at a 90 percent RH, there were essentially no viable spores of any type remaining after two hours of exposure. These conditions were more than twice as effective as the data with a RH of 75 percent and a greater than two-fold increase in ClO₂ concentration.

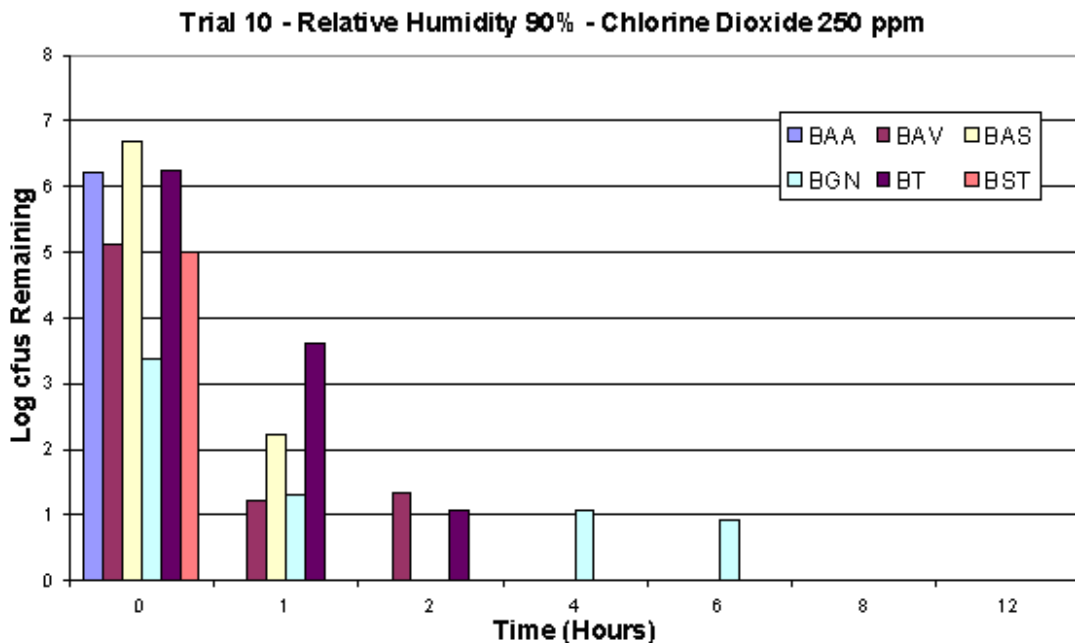


Figure 5.1-5. Log of Colony Forming Units (cfus) Remaining at Each Time Point for Trial 10; Laboratory Validation of Chlorine Dioxide Decontamination

NOTE: BAA – *Bacillus anthracis* var. *ames*, BAV – *Bacillus anthracis* var. *vollum*, BAS – *Bacillus anthracis* var. *sterne*, BGN – *Bacillus subtilis* var. *niger*, BT – *Bacillus thuringiensis*, BST – *Bacillus stearothermophilus*.

These experiments conducted at Dugway Proving Grounds clearly demonstrate the importance of relative humidity, time and ClO₂ concentration for the killing of dried *Bacillus* spores. The Dugway testing was not completed in time to help define the concentration, time, and RH to be specified in the crisis exemption allowing ClO₂ fumigation during remediation of the HSOB. However, these data validated the values selected for the HSOB fumigation, and have supported the conditions specified for subsequent fumigations.

The data presented above were for spores dried on glass slides. The scientists also conducted parallel experiments using the same spore slurry dried on filter paper. The spores on the filter paper possibly had a greater exposed surface area, since they were adhering to the three-dimensional fiber matrix of the paper. The data obtained from the filter paper indicated almost 100 percent killing of all spore types within one hour under almost all experimental conditions. It was suggested that the higher kill rate on the paper might be due to the potential ability of the

gas to penetrate the paper from both sides, whereas the spores applied to glass slides could be attacked only from one side. Another possibility is that clumping of the spores may have been more likely on the glass slides, where the high-concentration spore slurry would have resided in a pool as the liquid dried; the clumps could have been more resistant to the ClO₂.

EPA-Sponsored Evaluations of ClO₂ for Anthrax Decontamination – Washington, DC, Test Trailer

Since the Dugway testing could not be completed before the decisions had to be made regarding ClO₂ fumigation conditions for the HSOB, a brief series of tests was conducted in the Washington, DC, area to help define these conditions.

The tests utilized a trailer-mounted Sabre Technologies ClO₂ generator, piped to fumigate an adjacent empty truck trailer (Schaudies et al., 2003). Spore strips and Steri-charts containing three *B. anthracis* surrogates – *B. subtilis*, *B. stearothermophilus*, and *B. thuringiensis* – were placed inside the trailer. The average ClO₂ concentration to which the indicators were exposed was varied between 200 and 2,300 ppm over the series of 12-hour runs, giving CT values ranging from 2,000 to 28,000 ppm-hr. The average relative humidity inside the trailer was varied between 65 and 79% for different runs. The average temperature inside the trailer was held at 75 to 78 °F. Prior, preliminary lab tests conducted by DoD's Defense Advanced Research Products Agency (DARPA) had suggested that a CT above 4,000 ppm-hr, an RH above 75%, and a temperature above 75 °F would be preferred; the range of conditions for these trailer tests were selected on that basis.

Based on the results of these tests – and subsequent analysis – it was decided that the target ClO₂ fumigation concentration should be 750 ppm for 12 hr (CT = 9,000 ppm-hr), and that the RH and temperature should be “as high as possible” (Schaudies et al., 2003). Of the three spores tested, *B. subtilis* was the most susceptible to the ClO₂ gas.

EPA-Sponsored Evaluations of ClO₂ for Anthrax Decontamination – Beltsville Maryland

After fumigation of the HSOB, EPA conducted a series of seven fumigations in a trailer at the U.S. Department of Agriculture's (USDA) Agricultural Research Center in Beltsville, MD to decontaminate U.S. mail and private carrier packages transferred from the P Street Warehouse, as well as artifacts, critical items (items determined to be too important for destruction), and other items that were not treated with ethylene oxide sterilization. The two photographs in Figure 5.1-6a and 5.1-6b illustrate the chlorine dioxide generation system and the interior set up at the Beltsville remediation facility.

The first six runs were conducted between March 22 and March 28, 2002. The seventh run was conducted on April 10 and 11, 2002. The target exposure concentration was 1,000 ppm for 9 hours in runs one through six. In the seventh run, the target ClO₂ concentration was 450 ppm for a longer exposure time of 20 hours. Uncontaminated packaging materials were included in the



Figure 5.1-6a. Chlorine Dioxide Generation System at Beltsville, MD



5.1-6b. Interior Operations at ClO₂ Test Facility at Beltsville

last run to determine the penetration efficiency and other effects of ClO₂ on various materials. The target temperature for all runs was approximately 80 °F, with a target relative humidity of 80-85 percent. Actual measurements were taken for all three parameters at frequent intervals during each run and are presented and discussed below.

Spore strips were used to assess the effectiveness of the fumigations. As with other fumigations, *B. subtilis* and *B. stearothermophilus* were used. A combination of spore strips and Steri-charts were placed in 30 designated sampling locations in the treatment trailer during each run. The effectiveness of each fumigation was assessed using a total of 255 spore strips. Each array consisted of a negative control strip, three *B. subtilis* spore strips and one *B. stearothermophilus* spore strip. Steri-charts were included at half of the sampling locations, along with an additional negative control strip. Spore strips were in a Tyvek sleeve and all samples were handled with powder-free, sterile, nitrile gloves and alcohol-sterilized tweezers to prevent cross-contamination. Each spore strip included a location code and a unique identification number. Positive controls from each Steri-chart were used to assess viability of the spores on the test strips. Therefore, they were removed and placed in a pre-labeled key envelope prior to positioning of the charts and were never exposed to ClO₂ gas.

Sporicidal efficiency was calculated for each individual run for each of the two indicator organisms. The use of the steri-chart strips allowed for quantification of kill efficiencies of up to 10⁸ for *B. subtilis* and 10⁷ for *B. stearothermophilus*. Fractional exponents were calculated based on the raw data. In some cases there was positive growth at 10⁶ with both higher concentrations being growth negative. This could be the result of clumping on the spore strip, or handling and/or laboratory error. If the sample was subsequently analyzed by culture and the resultant organisms were not the indicator species, the culture data were considered growth negative. There were no cases in which growth of the target organism occurred after exposure to the lower concentrations of chlorine dioxide fumigant.

Two Beltsville 3D bar graphs were generated illustrating five factors: relative humidity, temperature, concentration of chlorine dioxide integrated over time (CT), log kill rate, and organism type (Figure 5.1-7, *B. subtilis*, and Figure 5.1-8, *B. stearothermophilus*). The graphs were generated from data in the table inserts shown on the figures. The graphs present kill rate, concentration of chlorine dioxide integrated over time (CT), and percent relative humidity (percent RH) on three axes. The fumigation temperatures are color coded in incremental ranges from <75.1 °F (blue) to >85 °F (red). The organisms are identified with different patterns on the bars of the graph. *B. subtilis* has vertical lines and *B. stearothermophilus* has horizontal lines. The same scaling was used on the axes of the two graphs to allow for easier comparison.

Temperature and Relative Humidity Data. Temperature and relative humidity values were calculated by taking the average of the readings for each data run from two machines, Model No. 8762, for the “Black” version (Serial No.: 01120527) and the “Grey” version (Serial No: 01120217). The temperature and humidity values used ranged from the time of initial treatment of ClO₂ to the final reading. After the average was obtained for each machine, an average of the two values was taken for the final temperature and relative humidity value listed for each test run.

Concentration Data. Concentration values were calculated by taking the average of the final concentration readings of the four sample locations for each test run.

B. subtilis var. *niger* was originally selected as a surrogate organism, because of its unique property of producing an orange color on agar growth plates. This makes the identification of this particular strain relatively easy in a subsequent culture analysis.

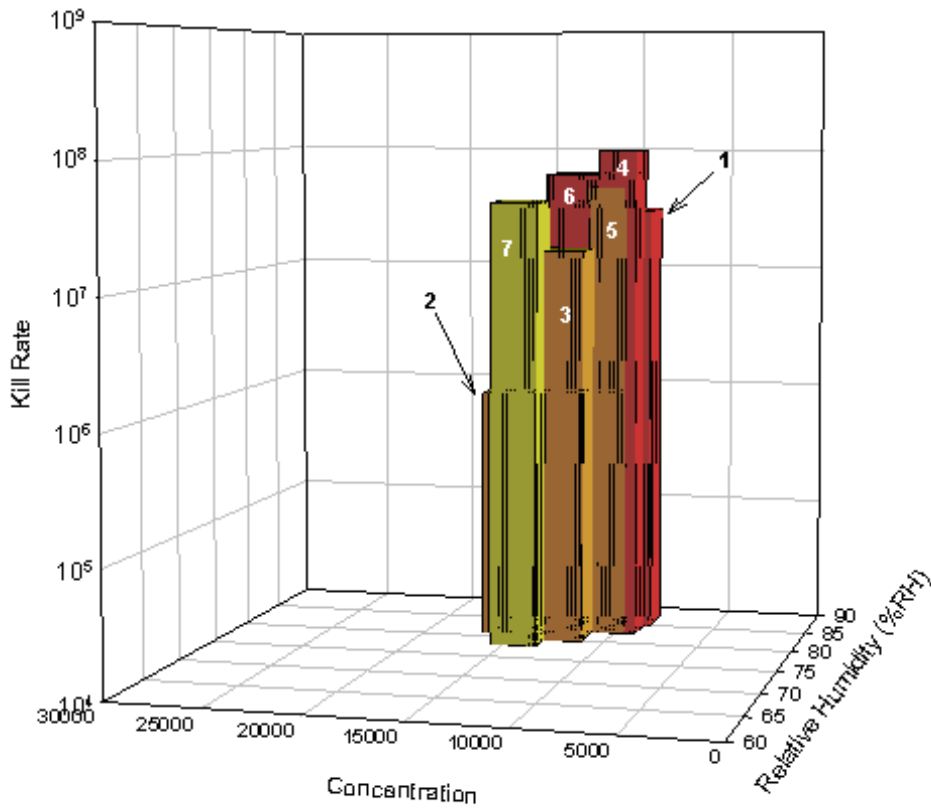
Run #1

The first run resulted in a chlorine dioxide CT value of 9,920 over a 9.7-hour period with an average concentration of 1022 ppm/hr. The average temperature was 85.7 °F with an average RH of 86 percent. All of these values were within the target range. The kill rate for *B. subtilis* was 10^{7.5} and the kill rate for *B. stearothermophilus* was 10⁶. These results were consistent with earlier data in which the killing efficiency for *B. subtilis* was generally an order of magnitude greater than that achieved for *B. stearothermophilus* under identical conditions.

Run #2

The second run resulted in a relatively high chlorine dioxide CT value of 15,345 over a 12-hour period with an average concentration of 1,278 ppm/hr. The average temperature was 82.4 °F with an average RH of 85 percent. All of these values were within the target range. The kill rate for *B. subtilis* was 10⁶ and the kill rate for *B. stearothermophilus* was also 10⁶. These results were inconsistent with earlier data in which the killing efficiency for *B. subtilis* was generally an order of magnitude greater than that achieved for *B. stearothermophilus* under identical conditions.

B. subtilis
RH vs. CT vs. Kill Rate



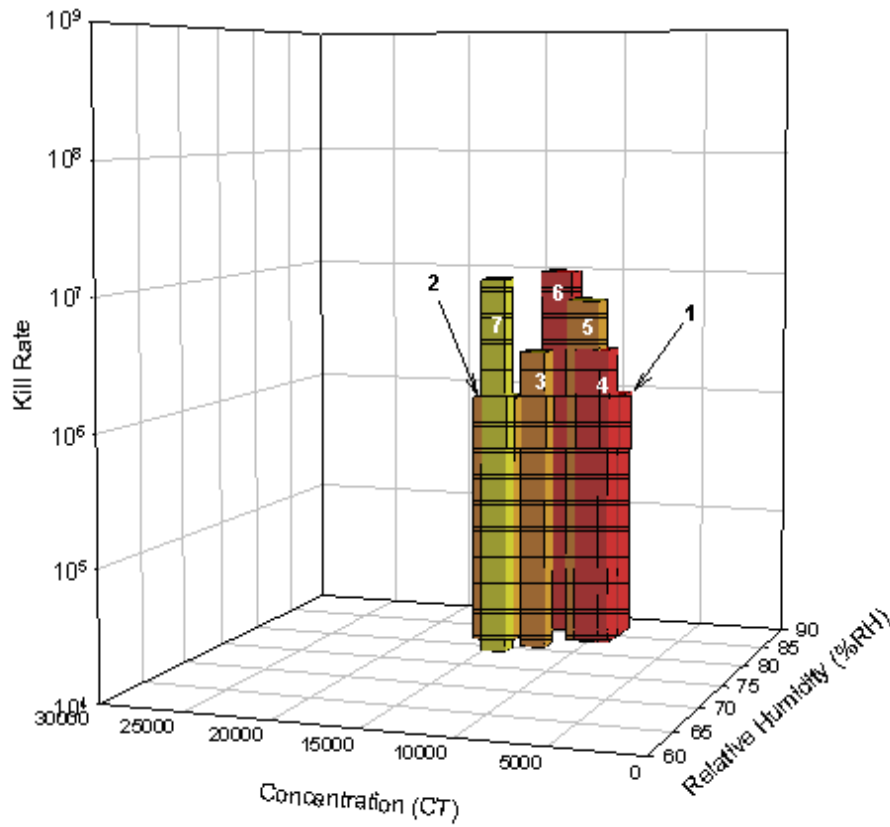
Beltsville—*B. subtilis*

Test Run	%RH	Temp (°F)	CT	Kill Rate	Run Duration (hours)	CT/Hour
1	86.0	85.7	9,920	10 ^{7.5}	9.7	1022
2	82.4	84.6	15,345	10 ⁶	12.0	1278
3	81.1	84.4	12,578	10 ^{7.2}	9.0	1397
4	83.8	85.7	9,772	10 ⁸	7.7	1269
5	83.8	84.1	10,325	10 ^{7.7}	8.0	1290
6	86.3	87.4	12,722	10 ^{7.8}	9.0	1413
7	79.3	80.2	14,374	10 ^{7.6}	21.0	684

Temp Range	Color Key
<75.1	Blue
75.1-77.5	Cyan
77.6-80.0	Green
80.1-82.5	Yellow
82.6-85.0	Orange
>85.0	Red

Figure 5.1-7. Beltsville data for *Bacillus subtilis* spore strip analysis at various conditions

B. stearothermophilus
RH vs. CT vs. Kill Rate



Beltsville—*B. stearothermophilus*

Test Run	%RH	Temp (°F)	CT	Kill Rate	Run Duration (hours)	CT/Hour
1	86.0	85.7	9,920	10 ⁶	9.7	1022
2	82.4	84.6	15,345	10 ⁶	12.0	1278
3	81.1	84.4	12,578	10 ^{6.4}	9.0	1397
4	83.8	85.7	9,772	10 ^{6.4}	7.7	1269
5	83.8	84.1	10,325	10 ^{6.8}	8.0	1290
6	86.3	87.4	12,722	10 ⁷	9.0	1413
7	79.3	80.2	14,374	10 ⁷	21.0	684

Temp Range	Color Key
<75.1	Blue
75.1-77.5	Cyan
77.6-80.0	Green
80.1-82.5	Yellow
82.6-85.0	Orange
>85.0	Red

Figure 5.1-8. Beltsville data for *Bacillus stearothermophilus* spore strip analysis at various conditions.

The efficiency in killing of *B. stearothermophilus* during the second run at the Beltsville location is analogous to the results from Run 1. The efficiency of killing *B. subtilis* was notably low in the second run. The temperature and humidity were within the target range. The CT value was actually 50 percent higher than the target level. The elevated chlorine dioxide concentration would lead one to predict a better killing efficiency based on previous data. In fact, the killing efficiency was six logs, but this was still below all other runs. Upon careful evaluation of the spore strip analysis, a potential explanation is evident. On this run the spore strips appear to be grouped by type and number of organisms rather than by location. For all other runs the spore strips were analyzed in groupings by location rather than by type. Stated in another way, spore strips containing the same amount of a particular bacterial spore were processed together. As a result of this organization, the spore strips containing 10^7 and 10^8 spores were processed at the end of the run. All of the last 21 samples prior to the positive controls demonstrated growth, including a negative control that was also positive.

An artifact in the strip processing may have created this large cluster of positive cultures. With the available data, it is impossible to determine the source of the contamination. None of these positive cultures was analyzed to determine if the bacteria were the same bacteria as present on the original spore strip.

Run #3

The third run resulted in a chlorine dioxide CT value of 12,578 over a 9-hour period with an average concentration of 1,397 ppm/hr. The average temperature was 84.4 °F with an average RH of 81 percent. All of these values were within the target range. The kill rate for *B. subtilis* was $10^{7.2}$ and the kill rate for *B. stearothermophilus* was $10^{6.4}$. These results were consistent with earlier data in which the killing efficiency for *B. subtilis* was generally an order of magnitude greater than that achieved for *B. stearothermophilus* under identical conditions.

Overall, runs 1-3 had the lowest killing efficiencies for both target organisms.

Run #4

The fourth run resulted in a chlorine dioxide CT value of 9,722 over a 7.7-hour period with an average concentration of 1,269 ppm/hr. The average temperature was 83.8 °F with an average RH of 86 percent. All of these values were within the target range. The kill rate for *B. subtilis* was 10^8 and the kill rate for *B. stearothermophilus* was $10^{6.4}$. These results were consistent with earlier data in which the killing efficiency for *B. subtilis* was generally an order of magnitude greater than that achieved for *B. stearothermophilus* under identical conditions.

While this run had the lowest CT value, it had the most effective kill rate for *B. subtilis*. The killing efficiency for *B. stearothermophilus* was also high, but not the highest in the series. The high temperature and relative humidity may have been responsible for the enhanced performance.

Run #5

The fifth run resulted in a chlorine dioxide CT value of 10,325 over an 8-hour period with an average concentration of 1,290 ppm/h. The average temperature was 84.1 °F with an average

RH of 84 percent. All of these values were within the target range. The kill rate for *B. subtilis* was $10^{7.7}$ and the kill rate for *B. stearothermophilus* was $10^{6.8}$. These results were consistent with earlier data in which the killing efficiency for *B. subtilis* was generally an order of magnitude greater than that achieved for *B. stearothermophilus* under identical conditions.

The operating conditions for runs 4 and 5 are essentially identical and the killing efficiency in the two runs is not notably different. Thus, the results may illustrate the range of values that can be expected under nearly identical conditions.

Run #6

The sixth run resulted in a chlorine dioxide CT value of 12,722 over a 9-hour period with an average concentration of 1,413 ppm/hr. The average temperature was 86.3 °F with an average RH of 87 percent. All of these values were within the target range. The kill rate for *B. subtilis* was $10^{7.8}$ and the kill rate for *B. stearothermophilus* was 10^7 . These results were consistent with earlier data in which the killing efficiency for *B. subtilis* was generally an order of magnitude greater than that achieved for *B. stearothermophilus* under identical conditions.

This run demonstrates among the highest killing effect for both indicator organisms. It may be important to note that this run has the highest temperature and relative humidity of all the runs.

Run #7

The seventh and final run resulted in a chlorine dioxide CT value of 14,374 over a 21-hour period with an average concentration of 684 ppm/hr. The an average temperature was 80.2 °F with an average RH of 79.3 percent. All of these values were within the target range. The kill rate for *B. subtilis* was $10^{7.6}$ and the kill rate for *B. stearothermophilus* was 10^7 . These results were consistent with earlier data in which the killing efficiency for *B. subtilis* was generally an order of magnitude greater than that achieved for *B. stearothermophilus* under identical conditions.

This final run was unique in numerous aspects. While it had the second highest overall CT value, the actual chlorine dioxide concentration within the enclosure was almost one-half of the concentrations of the previous six runs. In addition, this run had the lowest temperature and relative humidity values. Even with these lower temperatures and absolute chlorine dioxide concentrations, the killing efficiency was equivalent to the most effective kills measured in other runs. Although this is a single experiment, the data are clearly consistent with the concept that it is the overall chlorine dioxide exposures (concentration times exposure time), not the absolute ClO_2 concentration, that most significantly determines spore killing capability.

Summary of Beltsville Operations

The operational parameters of chlorine dioxide concentration, time of exposure, temperature and relative humidity chosen for the fumigation runs at Beltsville were all successful in achieving a minimum of a six log kill of the indicator organisms in a reproducible fashion. Although data from Washington, DC area and the HSOB indicated the importance of humidity and temperature, there was not an observable temperature or humidity enhancement in the

operational ranges tested at Beltsville. In fact, one of the best kill rates was obtained at the lowest temperature and relative humidity. This final run also employed a significantly lower absolute concentration of chlorine dioxide, but with an increased exposure time resulting in an increased final CT value. These conditions also resulted in an excellent killing efficiency.

Comparisons Between Different Operations

The data presented above represent chlorine dioxide generated via the three methods mentioned previously. The Johnson and Johnson experiments used gas generated as a result of passing dilute chlorine gas through a packed bed of flaked NaClO_2 . The Dugway report used the electrolysis system, and the Washington DC area EPA data were generated by the solution method by Sabre Technologies. All of the systems are believed to have generated fairly pure chlorine dioxide. While all of the systems demonstrate that the chlorine dioxide is capable of killing bacterial spores, the results do vary. It is possible that this variability is due to differences in temperature and humidity for the different experimental conditions. Uncertainty exists because the specific temperature and humidity measurements were not provided. Johnson and Johnson gave a humidity range of 75-90 percent relative humidity and the Dugway test did not present temperature data. The data that are presented are very compelling that chlorine dioxide is an effective agent for killing of spores if used correctly.

Materials Compatibility and Residue

Chlorine is known to react with an extensive variety of compounds, primarily through oxidation reactions, but it also participates in addition and substitution reactions (EPA, 1981). ClO_2 has a much more limited reactivity towards organics (Rav-Acha, 1984; Masschelein, 1980) and as such remains available as a biocide even in relatively dirty environments.

The bleaching effect of the gas is more apparent in synthetic rather than natural fibers. Most paints are relatively unaffected by the gas, but photographic emulsions are susceptible to bleaching as illustrated in Figure 5.1-9.

Figure 5.1-9 illustrates the effect of ClO_2 on two separate types of photograph color images. The small strip was not exposed to ClO_2 , the bottom portions were exposed to 700 ppm ClO_2 for 10 hours at 75 °F at 75 percent relative humidity. This experiment was conducted by the U.S. EPA Emergency Response Team at a Washington D.C. test trailer in November 2001.



Figure 5.1-9. Bleaching Effect on Photographic Materials

Chlorine dioxide is a strong oxidizer but does not chlorinate organic compounds or amines the way that chlorine gas does. Chlorine dioxide might penetrate into some materials – such as porous materials, plastics, and rubbers – resulting in an "off-gassing" period. For example, a video cassette tape exposed to 500 ppm of chlorine dioxide for eight hours still had a distinctive odor three weeks after exposure (personal communication: R. Paul Schaudies). An added advantage of chlorine dioxide over other gas sterilants, such as paraformaldehyde, is that it leaves no visible residue.

5.1.4.2 Experience with field fumigation of buildings

Experience at the Hart Senate Office Building

On October 15, 2001, an anthrax-containing letter was received in Senator Daschle's suite in the Hart Senate Office Building (HSOB). A second such letter, to Senator Leahy, was stopped in the mail processing system after the Daschle letter was received, and was discovered before it could be delivered. The letter to Senator Daschle resulted in significant contamination of the suite itself by anthrax spores. Spores were also drawn into the return ducting of the air handling system serving the suite (and adjoining suites), and were transported to some other HSOB suites and common areas by building air movement or occupant activities. Spores were also found in mail handling facilities in the HSOB and in other nearby Government buildings, resulting from the processing of the Daschle or Leahy letters, or of other letters that had been cross-contaminated by those two. Collectively, the buildings near Capitol Hill that were impacted by these two letters are referred to as the Capitol Hill Anthrax Site.

As was to become the pattern in subsequent building anthrax remediations, initial remediation activities included sealing of the HSOB to prevent further spread of the spores. Environmental sampling was conducted to define the extent of the contamination, demonstrating high levels of contamination in multiple areas within the Daschle suite, and lesser levels of contamination in the return ductwork of the air handling system and in other HSOB suites and common areas. Lesser levels of contamination were also found in the affected mail facilities within the Capitol Hill Anthrax Site.

EPA evaluated a number of alternative decontaminating agents for treatment of the Capitol Hill Site, including various liquids, foams, gels, and gaseous sterilants. Based upon evaluation by an interagency committee of advisors, it was decided to use a gaseous sterilant as a central component of the remediation strategy. For various reasons, including its penetrability, chlorine dioxide was selected as the gaseous fumigant. Initially, EPA considered fumigation of the entire HSOB (about 10 million cubic feet of volume). But ultimately, a tiered approach was settled upon, wherein the initial fumigation would address only the Daschle suite (93,000 ft³) – the most highly contaminated area. A decision regarding how to treat any other areas would be made based upon further environmental sampling, and the experience in the Daschle suite.

Using this approach, it was ultimately decided that – in addition to the Daschle suite itself – the one other space to be fumigated with ClO₂ would be the return ductwork for the air handler (3,000 ft³). All of the other areas in the HSOB, and other affected buildings, were decontaminated using various topical treatments (in particular, with aqueous ClO₂ or sodium hypochlorite).

This was the first time that gaseous ClO₂ sterilization had been utilized in microbial decontamination of a building.

Prior to the HSOB fumigation, all available experimental data had been obtained under controlled laboratory conditions in sealed chambers that would fit within a single room of the lab building. While mathematical calculations appeared to support the feasibility of the ClO₂ fumigation approach for the remediation of large buildings, such large-scale field fumigation using ClO₂ had not previously been attempted. As discussed in Section 5.1.4.1, in preparation for the HSOB remediation, EPA conducted testing in a trailer in Washington, DC, and initiated controlled laboratory experiments at Dugway Proving Ground, to help define the appropriate fumigation conditions for this new application.

The field experiments in the Washington, DC, trailer suggested that ClO₂ fumigation with a CT of 9,000 ppm-hr (750 ppm for 12 hr), with a temperature above 75 degrees Fahrenheit, and with a relative humidity above 75 percent, would provide a six-log kill of *Bacillus anthracis* spores. These conditions were consistent with prior laboratory results.

The first step in the fumigation process was to seal the area to be fumigated, to contain the fumigant (as well as to prevent the anthrax spores from being transferred into other areas of the building or outdoors). Comprehensive sealing of Senator Daschle's suite was achieved using heavy plastic sheeting around the suite's interior perimeter, to isolate it from the remainder of the building. Exterior windows were covered and sealed with light-blocking material, to isolate the suite from outdoors, and also to prevent UV radiation from entering the space, since sunlight causes decomposition of ClO₂. Other openings through the exterior shell were also sealed.

Relative to the fumigation activities at most of the subsequent remediation sites, the extent of source reduction in the Daschle suite prior to fumigation was modest. Except in the area immediately around where the anthrax-containing letter was opened, few building materials or furnishings were removed. Ceiling tiles, carpeting, furniture, etc., were largely left in place for decontamination by the fumigant. The exception was that selected valuable artifacts and critical items were removed for off-site treatment in an ethylene oxide gas sterilization chamber. Also, paper items were removed from surfaces, drawers, and cabinets, and sent either to an off-site ethylene oxide sterilization chamber, or to a medical waste incinerator. Topical cleaning of suite surfaces prior to fumigation – using liquid agents (such as aqueous ClO₂ or bleach), or vacuuming using a high-efficiency particulate air (HEPA) filter – was limited, with the expectation that the gaseous ClO₂ fumigation would adequately sterilize all surfaces.

Chlorine dioxide was generated using the Sabre Oxidation Technologies process. This system utilizes Equation 5 in Section 5.1.2. Sodium hypochlorite (bleach) solution is first reacted with HCl to produce chlorine gas (Cl₂), followed immediately by reaction of this chlorine with sodium chlorite solution to produce the ClO₂ in aqueous solution. The presence of free chlorine is minimized or avoided by utilizing excess sodium chlorite.

The trailer-mounted ClO₂ generator and its ancillary equipment was located outside the Hart Building, at street level below the suite. The aqueous ClO₂ solution was pumped up to the suite through exterior piping, and then passed through air strippers inside the suite to release the gaseous ClO₂ into the sealed space.

Prior to the introduction of ClO₂ during fumigation, the RH and temperature in the suite were first raised to the target values ($\geq 75\%$, ≥ 75 °F) by 12 heaters and humidifiers placed within the space (Schaudies, 2003). Maintenance of the high relative humidity proved to be an operational challenge in this initial application of this technology to building fumigation, revealing the humidification capacity required for this purpose. Following the humidification phase, feed of aqueous ClO₂ solution to the air strippers was initiated (the “conditioning” phase). The “CT clock” for the fumigation was started after the ClO₂ concentration in the space reached the desired level.

In an effort to achieve uniform mixing of the ClO₂, the steam, and the heated air throughout the suite, nine box-type mixing fans were operated during the fumigation process.

Gas samples for analysis were taken at 16 locations throughout the suite on 10- to 15-minute intervals, to verify whether ClO₂ concentrations were holding at the required level, and whether the required CT of 9,000 ppm-hr was being achieved. The results showed that the average CT throughout the suite during the fumigation period exceeded the minimum (averaging 9,600 ppm-hr in one part of the suite, and 10,900 ppm-hr in the other part), although there were individual sampling locations where the CT dropped below the target value (as low as 6,000 ppm-hr at one location) (Schaudies and Robinson, 2003).

Also, temperature and RH probes were installed at a number of locations throughout the suite to allow the heaters and humidifiers to be adjusted to maintain the objectives of ≥ 75 °F and $\geq 75\%$ RH. Unfortunately, these probes failed to function during the fumigation due to an electrical problem, and the temperature and RH measurements had to be made manually by staff inside the space. The temperatures generally met the target, ranging between 72 and 77 °F. The RH met the target in one part of the suite (ranging between 83 and 89%), but fell below the target in the other part (ranging between 57 and 75%).

Throughout the fumigation process, EPA’s Environmental Response Team (ERT) monitored the ambient air in the area around the HSOB using a mobile monitoring van, to confirm that hazardous amounts of ClO₂ gas were not escaping into the environment. A maximum ambient concentration of 25 ppb was detected over a very short time period; 100 ppb would have been required to shut down the generator. In addition, stationary air monitors placed in the area surrounding the HSOB did not measure significant levels of ClO₂ during the fumigation.

After the suite had been fumigated, the residual ClO₂ gas in the suite was removed by circulating the suite air through a scrubbing solution. This was accomplished by switching the liquid in the in-suite air strippers from aqueous ClO₂ to the scrubbing solution, thus converting them from ClO₂ emitters into scrubbers. Natural decay of the ClO₂ hastened the removal process.

Following EPA's issuance of a crisis exemption under FIFRA for the use of gaseous ClO₂ in this application, the fumigation of Senator Daschle's suite took place over a period ending on December 2, 2001. The effectiveness of the fumigation was determined in two ways:

1. Spore strips containing surrogates for the anthrax (*Bacillus anthracis*) spores. Over 3,000 spore strips containing *B. subtilis*, *B. cereus*, *B. thuringiensis*, and *B. stearothermophilus* spores were distributed around the suite – attached to walls, floors, and furniture, and placed under desks. The spore strips were positioned to verify whether a sufficient concentration of ClO₂ had been maintained for a sufficient time and at a sufficient relative humidity at each location in the suite to kill the surrogate spores on the strip.
2. Environmental sampling to verify whether any surviving *B. anthracis* spores remained at the sampling location. Environmental sampling methods included: surface sampling, using wet wipe and vacuum techniques; and aggressive air sampling, i.e., high-volume sampling of the suite air after room surfaces had been agitated (blown) in an effort to re-suspend any spores that might have been present.

The results from a number of the spore strips were positive, indicating that the concentration-time-RH-temperature conditions at some locations may not have been sufficient to kill all of the surrogate spores on the strip. Subsequent testing suggested that some of these apparent positives may have been due to secondary contamination of the spore strips at various points in the process: a) during the fumigation, when entries were made into the suite; b) during the post-fumigation collection and handling of the strips; and c) during analysis in the laboratory.

The results of the environmental sampling, performed after removal of the spore strips, indicated a highly significant reduction in contamination of the suite. However, a small percentage of the samples were positive for the growth of *B. anthracis* spores. Therefore, surface cleaning with aqueous chlorine dioxide was then performed in the suite. (As discussed under Section 3.2.4 of this report, EPA had issued a crisis exemption under FIFRA, allowing the use of aqueous ClO₂ against anthrax in this application.)

Following application of the topical aqueous solution, the final environmental samples in the suite were all negative for growth of anthrax spores.

As indicated previously, the return ducting and filter in the air handling system serving the Daschle suite had also tested positive for anthrax spores, and was fumigated with ClO₂. The filter was removed. The return ductwork from the Daschle suite – which connected to the returns from other suites that had not been impacted – was isolated from these other returns. Feed lines from the ClO₂ gas generator and the steam generator were connected into the return duct in the suite, and an exhaust fan was connected at the other end of the return ducting (i.e., by the air handler, several stories above the suite). The ducting was fumigated by using an exhaust fan to draw ClO₂ gas and steam through the contaminated section of return ducting. The ClO₂-containing outlet from the exhaust fan was designed to pass through a scrubber to remove the ClO₂ before being released.

Chlorine dioxide concentrations were measured at nine sampling locations throughout the ductwork and air handling system, and temperature and RH probes were installed at seven locations, to verify whether the concentration and environmental targets were met. Also, a total of 440 surrogate spore strips were suspended in the air stream at 11 locations within the air handling system to help assess fumigation efficacy.

Unfortunately, the first attempt at fumigating the return duct was unsuccessful due to difficulties in maintaining the required fumigation conditions. As a result, some spore strips showed incomplete kills of the surrogates. Some sections of the ductwork were wiped with aqueous ClO₂ solution, and the ducting was fumigated for a second time on December 28-31, 2001.

Subsequent environmental sampling showed no growth of anthrax spores in any of the samples. The HSOB was cleared for re-occupancy and re-opened on January 22, 2002.

Experience at the USPS Brentwood Processing and Distribution Center (Curseen-Morris)

The letters to Senators Daschle and Leahy, containing weapons-grade *B. anthracis* spores, were processed through the U. S. Postal Service's Brentwood Processing and Distribution Center (P&DC) in Washington, D.C. This facility was the primary Federal mail processing center for the Washington area. Some of the very fine spores escaped from the envelopes as they passed through the high-speed sorting machine on Line 17 and other postal equipment. The contamination was spread in large part through the operation of the mail equipment, and through the routine use of compressed air to clean the machines of dust and debris. The Brentwood P&DC was closed on October 22, 2001, after four workers at Brentwood developed inhalational anthrax. Environmental measurements to determine the extent of the contamination revealed the greatest number of positive samples at Line 17 and at the two adjacent mail sorting machines, Lines 16 and 18.

The lessons learned at the HSOB were valuable in guiding the Postal Service's efforts for remediation of the Brentwood P&DC.

The building was tightly sealed, to prevent *B. anthracis* spores from migrating from the facility prior to remediation. This sealing also served to prevent the large volume of ClO₂ gas that would be inside this building during fumigation from escaping out into the adjoining neighborhoods. And it served to prevent outside light from entering the building during fumigation, since ClO₂ gas decays quickly in the presence of UV light. In general, plywood or foam board was attached over exterior windows, doors, and other large openings in the exterior shell, with caulking and duct tape to ensure a good seal. Unintended openings in the building shell – e.g., seams between the roofing and the exterior wall – were caulked.

The initial remedial efforts at Brentwood included a series of source reduction steps and spot decontamination efforts (Princiotta, 2003; Canter, 2004). A significant amount of porous and non-porous material was treated with bleach, then packaged within the facility and taken off-site for disposal as infectious waste. Materials thus treated and removed included, for example, some ceiling tiles; carpeting was generally left in place. Some other materials, such as non-porous postal carts and other rolling stock, were decontaminated with bleach in accordance with

the crisis exemption granted by EPA for the use of this aqueous product, and then sent to other postal facilities for re-use. Surface cleaning of mail sorting machines with bleach was also conducted.

Following topical bleach treatment of Lines 16, 17, and 18, additional environmental sampling was performed. This sampling continued to show *B. anthracis* contamination, but at lesser levels.

Lines 16, 17, and 18 were then enclosed in a tent of plastic sheeting, and fumigated with gaseous ClO_2 in July 2002. As at HSOB, the selected fumigation conditions inside the tent were specified as: ClO_2 concentration ≥ 750 ppm; exposure time 12 hours; RH $\geq 75\%$; and temperature ≥ 75 °F. Surrogate spore strips were used to estimate the efficiency of this fumigation. Greater than 99% of the spore strips were negative for growth of spores following the fumigation.

Following this focused treatment of the most contaminated areas, the entire building was fumigated with a gaseous sterilant. In view of the experience at HSOB, it was again decided to use ClO_2 as the fumigant. However, in this case – rather than treating only selected sections of the building, as had been possible with Senator Daschle’s suite – the decision was made at Brentwood to fumigate the entire building (the entire 14 million cubic feet) at one time. This decision was based on the widespread contamination within the Brentwood facility, and the open nature of most of the facility.

The Sabre Oxidation Technologies process was again utilized to generate the ClO_2 gas for the fumigation, as it had been at the HSOB. However, because the Brentwood facility had 150 times the volume of the Daschle suite, the trailer-mounted gas generator used as HSOB was no longer adequate. A new, larger gas generator was built for this purpose. Also, more substantial ancillary equipment was required generate the steam needed for humidity control, to provide the quantities of NaOCl, HCl, and NaClO_2 needed to generate the required amount of ClO_2 , to distribute the aqueous ClO_2 throughout the building and air-strip it inside the building, to provide the quantities of Na_2HSO_3 and NaOH needed to generate the Na_2SO_3 required to scrub the ClO_2 gas from the building, and to handle the liquid wastes generated. (The chemistry involved with the Sabre process was discussed previously in connection with the HSOB remediation.)

As in the case of the HSOB fumigation, the objective was to maintain the building at a ClO_2 concentration at 750 ppm or above for 12 hours (for a total CT of at least 9,000 ppm-hr), at a relative humidity greater than 75% and a temperature of 80 °F.

At Brentwood, two large exhaust fans (referred to as “negative air units”, or NAUs) were used to maintain the entire building at negative pressure throughout the fumigation, to prevent escape of the ClO_2 into the ambient air. The objective was to control operation of the NAUs such that the average pressure across the building shell at the five most positive pressure measurement points was at least -0.02 inches of water (i.e., that the interior averaged at least 0.02 in. lower in pressure than the outdoors). The ClO_2 -containing exhausts from these two NAUs were passed through HEPA filters, sodium sulfite scrubbers, and carbon sorption beds (which served as a

polishing step for ClO₂-removal, and as back-up in the event of scrubber failure). The objective was to reduce the ClO₂ concentration in the NAU exhausts to 5 ppm or less.

Modeling calculations showed that – if the NAUs failed to maintain negative pressure in the building – the resulting leakage of high-ClO₂ building air into the ambient could theoretically result in ambient ClO₂ concentrations of 1 ppm half a mile from the site. While this is below the level considered Immediately Dangerous to Life and Health (5 ppm), it is above the OSHA/ACGIH 15-minute standard of 0.3 ppm, and underscores the importance of proper functioning of the NAUs.

In view of these concerns, three tests were conducted on one of the NAUs prior to fumigation. The test objectives were to ensure that the sodium sulfite scrubber would function effectively during the full-scale fumigation, and that the carbon bed alone had the capability to maintain the exhaust below 5 ppm in the event of a catastrophic failure of the scrubber. Following improvements to the scrubbers and the carbon beds based upon these tests, the concentration objectives were successfully achieved.

Following the modifications of the NAU scrubbers and carbon beds, a practice run was conducted at low ClO₂ concentration to confirm that all systems were functioning properly. This test demonstrated that a several-hundred-ppm ClO₂ concentration could be maintained throughout the building for several hours, that the NAUs could achieve and maintain negative air pressure inside the building, and that NAU exhaust concentrations could be maintained below 5 ppm. Based upon the results of this low-level run, EPA issued a crisis exemption under FIFRA to enable the full fumigation to proceed. The fumigation was successfully completed on December 14-15, 2002.

Throughout the fumigation process, EPA's Environmental Response Team (ERT) monitored the ambient air in the area around the HSOB using a mobile monitoring van, sampling for ClO₂. Measurements were also made at the Brentwood fence-line, and on the building itself. To protect the adjoining neighborhoods, the generator was to be shut down if ambient levels of ClO₂ were at or above 100 ppb for two consecutive 15-minute sampling periods at any of these ambient monitoring stations. The ambient concentration never reached 100 ppb.

As at HSOB, the success of the fumigation at Brentwood was determined through: 1) surrogate spore strips throughout the building, to verify that fumigation conditions had in fact been maintained adequately to kill surrogate spores; and 2) environmental samples taken after fumigation, including both surface sampling and aggressive air sampling. The U.S. Postal Service final report indicated that greater than 98% of the spore strips showed complete kills of the surrogate spores, and that all environmental samples were negative for growth of *B. anthracis* spores. Based on these results, the Environmental Clearance Committee recommended in September 2003 that the facility (now named the Curseen-Morris P&DC) was safe for re-occupancy.

Experience at the USPS Hamilton Processing and Distribution Center (Trenton, NJ)

Anthrax-containing letters to the New York Post and to the NBC-TV network offices in New York City were processed through the Hamilton P&DC on September 18, 2001. The two letters to Senators Daschle and Leahy were also processed through Hamilton on October 9, 2001. After five workers at Hamilton were diagnosed with cutaneous or inhalational anthrax, the facility was closed on October 18, 2001.

Hamilton has a volume of about 6 million cubic feet, less than half the size of the Brentwood facility. The decision was made that – as with Brentwood – a central component of the Hamilton remediation would be ClO₂ fumigation of the entire building at one time, using the Sabre Oxidation Technologies process. The fumigation process at Hamilton was postponed until after the cleanup at Brentwood was completed, so that the ClO₂ generators and much of the ancillary equipment that had been used at Brentwood could be transported to the Hamilton site and used in this fumigation. A number of refinements were implemented at Hamilton based upon the Brentwood experience.

The extensive experience at the two fumigations at the HSOB and at Brentwood enabled a more efficient remediation at Hamilton.

The building was extensively sealed, with the aid of thermal imaging. Exterior doors and windows were sealed with foam insulation board and layers of plastic sheeting. All openings in the building shell were sealed with silicone caulk (or expanding foam) and tape, including seams around the door and window covers, expansion joints in the exterior walls, utility penetrations through the shell, and gaps where the roof met the walls. Exhaust vents and the building's sewer system were sealed. All HVAC penetrations in the shell – including air intake and exhaust vents – were sealed. The sealing of exterior windows and glass doors serves not only to prevent spores and ClO₂ from escaping into the ambient air, but also prevents UV light from entering the building and increasing the decay rate of the ClO₂.

Significant source reduction activities were conducted at Hamilton prior to fumigation. Critical items (e.g., cash, mail, key files) were packaged and removed for off-site sterilization. Other porous materials were removed for disposal, including carpeting, upholstered furniture, ceiling tiles, some cubicle walls. Such porous materials were treated with modified (pH-neutral) bleach (sodium hypochlorite) prior to packaging and shipment off-site. Frame walls were left in place.

Many surfaces were cleaned by HEPA vacuuming and/or by wipe-down with modified bleach solution. Extensive efforts in this regard were made to clean the mail handling equipment that processed the four anthrax-containing letters. Special focus was placed on those sites within the building where initial environmental sampling had identified a problem, or where employees had been stationed who had contracted either cutaneous or inhalational anthrax. To the extent practical, the HVAC distribution ducting was cleaned with modified bleach, and the existing HVAC mixing boxes removed and replaced. The removed mixing boxes were cut into pieces, cleaned with modified bleach on-site, packaged, and shipped for disposal.

As in the prior fumigations, the target at Hamilton was to maintain at least 750 ppm ClO₂ for a period of 12 hours (for a CT of 9,000 ppm-hr), at an RH at or above 75%, and a temperature at or above 75 °F.

The ClO₂ was generated outside the building by the same dual (primary plus back-up) Sabre reactor system used at Brentwood, reacting aqueous NaOCl with HCl to produce Cl₂, followed instantaneously by reaction of this chlorine with NaClO₂ to produce aqueous ClO₂. The aqueous ClO₂ was pumped to 12 air strippers distributed inside the building, releasing gaseous ClO₂ into the building air. Relative humidity and temperature were controlled by steam from a boiler outside the building. During fumigation, the building was held at negative pressure, to avoid escape of the ClO₂ to the outdoors. This negative pressure was maintained by two large exhaust fans (“negative air units”), which exhausted the ClO₂-containing building air through a sodium sulfite scrubber, with a back-up carbon sorption bed, in order to reduce the stack exhaust concentration to the 1.8 ppm required by permit.

Between 300 and 400 fans, located throughout the building, were utilized in an effort to ensure uniform mixing of the ClO₂ during fumigation. These included 5,000 acfm tube-axial fans and 2,000-5,000 acfm box fans, as well as the building’s ceiling fans. The building’s internal HVAC air handlers were also used to assist in the distribution, in that ClO₂ released by Sabre’s emitters was drawn into the air handlers’ return ducting, and distributed throughout the zone served by each air handler.

The postal machinery inside the building was wired to be operated remotely during the fumigation process, in an effort to ensure that all components of the equipment were exposed to the ClO₂ gas.

Consistent with the fumigations at HSOB and Brentwood, this fumigation was conducted in four steps:

- 1) Humidification, in which steam from the exterior boiler (and, as necessary, heat from the building’s heating system) were used to bring the building up to the required conditions ($\geq 75\%$ RH, ≥ 75 °F). The building had to be held at those conditions throughout for at least one hour before ClO₂ was introduced.
- 2) Conditioning, in which aqueous ClO₂ introduction into the building began, and the indoor concentration was raised to the level at which the CT clock would start running. In this case, the minimum concentration required to start the clock (and to keep it running) was 500 ppm ClO₂ at all monitoring sites in the building, although the target concentration during fumigation was 750 ppm.
- 3) Decontamination, in which the ClO₂ concentration in the building would be maintained above the minimum value (and presumably above the target value) – and the RH and temperature maintained at or above the required values – for the duration necessary to achieve a total CT of at least 9,000 ppm-hr.

- 4) Neutralization, in which the ClO_2 concentrations in the building would be reduced below the OSHA 8-hour Permissible Exposure Limit (PEL) of 0.1 ppm following fumigation. Neutralization of the ClO_2 was achieved by replacing the aqueous ClO_2 flows into the air strippers with sodium sulfite – converting the ClO_2 emitters into scrubbers – and by continued exhausting of the building air through the sodium sulfite scrubbers and carbon beds associated with the negative air units. Natural decay of the ClO_2 also played a role.

Dehumidification is also implemented during the neutralization step, with RH being reduced to avoid mold growth and other moisture-related problems. Dehumidification to about 50% RH was achieved by chilling the sodium sulfite solution being delivered to the emitters-turned-scrubbers, so that these scrubbers would also serve as condensers. Further dehumidification to 20% RH – to ensure drying of all interior surfaces over the following two days – was achieved using silica desiccant dehumidifiers.

Following a series of tests to verify the performance of the negative air units, the building temperature and RH control system, the building air mixing, and the operability of the total system at a low ClO_2 concentration, EPA issued a crisis exemption for this ClO_2 fumigation to proceed. The four-step fumigation process was conducted beginning on October 24, 2003.

Concentrations of ClO_2 were measured using gas samples drawn on an hourly basis from each of 33 sampling locations distributed inside the building. Temperature and RH were monitored continuously at these same 33 locations, and at some additional locations. In accordance with the four-step process above, the CT clock for the fumigation was started at 7 pm on October 24, and continued uninterrupted for 12 hours (until 7 am on October 25), at which time ClO_2 generation was stopped. The total average CT exposure throughout the building during that 12-hour period was about 19,300 ppm-hr (ranging between 15,500 and 21,800 ppm-hr at the various monitoring locations throughout the building), all well above the 9,000 ppm-hr target.

Throughout the Hamilton fumigation process, EPA's Environmental Response Team (ERT) monitored the ambient air in the area around the HSOB using a mobile monitoring van, sampling for ClO_2 and Cl_2 . Measurements were also made at the fence-line, and on the building itself. The ambient concentration never reached the level that would have required generator shut-down. The ClO_2 concentration measured by the ERT remote from the building never exceeded the background level of 3 parts per trillion, well below the level of concern.

As at the other anthrax fumigation sites, the success of the fumigation at Hamilton was determined through: 1) surrogate spore strips throughout the building, to verify that fumigation conditions had in fact been maintained adequately to kill surrogate spores; and 2) environmental samples taken after fumigation, including both surface sampling and aggressive air sampling. Slightly more than one percent of the 4,885 individual spore strips were positive for growth. As a result, additional surface environmental samples were collected at locations where positive spore strips had been found. All environmental samples were negative for anthrax. Based on the totality of results, the Environmental Compliance Committee concluded in February 2004 that the remediation was successful, and recommended that the facility be re-opened.

5.1.5 Concerns for the User

Below is a summary of the Occupational Safety and Health Administration's guidelines for the use and storage of ClO₂. This information was extracted from the following website:

<http://www.osha.gov/SLTC/healthguidelines/chlorinedioxide/recognition.html>.

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chlorine dioxide is 0.1 ppm as an 8-hour time-weighted average (TWA) concentration (29 CFR 1910.1000, Table Z-1). The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limits (RELs) for chlorine dioxide of 0.1 ppm as a TWA for up to a 10-hour workday, and a short-term exposure limit (STEL) of 0.3 ppm. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorine dioxide threshold limit values (TLVs) of 0.1 ppm as a TWA for a normal 8-hour workday and a 40-hour workweek, and a short-term exposure limit (STEL) of 0.3 ppm for periods not to exceed 15 minutes. Exposures at the STEL concentration should not be repeated more than four times a day, and should be separated by intervals of at least 60 minutes.

Exposure to chlorine dioxide can occur through inhalation, ingestion, and contact with the skin or eyes. To limit or control exposure, the following preventative steps should be taken by the user: the area of use should be enclosed; local exhaust ventilation should be utilized; and personal protective equipment should be worn. Chlorine dioxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's Hazard Communication Standard (29 CFR 1910.1200). Containers of chlorine dioxide should be protected from physical damage, ignition sources, and light, and should be stored separately from carbon monoxide, dust, fluoroamines, fluoride, hydrocarbons (e.g., butadiene, ethane, ethylene, methane, propane), hydrogen, mercury, non-metals (phosphorus, sulfur), phosphorus pentachloride-chlorine mixture, platinum, potassium hydroxide, water, or steam. To avoid an explosion hazard, chlorine dioxide should be stored only in diluted forms. Solutions of more than a 10 percent concentration should not be handled. Empty containers of chlorine dioxide should be handled appropriately.

The guidelines provide exposure limits and safety considerations for the use of chlorine dioxide for numerous applications. One might anticipate that, because the gas kills spores, it is also toxic to humans. It is important to note that the concentrations reported as flammable or explosive are orders of magnitude higher than those required for sterilization, and are not achieved in normal operations.

5.1.6 Availability of the Technology for Commercial Applications

There are numerous commercial vendors for the supply of ClO₂. Table 5.1-2 presents data for domestic and foreign manufacturers. While the applications section reflects the information from the company's website, it is fair to conclude that the chlorine dioxide generated by any of these systems could conceivably be utilized for decontamination of bacterial spores in buildings or enclosed spaces. However, some of these technologies have not been tested on a building scale, and it is possible that practical technical or economic considerations could impact the applicability of some of these technologies to building applications.

Table 5.1-2. Vendors for ClO₂

Vendor Name and Address	Contact Info. (Website, Phone, Email)	Products	Chlorine Dioxide Generation Chemistry	Applications
CDG 140 Webster Street Bethlehem, PA	(Tel):(888) 610-2562 (Fax): (610) 974-9721 (Email): info@cdgtechnology.com www.cdgtechnology.com	Bench-scale and plant scale systems available.	$2 \text{NaClO}_2(\text{solid}) + \text{Cl}_2(\text{gas}) \rightarrow 2 \text{NaCl} + 2 \text{ClO}_2(\text{gas})$	Decontamination Waste water Process water Food processing Medical device sterilization
DELUWA GmbH Jakob-Kaiser-Strasse 8 D - 47877 Willich, Germany	http://www.deluwa.de/english/frameone.htm www.deluwa.de www.chlordioxid.de (Tel) +49 (0) 2154 / 48 68 80 (Fax) +49 (0) 2154 / 48 68 98 (email) info@deluwa.de	DELUDOX chlorine dioxide; Dosing stations; ACODOX disinfection systems.	$2 \text{NaClO}_3 + \text{Na}_2\text{S}_2\text{O}_8 \rightarrow 2 \text{ClO}_2 + 2 \text{Na}_2\text{SO}_4$ Reaction conducted in solution German standard EN12671 <i>Chemicals used for treatment of water intended for human consumption - Chlorine dioxide</i>	Destruction of legionella in warm water systems Disinfection of pools and whirlpools Prophylaxis of legionella in therapy basins (Emergency) disinfection of waterworks Sterilization of air, air humidifiers and air duct systems Disinfection of cooling circuits and cooling towers Disinfection for the brewing industry and of ion exchangers Sterilization and cleaning-up of pipes in house installations Deodorization and disinfection of filters in the disposal industry Disinfection of slaughterhouse sewage Disinfection of water tanks Disinfection of Cip-plants Disinfection of dental instruments Decentralized washing of fruit and vegetables Disinfection of tankers for food transport Destruction of salmonella on chicken and eggs Sterilization of containers for spraying/ painting parts (e.g., car parts) Sterilization of cleaning water and bottle rinsing water Sterilization of containers and production pipes Cleaning of empties for the beverage industry

Vendor Name and Address	Contact Info. (Website, Phone, Email)	Products	Chlorine Dioxide Generation Chemistry	Applications
<p>ERCO Worldwide</p> <p>Information Request Coordinator: Sherrie Tack 302 The East Mall, Suite 200 Toronto, Ontario, Canada M9B 6C7</p>	<p>http://www.clo2.com (Tel) 416-239-7111 (Fax) 416-239-8091 (email) info@clo2.com</p>	<p>Chlorine dioxide generators:</p> <ul style="list-style-type: none"> - ERCO R3 - ERCO R3H - ERCO R5 - ERCO R7 - ERCO R8 - ERCO R9 - ERCO R10 - ERCO R11 - ERCO R12 - ERCO R13 	<p>ERCO R-2 and ERCO R-3 processes $\text{NaClO}_3 + \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{ClO}_2 + 1/2 \text{Cl}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$</p> <p>ERCO R-5 process $\text{NaClO}_3 + 2\text{HCl} \rightarrow \text{ClO}_2 + 1/2 \text{Cl}_2 + \text{NaCl} + \text{H}_2\text{O}$</p> <p>ERCO R-8 and ERCO R-10 processes $3 \text{NaClO}_3 + 2 \text{H}_2\text{SO}_4 + 0.85 \text{CH}_3\text{OH} \rightarrow 3 \text{ClO}_2 + \text{Na}_3\text{H}(\text{SO}_4)_2 + \text{H}_2\text{O} + 0.05 \text{CH}_3\text{OH} + 0.6 \text{CHOOH} + 0.2 \text{CO}_2$</p> <p>ERCO R-11 process $\text{NaClO}_3 + 1/2 \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{ClO}_2 + \text{NaHSO}_4 + \text{H}_2\text{O} + 1/2 \text{O}_2$</p>	<p>Generators designed and engineered for pulp mills to meet desired whiteness and strength of the final bleached product</p>
<p>Lenntech Water Treatment and Air Purification Holding B.V.</p> <p>Rotterdamseweg 402 M 2629 HH Delft The Netherlands</p>	<p>http://www.lenntech.com/chlorine_dioxide.htm (Tel) (+31)(0)15 2610900 (Fax) (+31)(0)15 2616289 (email) info@lenntech.com</p>	<p>Stabilized chlorine dioxide</p>	<p>Information requested online</p>	<p>Hot and cold water systems Vegetables washing Biofilm prevention and control Cooling towers Scrubbers Potable water Treating iron bacteria Legionella</p>

Vendor Name and Address	Contact Info. (Website, Phone, Email)	Products	Chlorine Dioxide Generation Chemistry	Applications
PureLine Treatment Systems 25612 Commercenter Drive Lake Forest, CA 92630	http://www.pureline.com (Tel) (949) 716-4615 (Fax) (949) 716-4645 (email) inquiries@pureline.com	Pureline is a water treatment company with electrochemical chlorine dioxide generation systems	Electrochemical process Anode reaction: $\text{ClO}_2^- \rightarrow \text{ClO}_2 + e^-$ Cathode reactions: $\text{H}_2\text{O} + e^- \rightarrow 1/2 \text{H}_2 + \text{OH}^-$ $\text{Na}^+ + \text{OH}^- \rightarrow \text{NaOH}$	Decontamination Waste water Process water Food processing Medical device sterilization
Sabre Technologies Contact: John Mason, President 2642 Marco Avenue, Odessa, TX 79762	http://www.sabretechnologies.com/ (Tel) (209) 482-8199 (Fax) (915) 368-4491 (email) jmason@sabretechnologies.com (email) gkielman@4clo2.com	Generators – Typical 140 – S500-2A – Diklor	Two step solution process $\text{HCl}(15\%) + \text{NaOCl}(5-15\% \text{ avail Cl}) \rightarrow \text{Cl}_2 + \text{NaOH}$ $2 \text{NaClO}_2(25\%) + \text{Cl}_2 \rightarrow 2 \text{NaCl} + 2 \text{ClO}_2$ Undisclosed approach – patent pending	ClO_2 fumigation Bioterrorism response Water Wastewater Industrial wastewater Process water Food processing Well stimulation ClO_2 evaluations
Scotmas Limited Lindsay House Poynder Place Kelso, Borders TD5 7EH Scotland	http://www.chlorine-dioxide.com http://www.scotmas.com (Tel) +44 (0)1573 226901 (Fax) +44 (0)1573 226026 (email) enquiries@scotmas.com	Stabilized ClO_2 – Biox Industrial ClO_2 – Cidox ClO_2 generators – Adox	Proprietary approach	Building services Water treatment Agriculture Food hygiene Industrial Healthcare Formulated products (Website under construction)

Vendor Name and Address	Contact Info. (Website, Phone, Email)	Products	Chlorine Dioxide Generation Chemistry	Applications
Vernagene, Ltd. Units 2 and 3, Waters Meeting Britannia Way Bolton Lancashire BL2 2HH UK	http://www.vernagene.com (Tel) +44 (0) 1204 550820 (Fax) +44 (0) 1204 550821 (email) enquiries@vernagene.com	Stabilized chlorine dioxide: – Purogene (small scale) – Harvest Wash (medium/large scale) – Sanogene (large scale) Chlorine dioxide precursor chemicals; Specialist chlorine dioxide dosing systems; Chlorine dioxide generators; Chlorine dioxide monitoring equipment.	Information requested online	Disinfection of systems and surfaces Food processing aid for vegetable wash waters Speciality applications in fish processing Post-harvest citrus/top fruit/root vegetable/salad washing and storage

5.1.7 Cost for generation of ClO₂

In an effort to obtain some cost data for the generation of gaseous ClO₂, SAIC approached several vendors in an attempt to get a cost estimate for a chlorine dioxide facility having a capacity of 30,000 lb ClO₂/day. This would have been more than adequate to treat the Hamilton P&DC, making reasonable assumptions regarding the ClO₂ decay rate in the building and the building exhaust rate. However, the vendors declined to provide costing information, saying that more information would be required about the envisioned site to permit a meaningful estimate.

5.1.8 Advantages and Disadvantages

All gaseous bioremediation technologies require a gas that is, by definition, reactive. As such, the material is dangerous to living things. Following are disadvantages for the use of ClO₂ in remediation.

1. The gas is unstable and must be constantly replaced to attain the target concentration for the required time.
2. The gas must be generated onsite, and the equipment required to do this can be significant.
3. The killing efficiency decreases significantly at relative humidity levels below 70 percent. Maintenance of humidity is critical.
4. A large volume of liquid waste materials is generated.
5. Some reports from field fumigations suggest that some collateral damage may occur to the surfaces of machinery and electrical systems, resulting from condensation.

The advantages of ClO₂ include:

1. ClO₂ is well documented as a disinfectant for spores, vegetative bacteria and viruses.
2. Rapid natural breakdown of ClO₂ eases its removal after application.
3. The gas is very soluble and stable in water.
4. The gas is effective on porous and non-porous surfaces and reaches all regions within an enclosure except for the hardest to reach, isolated areas (e.g., closed employee lockers).
5. The gas can be commercially generated by several methods.
6. The gas leaves no residue.
7. The gas odor can be detected by humans at a concentration (0.1 ppm) equal to the PEL.

Regarding the potential problem of collateral damage, mentioned above, there have been undocumented reports from some of the field remediation sites that electrical circuit breakers needed to be replaced following ClO₂ fumigation, potentially due to condensation of moisture and aqueous ClO₂ at the high-humidity conditions. Post-fumigation inspections have indicated some collateral damage to machinery, equipment, and materials. No electrical shorts have been observed during fumigation. Collateral damage may be limited in part due to the quick dehumidification of the buildings following fumigation.

5.1.9 Potential Areas for Future Research

Although significant data exist documenting the effectiveness of ClO₂ against spores, bacteria, and viruses, there remain key questions about the combinations of time, concentration, temperature, and relative humidity for effective killing, about the effectiveness of ClO₂ on spores on different surfaces, about which *Bacillus* species should be used as surrogates, and about the performance of ClO₂ generation systems in large buildings. To this end there needs to be a unified method for preparation of bacterial and viral standards for remediation technology validation. The work at Dugway Proving Ground clearly demonstrates that remediation activity is spore preparation and surface dependent. The spore preparations dried on filter paper were significantly more susceptible to the ClO₂ than preparations dried on glass slides. Finally, testing of ClO₂ should be conducted on a field scale for some of the commercially available products to assure that they will perform as intended in large volume structures.

In order to predict the effectiveness of ClO₂ in differing building remediation scenarios, data need to be generated demonstrating the effectiveness against various agents in differing circumstances.

Measurement of ClO₂ levels is important for remediation operations. Inexpensive accurate real-time measurements are needed for routine use of this method for building remediation. Spectrophotometric methods are available, but the equipment is costly. Air impingers are used to partition the gas into water for chemical analysis, but this is time consuming.

A final area that deserves significant attention regarding future research is the use of ClO₂ for the remediation of chemical warfare agents. While it is unlikely that the gas phase of ClO₂ will have an effect on liquefied chemical agents because of limited access of the gas to chemical liquids, chlorine dioxide in solution may be very effective at degrading chemical warfare agents. The gas phase may be effective against the chemical warfare vapor. In addition, it is very likely that ClO₂ in water will be effective at oxidizing reactive chemical agents that are harmful but not considered chemical warfare agents. We are unaware of any testing in this promising research area.

5.1.10 References for Section 5.1

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5.2 Hydrogen Peroxide Vapor

The use of aqueous hydrogen peroxide as a decontaminant has a long history (see Section 3.3 of this report). One of the earliest published records for use of aqueous H_2O_2 is from 1883, when hydrogen peroxide was used as a bactericide to preserve milk (Schrodt, 1883). A comprehensive review of the early uses of aqueous hydrogen peroxide as a disinfectant was published in 1972 (von Bockleman and von Bockleman, 1972). In 1989, the U.S. Environmental Protection Agency (EPA, 2004a) approved the use of vapor-phase hydrogen peroxide as a sterilization process.

5.2.1 Description of the Technology Alternative

A number of hydrogen peroxide vapor generation systems are commercially available for small-scale chamber sterilization of, for example, pharmaceutical equipment. Several of these have been adapted for potential use in the fumigation of larger volumes, applicable to buildings.

In all cases, the hydrogen peroxide vapor is generated from a concentrated aqueous solution of hydrogen peroxide ($\geq 30\%$ H_2O_2). The vapor may be generated by controlled heating of the liquid, in a manner that reduces decomposition of the H_2O_2 . Other methods, such as heated aerosolizers, have been considered. Like other oxidizing fumigants, the peroxide decays with time – at a rate even faster than ClO_2 – and it is thus necessary to continuously supply fresh peroxide into the space at a rate sufficient to maintain the desired concentration. As discussed later, typical H_2O_2 vapor concentrations (e.g., 200 ppm, or about 0.3 mg/L) might require perhaps 2 to 6 hours of contact time to destroy anthrax spores, depending on the substrate. At the end of the operational cycle, the

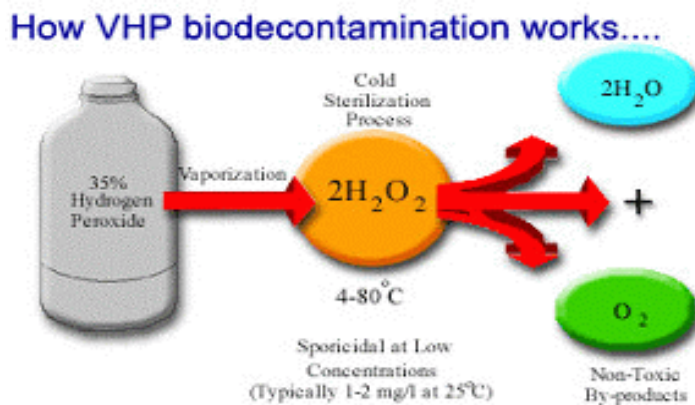


Figure 5.2-1. Chemical Reactions to Generate and Remove Hydrogen Peroxide from the Air
(Source: STERIS Corporation)

H_2O_2 generator is turned off, and hydrogen peroxide vapor is withdrawn from the space and passed over a catalyst (complementing the natural decay) to convert it into water and oxygen, thus leaving no toxic residue (Lauderback et al., 2002). Figure 5.2-1 shows a schematic of the process.

Relative humidity is an important parameter in determining the performance of hydrogen peroxide vapor, although the optimal RH level varies with the specific H_2O_2 process. The STERIS process, discussed below, maintains a low humidity in the space (below 40% RH at the start of fumigation), in an effort to keep the peroxide in the vapor phase for improved penetration of substrate surfaces. By comparison, the BIOQUELL process permits higher RH values, attempting to achieve “micro-condensation” of a thin film of peroxide over the surface to be decontaminated.

5.2.2 Technical Maturity



Figure 5.2-2. The BIOQUELL Clarus C and Claris L Units for hydrogen peroxide vapor generation.

Hydrogen peroxide vapor is well documented in the literature as an effective sterilizer of viruses, fungi, bacteria, and spores in controlled laboratory environments (Block, 2001; Klapes and Vesley, 1990; Kokubo et al., 1998). It has been registered by EPA for use as an antimicrobial pesticide for sterilization of sealed enclosures such as isolators, workstations, and pass-through rooms in commercial, institutional, and industrial settings (EPA, 2004a). The process is commercialized and hydrogen peroxide vapor generation systems are offered as turnkey operations. Hydrogen peroxide vapor is

generated from concentrated aqueous hydrogen peroxide solution (Lauderback et al., 2002). Figures 5.2-2 and 5.2-3 show hydrogen peroxide vapor generation systems that are commercially available from BIOQUELL and STERIS.

The BIOQUELL Clarus C was designed for use in the pharmaceutical industry for the sterilization of filling lines, isolators, and clean rooms. This unit is being considered for adaptation to address building fumigation applications. The smaller unit, Clarus L, is designed for smaller applications such as incubators and equipment sterilization. The hydrogen peroxide product used in BIOQUELL's Clarus C and Clarus L systems is not registered with EPA under FIFRA.

STERIS Corporation is another manufacturer of hydrogen peroxide vapor equipment (referred to as Vaporized Hydrogen Peroxide®, or VHP). Their larger unit, the VHP 1000 (shown in Figure 5.2-3), has been used for decontamination of chambers and enclosed areas for ten years and is applicable for rooms up to 6,000 ft³ in size. The STERIS hydrogen peroxide product has been registered by EPA under FIFRA. In more recent operations, multiple units were combined in a single operation to remediate significantly larger rooms. Scaled-up versions of the VHP 1000 have recently been tested by STERIS, with multiple units being combined to treat volumes up to 200,000 ft³ in actual applications (SAIC, 2003). This represents a significant enhancement in capability.

The STERIS Corporation was contracted to conduct fumigation of the two U.S. Government mail facilities that were contaminated with *Bacillus anthracis* spores via the mail system: the General Services Administration's Building 410 in Washington, D.C. and the U.S. State Department Mail Facility in Sterling, Virginia, (Loudoun County, 2004). The buildings were sectioned into smaller areas (approximately 100,000 to 200,000 ft³ each) and fumigated with the hydrogen peroxide vapor. The experience at the State Department facility is discussed further in Section 5.2.4 of this report.



Figure 5.2-3. The STERIS VHP 1000 Vaporized Hydrogen Peroxide system.

5.2.3 Applications for Hydrogen Peroxide Vapor

Hydrogen peroxide is a strong oxidizing agent with a wide variety of applications. As a dilute aqueous solution (3 percent) it is sold for home use for disinfecting minor cuts and scrapes. More concentrated (10 percent) solutions are used for home hair bleaching treatments. See Section 3.3. The strong oxidizing potential of hydrogen peroxide is highlighted by the incorporation of hydrogen peroxide in ecologically friendly rocket propellants (Lauderback et al., 2002).

Aqueous hydrogen peroxide has been in use for over one hundred years for its ability to kill bacteria (Schrodt, 1883). Specific aqueous H₂O₂ products (including hydrogen peroxide and peroxyacetic acid mixtures) have been registered for indoor use on hard surfaces (e.g., in food establishments, medical facilities, and home bathrooms) since as early as 1977, and have been granted crisis exemptions by EPA for use on hard surfaces for destruction of anthrax spores (EPA, 2004b). Hydrogen peroxide in the vapor form is registered as a pesticide by EPA for use in killing bacterial spores on environmental surfaces within enclosed areas in commercial, institutional, and industrial settings (EPA, 2004a). More recently, H₂O₂ vapor has been granted crisis exemptions for treatment of anthrax spores specifically in the fumigations of GSA Building 410 and the State Department mail annex, mentioned above.

Vaporized hydrogen peroxide generators generally use a 35 percent aqueous hydrogen peroxide solution (Lauderback et al., 2002). The aqueous hydrogen peroxide is vaporized at temperatures of 70-140 °C. In this vaporized form, hydrogen peroxide has been reported to inactivate pathogenic bacteria, yeast, and bacterial spores. The rate of activity of peroxide is sharply increased by heat, ultraviolet light, and ultrasonic energy. There have been promising results from experiments using peroxide vapor for space decontamination of rooms and biologic safety cabinets (Kirk-Othmer, 1993).

Hydrogen peroxide vapor is registered as an antimicrobial pesticide for use in commercial, institutional, and industrial settings, for the decontamination or sterilization of sealed enclosures including scientific workstations, isolators, pass-through rooms, and medical and diagnostic devices (EPA, 2004a). Hydrogen peroxide vapor decontamination technology has been used in the pharmaceutical industry for over ten years. More than 700 hydrogen peroxide vapor systems are used in this industry worldwide, and they have proven to be effective against a variety of microorganisms (STERIS, 2004).

Vaporized hydrogen peroxide is also used in plasma sterilizers. These commercially available sterilizers use hydrogen peroxide and a vacuum as in the standard hydrogen peroxide vapor generators, but also use low pressure plasma. The plasma induces free radicals and ions, enhancing the hydrogen peroxide vapor's effectiveness at killing microbes. Experiments using hydrogen peroxide vapor conducted with and without plasma suggest that the addition of plasma to the equation results in a better, faster decontamination (Sias, 2003). This decontamination technology is used for sterilizing surgical instruments. A patent exists for the use of peroxide vapor and a radio frequency energy generated plasma which releases free radicals, ions, excited atoms, and excited molecules in a sterilizing chamber (U.S. Pat. 4,643,876, 1987, P.T. Jacobs and S.M. Lin) (Kirk-Othmer, 1993). Yet another variation of hydrogen peroxide vapor decontamination technology exists, Binary Ionization Technology (BIT). BIT also uses

hydrogen peroxide and plasma, but it does not require a vacuum environment or containment within a chamber (Sias, 2003).

Although vaporized hydrogen peroxide and hydrogen peroxide plasma technologies have proven to be effective decontamination methods, they did not have widespread acceptance as of 1996. Historically, steam, ethylene oxide, and dry heat have been the preferred methods of sterilization of biomedical devices (Kirk-Othmer, 1997).

5.2.4 Evaluation of Available Data

5.2.4.1 Data from laboratory testing

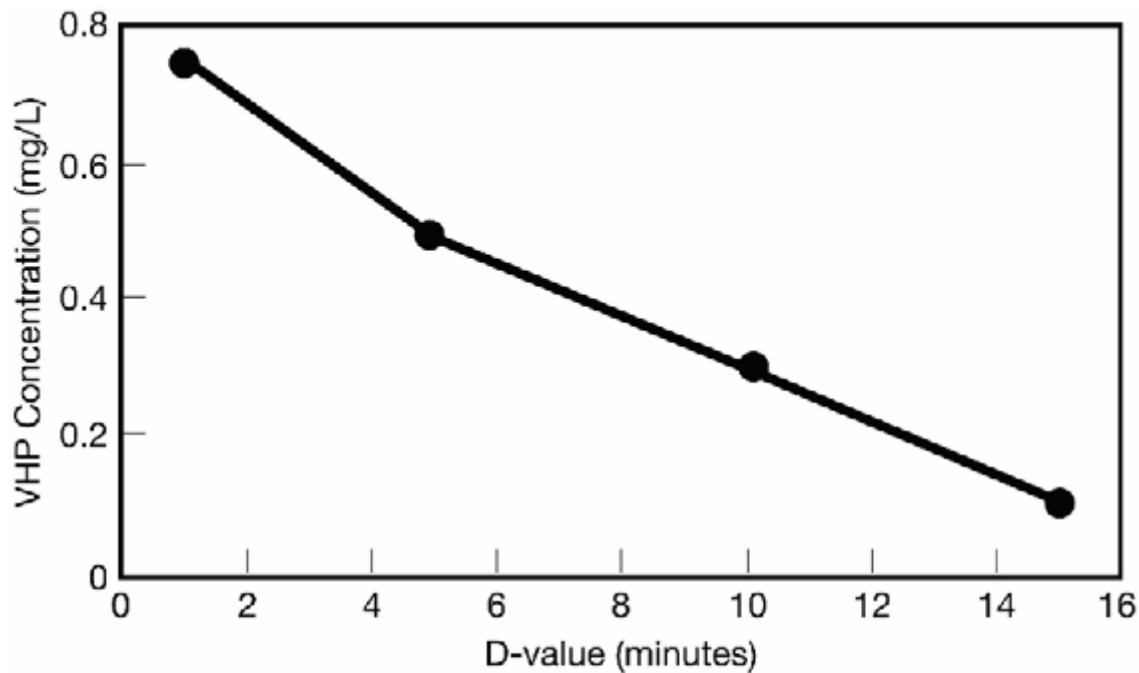
The efficacy of a chemical as a sporicide is expressed in terms of log kills and D-Values. A one log kill represents 90 percent killing efficiency. A six log kill, required for sterilization is a 99.9999 percent killing efficiency. A D-value is the contact time required for a one log kill. In a 1991 published report the D-values of liquid and hydrogen peroxide vapor were compared using three different bacterial spore types. As shown in Table 5.2-1, the concentration of hydrogen peroxide in water is over 200-fold greater than the concentration required in the vapor-phase to achieve similar microbial activity (Block, 2001).

Table 5.2-1. Effectiveness of Hydrogen Peroxide Liquid and Vapor on Spores

Test Organism (spores)	D-value (time to kill one log of test organism in minutes)	
	Liquid H ₂ O ₂ Concentration 370 mg/L Temp 24-25 Celsius	Vapor H ₂ O ₂ Concentration 1-2 mg/L Temp 24-25 Celsius
<i>B. stearothermophilus</i>	1.5	1-2
<i>B. subtilis</i>	2.0-7.3	0.5-1
<i>C. sporogenes</i>	0.8	0.5-1

STERIS Corporation provided the data shown in Figure 5.2-4.

The D-values (time required to kill 90 percent of the initial population) for a variety of bacterial spores were determined with hydrogen peroxide vapor. Spore populations of 10⁶ were deposited onto 316 stainless steel coupons. The contaminated coupons were exposed to Vaporized Hydrogen Peroxide at a concentration of 1,370 ppm at approximately 30-37 °C. The thermophilic *Geobacillus stearothermophilus*, which is used on many commercial biological indicators, exhibited the greatest resistance to the process as shown in Table 5.2-2.



VHP Concentration/D-value graph

**B. stearothermophilus* spore D-values were determined at various VHP concentrations. The average D-value is shown for each concentration, as determined from an initial spore population inoculated onto stainless steel coupons, exposed to VHP over time and D-values determined by direct enumeration. The D-value is the average time in minutes for a log reduction of spores.

Figure 5.2-4. Hydrogen Peroxide Vapor Concentration versus D-value

Table 5.2-2. D-Values of bacterial spores exposed to 1,370 ppm hydrogen peroxide vapor at 30-37 °C

Organism	D-Value (seconds)
<i>Geobacillus stearothermophilus</i>	42.3
<i>Bacillus subtilis</i>	18.7
<i>Clostridium sporogenes</i>	15.6
<i>Bacillus circulans</i>	14.4
<i>Bacillus cereus</i>	9.9

The performance of hydrogen peroxide vapor is sensitive to temperature and humidity conditions. Hydrogen peroxide vapor was applied at different temperatures, and D-values were determined. As seen in Table 5.2-3, a higher equilibrium concentration of the hydrogen peroxide vapor was achieved at higher temperatures since the air was less saturated with water

vapor. The process was more effective at the higher temperatures due to the increased concentration, as well as the faster reaction rates of hydrogen peroxide vapor reacting with the target cell constituents.

Table 5.2-3. Hydrogen peroxide vapor efficacy at various temperatures against *Geobacillus stearothermophilus* spores

Temperature (°C)	Hydrogen Peroxide Vapor Concentration (ppm)	Typical D-Value
4	350	8 – 12 minutes
25	700 – 1500	1 – 2 minutes
37	2000 - 3000	30 – 60 seconds
55	> 7000	One second

In pharmaceutical manufacturing, the performance of hydrogen peroxide vapor is routinely monitored by the use of biological indicators (BIs). The BIs are either strips of polymeric non-woven fabric or stainless steel coupons inoculated with spores of *Geobacillus stearothermophilus* or other appropriate indicator microorganism. A successful decontamination cycle is determined by complete inactivation (sterilization) of the biological indicator. *Geobacillus stearothermophilus* spores have been identified as the most resistant organism to the hydrogen peroxide vapor process (Rickloff and Oreiski, 1989).

In response to the anthrax containing letters delivered to Florida, New York, and Washington, D.C., the U.S. EPA in Denver Colorado contracted the West Desert Test Facility at Dugway Proving Ground to test the effects of ClO₂ and hydrogen peroxide vapor on a variety of dried *Bacillus* spores:

- BAA – *Bacillus anthracis* var. *ames*,
- BAV – *Bacillus anthracis* var. *vollum*,
- BAS – *Bacillus anthracis* var. *sterne*,
- BGN – *Bacillus subtilis* var. *niger*,
- BT – *Bacillus thuringiensis*, and
- BST – *Bacillus stearothermophilus*.

The ClO₂ data from this testing were discussed in Section 5.4.1.1. The data obtained from the one trial with H₂O₂ vapor are discussed and illustrated below, excerpted from the study report (West Dugway Test Center, 2002).

Spores from three strains of *Bacillus anthracis* (BA) and three BA simulants were applied as a liquid slurry and dried on either glass cover slips (all six organisms) or porous filter paper (BAA and BAV only), and were exposed to hydrogen peroxide vapor in a chamber under controlled conditions for 12 hours. The Dugway team did not control for temperature; discussions with the team indicated that they operated at ambient temperatures (70-75 °F).

During the course of the 12-hour run, triplicate slides were removed from the sterilization chamber at specific time intervals, and cultured to determine presence of viable spores.

Hydrogen peroxide vapor was used during Trial 6. The vapor was generated using a STERIS VHP1000 unit in accordance with the manufacturer's instructions (STERIS, 1996), heating 30 to 35 percent aqueous H₂O₂ to form the vapor. The VHP1000 unit operates on a four-phase cycle. In the first phase – which occurred prior to the introduction of gas into the Dugway chamber – the chamber was dehumidified utilizing a dehumidifier incorporated into the VHP1000 unit. Dehumidification is important in the VHP process, to reduce condensation of aqueous H₂O₂. Dehumidification was followed by the second, conditioning phase. In this phase, the generator introduced hydrogen peroxide vapor into the chamber at a rapid rate, to reach the desired chamber operating concentration as quickly as possible. After the desired concentration was achieved, the VHP1000 unit switched to the third, or fumigation, phase, reducing the hydrogen peroxide vapor generation rate to the level required to maintain the desired concentration at steady state for 12 hours. (This steady-state peroxide concentration was determined by the vendor's settings on the VHP1000 unit, and was not measured during this study.) The fourth and last phase of operation was the aeration phase, in which the residual hydrogen peroxide vapor in the chamber was removed so that the chamber could be opened without causing harm to personnel.

The data obtained for this experiment is illustrated in Figure 5.2-5, as excerpted from the EPA report. These results show that – at the potentially high gaseous H₂O₂ concentrations in the chamber – all of the *B. anthracis* surrogates (BGN, BT, BST, and non-virulent *B. anthracis* v. *sterne*) had been completely killed on the glass cover slips within 1 hour (a 6- to 8-log reduction in spores). The virulent *B. anthracis* v. *ames* strain (BAA) experienced a 6-log kill in 1 hour, and complete (7-log) kill in 2 hours. *B. anthracis* v. *vollum* (BAV) proved to be the most resistant to H₂O₂ vapor, requiring 4 hours to sustain a 6-log kill, and 6 hours to experience total (8-log) kill.

Hydrogen peroxide vapor does interact with many materials, decaying in contact with the surface, but it does not appear to be corrosive. Discoloration of dyes can occur and interactions with nylon are not favorable. It has been reported that nylon and other porous surfaces interact with the hydrogen peroxide and degrade it, thereby making it inactive. In a personal communication with STERIS representatives during the anthrax response in Washington, D.C., they reported that the gas was inactivated by celluloid compounds. This includes paper and paper products. In a more recent communication with Dr. Peter Burke of STERIS, he claimed to have more recent data indicating less rapid decay of the vapor against porous surfaces (SAIC, 2003).

Research is underway through a work-in-kind cooperative research and development agreement between Lawrence Livermore National Laboratory and STERIS Corporation to evaluate the use of heating, ventilation, and air conditioning (HVAC) systems as a means to convey Hydrogen peroxide vapor into building environments. The experiments are evaluating the delivery of VHP through the HVAC system, and quantifying the spore kill by culturing indicator strips (Carlson and Raber, undated).

Trial 6 - Hydrogen Peroxide

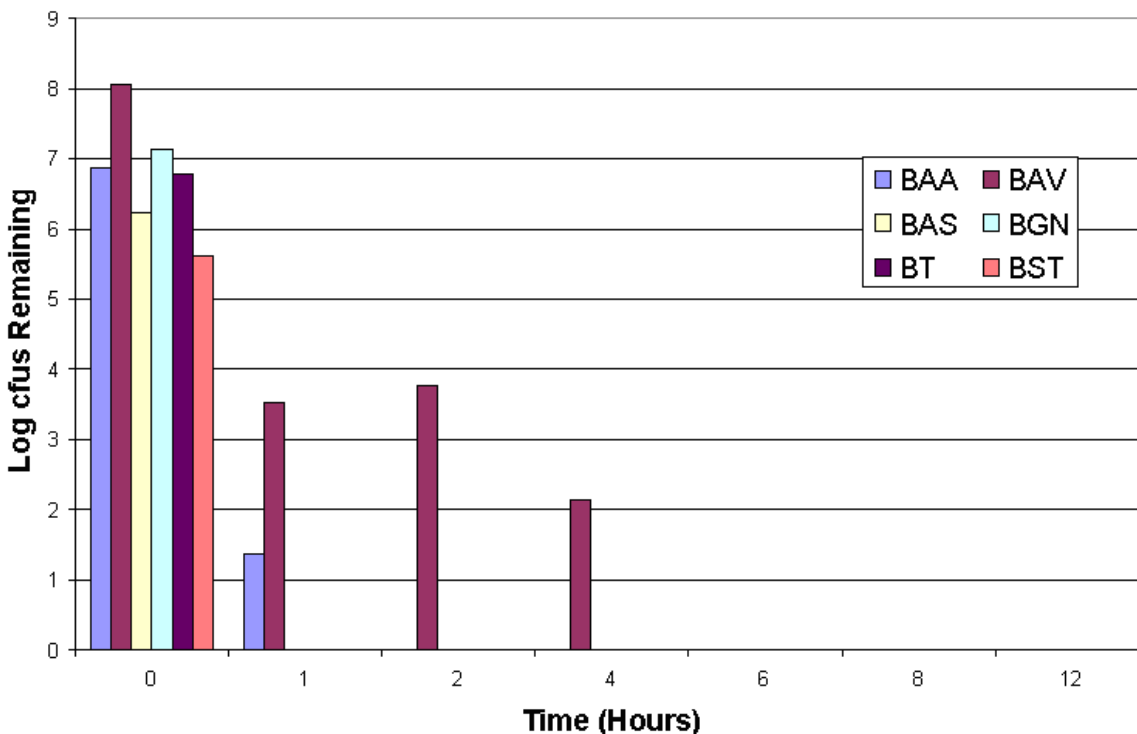


Figure 5.2-5. Log of Colony Forming Units (cfus) Remaining at Each Time Point for Trial 6; Laboratory Validation of Hydrogen Peroxide Decontamination

NOTE: BAA – *Bacillus anthracis* var. *ames*, BAV – *Bacillus anthracis* var. *vollum*, BAS – *Bacillus anthracis* var. *sterne*, BGN – *Bacillus subtilis* var. *niger*, BT – *Bacillus thuringiensis*, BST – *Bacillus stearothermophilus*.

5.2.4.2 Experience with field fumigation of buildings

Experience at the U.S. Department of State Mail Annex (SA-32), Sterling, VA

This State Department mail processing facility (SA-32) in Sterling, VA, was contaminated with *B. anthracis* spores in October 2001, possibly because the anthrax-containing letter addressed to Senator Leahy may have been mis-directed to SA-32 prior to being returned to the Brentwood P&DC (discussed in Section 5.1.4.2). SA-32 contains 1.4 million cubic feet of volume, making it about one-quarter the size of the USPS Hamilton P&DC, and about one-tenth the size of the Brentwood P&DC.

As with all of the buildings impacted by the 2001 anthrax mail attack, the initial step in the remediation process for SA-32 was environmental sampling (swab sampling and vacuum sock sampling) to characterize the extent of the contamination. Four such sampling events took place in October and November 2001.

With confirmation that the facility was contaminated, a significant effort was undertaken to seal the building, to prevent release of the spores to the outdoor environment and, ultimately, to prevent escape of the as-yet unselected fumigant. All exterior doors (including loading dock doors), windows, and vents were sealed with caulked polyethylene sheeting, and covered with plywood to prevent puncture of the sheeting. The rooftop HVAC units that served the building were all removed (after having been cleaned from inside the building), and the resulting openings in the roof were sealed in the manner described above. All plumbing fixtures inside the building were removed, and the water lines and plumbing vents capped. Following subsequent testing for leak-tightness, additional sealing was also performed, including caulking around the joint where the exterior walls meet the roof.

In addition, five exhaust fans (“negative air machines”, or NAMs) were installed on the building – exhausting through HEPA filters, to capture any anthrax spores that could be in the exhaust – to maintain the building under negative pressure throughout this entire process. This was intended to prevent any spores inside the building from escaping into the ambient air.

Critical and salvageable items were decontaminated by several approaches for re-use. Over 70,000 lb of flat mail was treated by irradiation. Bulk parcels were cleaned by HEPA vacuuming, then tested for *B. anthracis* to verify the effectiveness of treatment. Personal and office items, including file cabinets and document storage units, were treated off-site using ethylene oxide sterilization. Over 46,000 diplomatic mail pouches were sterilized using paraformaldehyde, using pre-constructed chambers set up in the SA-32 building for this purpose.

All interior finish and all postal equipment was removed from the building, reflecting the most substantial source reduction effort of any of the remedial actions taken in response to the anthrax mail attack. All interior frame walls, ceilings, carpeting, furnishings, etc., were removed, broken down, treated with amended bleach (pH-adjusted sodium hypochlorite with acetic acid) or with an aqueous hydrogen peroxide/ peroxyacetic acid product (Spor-Klenz®), packaged, and sent for destruction at a permitted medical waste facility. Large metal items, such as the mail handling equipment, were washed with soap and water, broken down, and placed in large containers, which were shrink-wrapped in plastic. The exterior of the shrink-wrap was cleaned with Spor-Klenz, the containers were shipped for off-site ethylene oxide treatment, and the resulting sterilized metal was recycled as scrap.

Following the removal of this interior finish and equipment, only the building shell remained – the exterior walls (and a few interior structural walls), the slab, the metal sheeting supporting the flat built-up roof overhead, and the metal roof trusses, along with the electrical system. All of these remaining interior surfaces were HEPA vacuumed, and washed with soap and water. In six areas known to have been contaminated by anthrax, based on the pre-remediation environmental sampling, the surfaces were also wiped down with the amended bleach or Spor-Klenz.

The original intention had been to fumigate the entire facility with paraformaldehyde. However, following evaluation of alternative building remediation approaches, the State Department selected gaseous H₂O₂ as the fumigant to be employed, using the STERIS Vaporized Hydrogen Peroxide process.

For the fumigation utilizing the STERIS VHP gaseous H₂O₂ process, the cleaned and basically empty 1,400,000 ft³ building was physically subdivided into zones using plastic sheeting. Initially, there were seven zones, each approximately 200,000 ft³ in volume. These zones would be fumigated one at a time. The decision was made to subdivide the building, in part, in order to reduce the H₂O₂ generation capacity that would have been required on-site were the entire building volume to be fumigated at once. In addition, the VHP process had not previously been used to treat volumes of this size, except at GSA Building 410, which also had been subdivided into 200,000 ft³ zones. This subdivision into zones was achieved using polyethylene sheeting that extended the entire width of the building, anchored to the floor slab, to the metal underside of the roof, and to the front and rear walls.

The target fumigation conditions were that the vaporized H₂O₂ concentration in each zone would have to be held at or above 0.3 mg/L (216 ppm) for 4 hours; the temperature would have to be ≥70 °F; and the “saturation level” would have to be ≤80%, to avoid condensation. The saturation level is defined as the concentration of water vapor plus H₂O₂, expressed as a percentage of the dew point concentration of these two compounds in combination at the prevailing temperature. It is noted that this peroxide concentration and exposure time (a total CT of 860 ppm-hr) are much lower than the values specified for ClO₂ fumigation, discussed in Section 5.1.4.2 (750 ppm for 12 hr, or 9,000 ppm-hr), reflecting a higher reactivity of H₂O₂.

Sensor bundles were placed at six locations within each zone during its fumigation (with H₂O₂ monitors at two additional locations), to continuously monitor the concentrations of H₂O₂ and water vapor, and the temperature, to ensure that the target process conditions were achieved. Among the buildings remediated following the 2001 anthrax mail attack, this was the only fumigation in which real-time monitoring of fumigant concentration occurred. In addition, chemical indicators (strips that changed color when exposed to a certain H₂O₂ CT) and biological indicators (stainless steel spore strips containing 10⁶ spores of an anthrax surrogate, *Geobacillus stearothermophilus*) were distributed throughout each zone, with approximately one of each type of strip per 100 ft² of zone floor area. The chemical and biological indicators were co-located. Fumigation of a given zone was judged to be complete when the target fumigation conditions had been satisfied in that zone, when all chemical indicators had changed color, and when all biological indicators were negative for growth of the indicator spores when cultured following fumigation.

The STERIS H₂O₂ generation system was installed outdoors, near one corner of the SA-32 facility. This system consisted of multiple (four to six) generators – each representing a specially-designed adaptation of the VHP 1000 unit pictured in Figure 5.2-3 above – having a total combined capacity initially deemed to be more than adequate to treat each of the seven 200,000 ft³ zones. These generators produced gaseous H₂O₂ by vaporizing an aqueous 35% H₂O₂ feed solution.

In commercial practice, in the fumigation of small volumes, the VHP units automatically cycle the treated volume through four phases. These four phases include: dehumidification, in which the RH of the space is reduced to 40% or less; conditioning, in which the introduction of H₂O₂ vapor at high concentration is initiated, to bring the space up to the target fumigation concentration as quickly as possible (while maintaining the saturation level at 80% or less); decontamination, in which the space is maintained at or above the target concentration, at or

above the target temperature, and below the target saturation for the specified time; and finally aeration, in which the air within the space is cycled through a catalyst bed to destroy the residual H_2O_2 , reducing concentrations to a safe level. (The H_2O_2 concentration considered Immediately Dangerous to Life and Health is 75 ppm – less severe than the 5 ppm for ClO_2 – and, commonly, the objective is to reduce the concentration below 1 ppm, the OSHA Permissible Exposure Limit, during the aeration phase.)

The specially-designed large-volume VHP system installed at SA-32 was configured to put the 200,000 ft^3 zone through this same cycle. A blower near the generators recirculated the zone air. The galvanized metal ductwork system associated with this blower was manifolded such that it could withdraw air from, and supply air to, any one of the original seven zones, as controlled by dampers within the ductwork. Air would be supplied to one end of the selected zone, and withdrawn from the other end of that zone. The modified VHP generators introduced vaporized H_2O_2 into the supply side of this blower during the conditioning and decontamination phases for the selected zone.

A regenerative desiccator was incorporated into this recirculation loop. During the dehumidification phase, zone air was circulated through this dryer without the VHP generators operating, in order to reduce the relative humidity in the zone to 40% or less before conditioning began. During conditioning and decontamination, the desiccator served to reduce the observed increase in the zone's RH, helping prevent the zone's calculated saturation level from exceeding 80%.

The return air drawn out of the zone was passed through a HEPA filter (to remove any spores or dust) and a catalyst bed (to destroy the H_2O_2 in the extracted air stream) before entering the dryer and blower. The residual H_2O_2 was destroyed during conditioning and decontamination to facilitate control of the process. During the aeration phase, recirculation of zone air through this catalyst bed helped reduce concentrations below 1 ppm H_2O_2 .

During the fumigation of each zone, at least 20 mixing fans were in operation within that zone, in an effort to distribute the H_2O_2 uniformly throughout the zone.

While the fumigation of a given zone was underway, a 5,000 cfm exhaust fan drew air from all of the zones not being fumigated, keeping the remainder of the building at negative pressure relative to the fumigated zone and relative to outdoors. The H_2O_2 -containing exhaust from this fan was passed through a catalyst bed, to reduce the H_2O_2 concentration to a very low level prior to release to the atmosphere. The building was maintained under negative pressure to prevent the H_2O_2 vapor from escaping through the building shell into the outdoor air.

The fumigation of the first of the seven zones was initiated in June 2003. Difficulties were encountered in achieving the desired 216 ppm H_2O_2 in the zone. It became apparent that a major reason for this problem was that the vapor-phase H_2O_2 was reacting more rapidly than anticipated with the limited remaining building surfaces inside the empty zone, and perhaps with the galvanized metal supply ducting. The supply ducting was replaced with (or lined with) high-density polyethylene, considered to be less reactive with H_2O_2 . Three of the 200,000 ft^3 zones (including the first) were eventually further subdivided into two zones, with the new sub-zone

that was thus created ranging in size from 40,000 to 100,000 ft³. The total number of treated zones was thus increased from seven to ten. For some fumigations, the number of VHP generators was increased, to increase capacity where necessary to maintain the concentration above 216 ppm at one or more of the continuous monitors.

During all fumigation activities, sensitive H₂O₂ sensors were located at various positions outside the building, along the fence-line, and on some neighboring buildings. At no time did any of the fence-line monitors detect ambient H₂O₂ concentrations above background.

In August 2003, the last of the zones was successfully fumigated according to the specified process conditions: ≥ 216 ppm H₂O₂ for 4 hours, ≥ 70 °F, saturation level $\leq 80\%$. (Concentration, temperature, and saturation typically varied within a zone during fumigation, but remained in the specified ranges for 4 hours.) For all ten zones, chemical and biological indicator requirements were also met. One zone had to be re-fumigated when one of the biological indicators showed growth of the indicator organism, but all indicators tested negative after the second fumigation.

The difficulties that were encountered in maintaining the H₂O₂ concentration in some of the zones during this fumigation underscore the need to more thoroughly understand the decay rate of H₂O₂ upon contact with various building surfaces, and to ensure that adequate generation capacity is available to compensate for the H₂O₂ losses that will result.

Significant post-fumigation environmental monitoring was conducted for *B. anthracis*, using both surface sampling and aggressive air sampling techniques. The air sampling took place after the interior surfaces of the zone to be sampled had been aggressively disturbed using a leaf blower to re-suspend any residual spores. All 619 samples cultured negative for *B. anthracis*. On the basis that all environmental samples were negative for spore growth, and that the fumigations had been successful in achieving both the target process conditions and the required chemical and biological indicator results, the Environmental Clearance Committee concluded that the remediation had been successful, and recommended in November 2003 that the facility be re-opened. The Department of State subsequently renovated and refurbished the building, incorporating a number of design and operational changes to better protect the workers should such an incident ever reoccur in the future.

5.2.5 Concerns for the User

Hydrogen peroxide vapor is acutely toxic at high concentrations. The byproducts of the vapor are harmless. The U.S. Occupational Safety and Health Administration (OSHA) has an eight-hour Permissible Exposure Limit (PEL) for hydrogen peroxide gas of 1.0 ppm. The short-term limit (Immediately Dangerous to Life or Health, or IDLH) is 75 ppm for a 30-minute exposure. One positive feature about this gas is that it is an irritant at levels above 1.0 ppm, minimizing the inadvertent exposure to dangerous levels of the gas. The gas has a discernable, slightly pungent or acidic odor at levels below the IDLH level, which adds to the safety factor.

5.2.6 Availability of the Technology for Commercial Applications

There are multiple vendors offering commercial H₂O₂ vapor systems for sterilizing relatively small volumes, such as sterilization chambers and pass-through rooms. In addition, the experience at the Department of State mail facility SA-32, and at GSA Building 410, has demonstrated that it may be practical to adapt some of these commercial systems such that volumes of 100,000 to 200,000 ft³ can be treated, perhaps by the use of multiple generators. A key consideration in this scale-up is the need to understand how rapidly the highly reactive H₂O₂ vapor will decay in contact with typical building surfaces, so that the generation capacity can be reliably estimated for cases where the building is not as thoroughly gutted as SA-32 was.

5.2.7 Advantages and Disadvantages

There are three main advantages to this technology application. The first is that it has been documented by many sources over a long period of time to be effective against viruses, bacteria, and spores. The second is that the technology is currently available for implementation and additional research. The third advantage is that the end products, after catalytic breakdown, are water and oxygen.

One main disadvantage of this technology is that the vapor is reactive and can break down upon contact with certain materials such as galvanized steel and porous surfaces such as paper and unpainted cinderblock. The thought is that the high degree of surface area catalyzes the conversion of the active gas to water and oxygen. This is thought to be the cause of the difficulties encountered at SA-32, described in Section 5.2.4.2 above.

5.2.8 Potential Areas for Future Research

The issue of surface inactivation should be addressed by testing the reactivity of hydrogen peroxide vapor with different common building materials and office products, determining the sterilization capability on various surfaces found indoors. As with all scientific experimentation, independent verification of the results is recommended.

Scalability of the technology is another area for future research. It is not clear if the limitations of size are a function of the generation of the vapor or the stability of the vapor. Clearly, multiple H₂O₂ generation units could be linked together to generate vapor in a large enclosure, as was done in SA-32, with a separate system to maintain negative air pressure of the larger enclosure. The individual peroxide generators would be designed to remove the vapor in their respective locations during the “aeration phase” following fumigation.

Another key area for future research is the compatibility of H₂O₂ vapor with the materials found inside buildings, in particular, with sensitive equipment. This is an issue of concern for all fumigants, not only hydrogen peroxide.

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5.3 Paraformaldehyde

Paraformaldehyde is a polymerized form of formaldehyde, $(\text{CH}_2\text{O})_n$. It is a stable white crystalline powder. Upon heating, it generates formaldehyde gas, which has antimicrobial properties. The antimicrobial properties of formaldehyde are believed to result from its reactivity in the alkylation of proteins, nucleic acids, and DNA and RNA (Wickramanayake, 1990). Because pure formaldehyde is unstable at ambient temperatures (resulting in polymerization), and is not commercially available (Kirk-Othmer, 1994), paraformaldehyde is a material which can provide a readily-usable form of formaldehyde at use sites. Both paraformaldehyde and formaldehyde have been used in decontamination for more than 30 years, although the extent of this use (e.g., annual use quantities) is largely unknown.

5.3.1 Description of the Technology Alternative

Paraformaldehyde is used to generate formaldehyde gas for the decontamination of rooms, storage cabinets, and equipment. A typical procedure for the use of paraformaldehyde is to isolate the material or area being sterilized (e.g., sealing with tape or sheeting), using hot plates to sublime the paraformaldehyde and fans to distribute the vapor within the space for a specified time period, and finally to introduce a compound that will neutralize the formaldehyde vapor once treatment is complete (Munro et al., 1999). The standard method for neutralizing the formaldehyde is the use of ammonia generated by the heating of ammonium bicarbonate.

Alternatively, a more sophisticated approach – particularly applicable when treating larger volumes – is to use a formaldehyde generator. In a generator, the heating of the paraformaldehyde takes place inside a closed system, and the resulting formaldehyde is introduced into the room to be treated (Certek, 1980). One vendor of such generators is Certek Inc.

Following removal of formaldehyde gas, some studies report that surfaces are cleaned with water to remove any remaining residue. In particular, high humidity or high concentrations can result in either the precipitation of paraformaldehyde or the condensation of formaldehyde in water. Condensed formaldehyde/water mixtures would likely result in paraformaldehyde deposits on the surfaces after the water evaporated (Hoffman and Spiner, 1990).

In addition to paraformaldehyde, formalin has also historically been used as a source of airborne formaldehyde for sanitizing or decontamination purposes. Formalin is a 37 percent aqueous solution of formaldehyde, stabilized by small quantities of methanol. Formalin is dispersed into the air such as through a fogging apparatus (Wickramanayake, 1990). Because both paraformaldehyde and formalin generate formaldehyde as the active ingredient, this chapter addresses both the use of formalin fog and the use of paraformaldehyde to generate formaldehyde gas for building decontamination, but with emphasis on the latter methodology.

5.3.2 Technical Maturity

Paraformaldehyde vaporization is fully mature and has been routinely used worldwide for sanitizing and disinfecting rooms and equipment in the health services industry (Coldiron and Janssen, 1984) and in U.S. Army Medical Research Institute of Infectious Diseases (USAMRIID) biological laboratories (Alexander, 1998). It was also used to decontaminate two pieces of postal equipment, which had been enclosed within a fumigation tent, in the Department of Justice mail facility in Landover, MD, which had become contaminated with *B. anthracis* spores in connection with the October 2001 anthrax mail incident.

Paraformaldehyde technology has been applied to rooms and small spaces (such as laboratories and safety cabinets), and to individual equipment items enclosed in chambers or tents. However, it has been used in at least one building decontamination project. The fumigant was used to destroy Ebola virus throughout the Hazelton Research Center in Reston, Virginia. A concentration of 12,000 mg/m³ paraformaldehyde was used for the building. The size of this building was not given, but – based on the back-calculation from other available data – it was estimated to be 78,000 ft³ (2,200 m³) (Alexander, 1998).

5.3.3 Applications of the Technology

Paraformaldehyde (a solid) is used as a source of either gaseous formaldehyde or solution (aqueous) formaldehyde. When the crystalline paraformaldehyde powder is heated, it releases formaldehyde gas. When dissolved in water, paraformaldehyde behaves like aqueous methanol-free formaldehyde.

Both paraformaldehyde and formaldehyde are primarily used in resin manufacturing, for uses such as adhesives and binders in consumer and industrial applications. Paraformaldehyde is used by resin manufacturers seeking low water content or enhanced reaction rate control, and in the production of phenol-, urea-, resorcinol-, and melamine-formaldehyde resins (Kirk-Othmer, 1994). Paraformaldehyde is also used in dentistry as a fixative. In these applications, the paraformaldehyde is dissolved in a solution to prepare aqueous formaldehyde.

Paraformaldehyde was registered by EPA under FIFRA as a sanitizer and fungicide for use on barber and beauty shop equipment in 1964. Since then, it has been registered and used as a disinfectant, sanitizer, fungicide, and microbicide in household and domestic dwellings, in ships and ship holds, on bedding and clothing, and in non-food/non-feed-transporting trucks (EPA, 2004). It is unclear which of these applications use aqueous formaldehyde and which use gaseous formaldehyde.

Under FIFRA definitions, a “sanitizer” is defined as a substance that significantly reduces bacterial populations, but does not destroy all bacteria or other microorganisms. A “disinfectant” destroys a specific species of microorganism – in particular, infectious (viral) microorganisms – but not necessarily bacterial spores. A “sterilant” destroys all forms of microorganisms, including all vegetative bacteria, bacterial spores, fungi, fungal spores, and viruses. Paraformaldehyde has never been registered as a sterilant, although it has been demonstrated to be effective in killing *B. anthracis* spores under certain prescribed conditions.

Paraformaldehyde has been used as a fumigant for more than 30 years. It has been used to decontaminate laboratory facilities and to disinfect sickrooms, clothing, linen, and sickroom utensils (EPA, 2004). In these applications, paraformaldehyde is heated to form gaseous formaldehyde.

Paraformaldehyde was registered and used to control microbial growth in laboratories and to decontaminate animal facilities until recently, when all registrations for this use of the chemical were canceled due to nonpayment of fees by the manufacturer (the name of the manufacturer was not identified in the source). Quarantine use of paraformaldehyde has been allowed in a poultry health laboratory in Arkansas (a use which was in effect through June 15, 2004). Similarly, the Department of Defense was authorized to utilize paraformaldehyde for quarantine use since 1993 (effective until July 6, 2002). Similar exemptions for the use of paraformaldehyde to decontaminate high-containment microbiological laboratories at Plum Island, NY, and Ames, IA (effective until June 15, 2001) have also been granted to the USDA (EPA, 2004).

A related use of gaseous formaldehyde is in low temperature steam formaldehyde (LTSF) technology, a technique for decontamination of small items developed in the late 1960s. In this method, small non-disposable items are placed inside an apparatus which uses sub-atmospheric (i.e., relatively low temperature) steam and gaseous formaldehyde. Typical conditions include temperatures of 73 °C and formaldehyde levels of 8,000 mg/m³ (Hoxey et al., 1985). These temperatures are impractical for larger scale (e.g., room) decontamination.

5.3.4 Evaluation of Available Data

More than 30 years of performance data regarding paraformaldehyde decontamination are available, most in small-scale applications in clinical or research settings. This is likely to be a reflection of its long use in the medical services industry for decontamination of biological safety cabinets, laboratories, and reusable equipment.

While much of the testing and application of paraformaldehyde has focused on microorganisms other than (or in addition to) bacterial spores, some of this testing has utilized bacterial spore strips as a convenient means for assessing the antimicrobial impacts of fumigant. Among the spores utilized in this spore strip testing are *B. stearotherophilus*, *B. subtilis*, and *B. globigii* (*B. subtilis* v. *niger*).

In one study addressing spores directly, aqueous formaldehyde was used in the treatment of soil contaminated with *B. anthracis* (Manchee et al., 1994). No data were reported from this study relevant to the use of gaseous formaldehyde against this organism.

Coldiron and Janssen (1984) describe an example of paraformaldehyde use in decontaminating a hospital autopsy suite at the University of Texas. This area consisted of three rooms, 73 meters of connecting exhaust ductwork, and three exhaust air incinerators. Concerns were for various, unidentified microorganisms present throughout the suite, as a result of prior use, which would pose potential risks to construction personnel. Commercially available indicator strips of *B. stearotherophilus* and *B. globigii* were used to determine disinfection completeness. Based on

‘no growth’ results of the test strips placed throughout the room, successful decontamination resulted from the use of 10.6 to 17.7 g/m³ paraformaldehyde, 3 to 4 hours of contact time, and relative humidity of 65 percent (Coldiron and Janssen, 1984).

Munro et al. (1999) conducted tests to determine optimum decontamination conditions for metal biological safety cabinets using paraformaldehyde. Organisms tested included polio virus, *Mycobacterium bovis* bacillus Calmette-Guérin (BCG), *B. stearothermophilus*, and *B. subtilis*. All testing was conducted on stainless-steel coupons placed at various locations inside a metal cabinet. Optimal decontamination conditions were identified as 66 percent relative humidity, a minimum temperature of 28 °C, and a paraformaldehyde concentration of 10.5 grams/cubic meter. Figures 5.3-1 to 5.3-3 display the results of these studies, with independent variables of concentration, relative humidity, and temperature, respectively (a 15 hour decontamination time was used for all studies). The dependent variable in each case (percent survival) was measured as the ratio of growth on the treated coupons versus growth on untreated controls (Munro et al., 1999). Growth was measured in terms of 50 percent tissue culture infected dose (TCID₅₀) for polio, and colony-forming units (CFU) for other organisms. Figures 5.3-1 and 5.3-2 show that the effectiveness of decontamination increased with concentration and humidity, while effects of temperature resulted in marginal variability based on Figure 5.3-3. Table 5.3-1 shows the survival of organisms as a function of location in the cabinet. The authors conclude that *B. stearothermophilus* was killed more readily than *B. subtilis*, although completely successful decontamination (total kill) was demonstrated for 7 of 144 coupons containing *B. subtilis*.

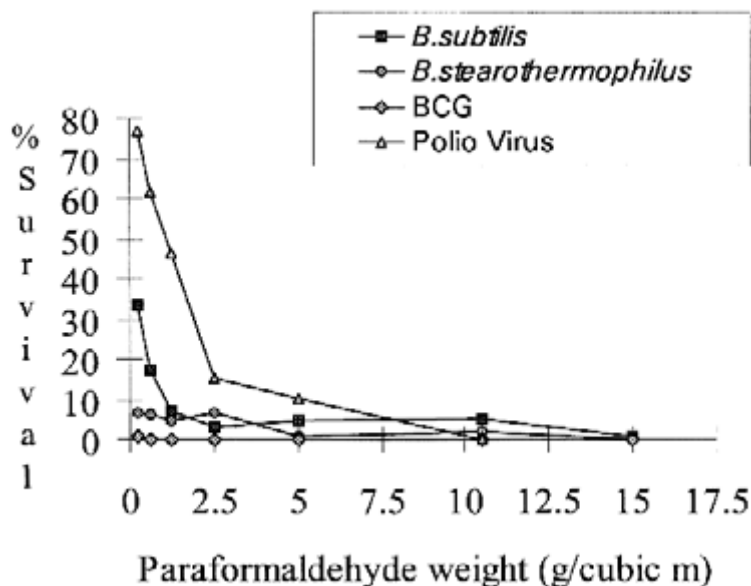


Figure 5.3-1. Percent Survival of Test Organisms after Decontamination with Various Concentrations of Formaldehyde.

Survival was measured as a percentage of the growth (CFU or TCID₅₀) of that for the untreated control for each test organism. The data were for test pieces placed inside the cabinet on the side wall. (The relative humidity was <58 percent, and the temperature was <27 °C.) (Munro et al., 1999)

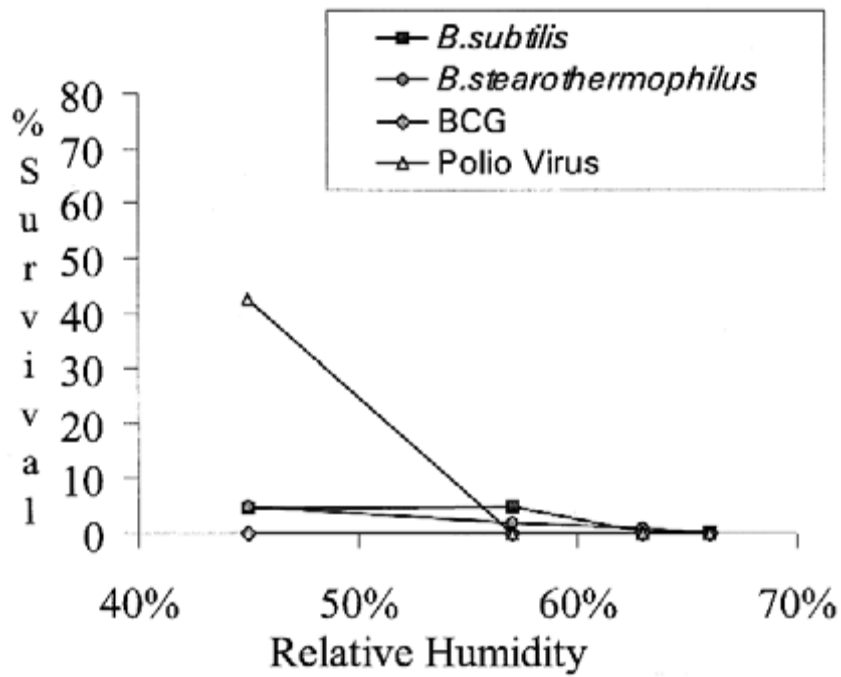


Figure 5.3-2. Percent Survival of Test Organisms after Decontamination at Various Relative Humidities.

Paraformaldehyde weights were $\geq 5 \text{ g/m}^3$, and the temperature was approximately 25 °C. (Munro et al., 1999)

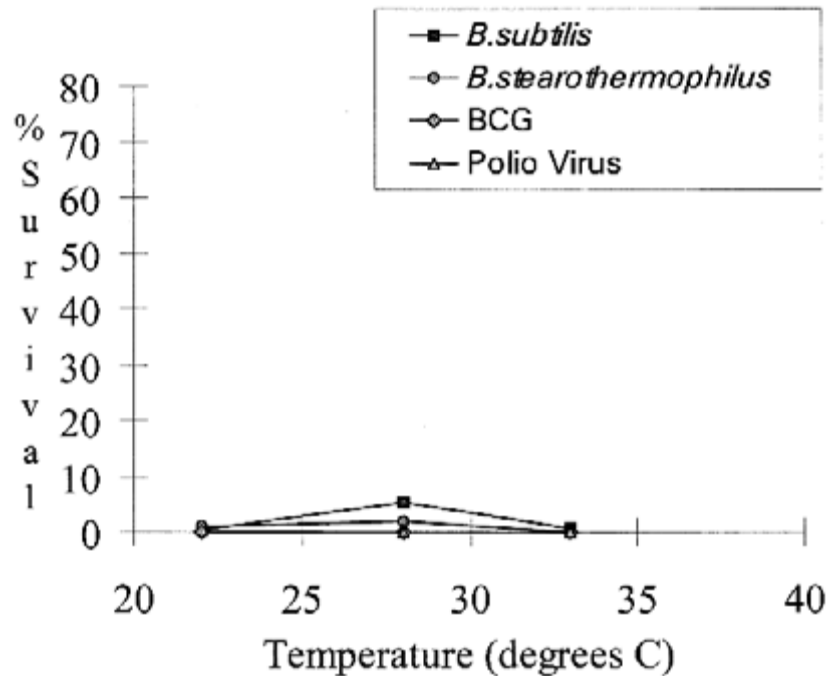


Figure 5.3-3. Percent Survival of Test Organisms with Variation of Temperature During Decontamination with Paraformaldehyde at $\geq 10.5 \text{ G/m}^3$ and a Relative Humidity of Approximately 58 Percent. (Munro et al., 1999)

Table 5.3-1. Survival of Test Organisms on Strips Positioned at Different Test Locations During Decontamination ^a

Location of strip	<i>B. subtilis</i> (CFU)	<i>B. stearothermophilus</i> (CFU)	BCG (CFU)	Polio virus (TCID ₅₀ /0.2 ml)
Under the cabinet tray	15,000	47.4	<10	0
Cabinet tray	20,000	46	<10	0
Cabinet side	21,000	73.8	<10	0
Beyond the exhaust filters	19,000	293.2	<10	10 ^{0.66}
Initial inoculation level	1.76x10 ⁶	4x10 ⁵	1.39x10 ⁶	10 ^{12.5}

a. Data are averages of three determinations. Decontamination conditions were as follows: paraformaldehyde, 10.6 g/m³; relative humidity, 57%; temperature, 28 °C; time, 15 hours. (Munro et al., 1999).

Table 5.3-2 provides additional data summarized by G.B. Wickramanayake (1990). The formaldehyde concentrations and decontamination time for testing are much lower than used by Munro et al. above, but nevertheless show inactivation to some degree. In particular, Table 5.3-2 shows 6-log inactivation of *B. subtilis* which is apparently higher than the results by Munro et al. (1999), despite the higher concentrations and increased decontamination times used by Munro.

Table 5.3-3 presents data by V.H. Lach (1990), which provides results of five different procedures in decontaminating a 38 m³ test room, using either formalin or paraformaldehyde as a source of formaldehyde. Part of the purpose of this work was to attempt to reproduce conditions of previous studies, such as Taylor (1969), discussed below. Therefore, comparisons of results between these studies are useful in assessing reproducibility. Unfortunately, the author noted that the low kill rate observed for the paraformaldehyde test in Table 5.3-3 was due to difficulties in simulating the conditions and formaldehyde release rate between the two tests.

Based on the results by Lach, the author notes that the theoretical airborne concentration of formaldehyde (i.e., based strictly on quantity introduced divided by room volume) was always significantly greater than the measured concentrations. A possible explanation for this includes the condensation of water and formaldehyde, in which case the use of lower quantities of formaldehyde could result in the elimination of condensed quantities. If this were true, a lower formaldehyde feed rate could have an effectiveness equivalent to a higher feed rate, if the losses due to condensation are eliminated at the lower rate. Such a hypothesis would require testing.

Many variations in decontamination as a function of bacteria or toxin placement were tested at Fort Detrick, Maryland (Taylor et al., 1969). The results of these tests are shown in Table 5.3-4. As shown, materials tested included laboratory equipment and various surfaces, while the size of the facilities also varied from small to large rooms. For experiments involving rooms, test strips containing the organism were typically placed at various locations inside the room.

Table 5.3-2. The Effects of Formaldehyde on Various Organisms

Organism	Matrix	Formaldehyde Concentration	Temp. (°C)	Relative Humidity (%)	Time	Inactivation	Source
Bacteria							
<i>E. coli</i>	Dried on steel rings	20 mg/m ³	20 to 27	80	10 min	90%	(1)
<i>E. coli</i>	Dried on steel rings	180 mg/m ³	20 to 27	80	<3 min	90%	(1)
<i>B. globigii</i>	Dried on steel rings	20 mg/m ³	20 to 27	80	120 min	90%	(1)
<i>B. subtilis</i>	Not identified	300 mg/m ³	20	100	1.5 hr	99.9999%	(2)
Fungi							
<i>A. sydowi</i>	Dried spores	2.5 mg/m ³	20 to 22	65	24 hr	99.99%	(3)
<i>A. flavus</i>	Dried spores	2.5 mg/m ³	20 to 22	65	24 hr	99.99%	(3)
<i>A. candidus</i>	Dried spores	2.5 mg/m ³	20 to 22	65	24 hr	99.99%	(3)
<i>Scopuloriopsis brevicaulis</i>	Dried spores	2.5 mg/m ³	20 to 22	65	24 hr	99.99%	(3)
<i>Paecilomyces varioti</i>	Dried spores	2.5 mg/m ³	20 to 22	65	24 hr	99.99%	(3)
<i>A. sydowi</i>	In dust samples	2.5 mg/m ³	20 to 22	65	24 hr	17%	(3)
<i>A. repens</i>	In dust samples	2.5 mg/m ³	20 to 22	65	24 hr	96%	(3)
<i>A. chevalieri</i>	In dust samples	2.5 mg/m ³	20 to 22	65	24 hr	82%	(3)
<i>A. versicolor</i>	In dust samples	2.5 mg/m ³	20 to 22	65	24 hr	50%	(3)
Source: Tables 4 and 6 of Wickramanayake (1990). The Wickramanayake article summarizes data previously published in the following sources, which were not reviewed for the present report): (1) Bovallius and Anas, 1977; (2) Caputo and Odlaug, 1983; and (3) Klein and Deforrest, 1983.							

Table 5.3-3. Measured Average Conditions and Experimental Kill of *B. Globigii*

Formaldehyde Source	Time (hr)	Matrix	Formaldehyde Concentration (mg/m ³)		Relative Humidity (%)	Kill (log ₁₀ cycles)
			Theoretical	Measured		
Formalin	18	Filter discs	7,060	240-800	89 to >99	>9 (all five locations)
Formalin	2.5	Filter discs	7,060	339-1,100	45 to 74	5 to >9
Paraformaldehyde	2.5	Filter discs	10,600	393-805	35 to 42	4 to 5 ^a
Formalin	3	Filter discs	2,830	102-261	91 to >99	6 to >9
Formalin	18	Filter discs	2,830	89-347	84 to >99	>9 (all five locations)

Source: Lach, 1990. In each test, five sensors were placed throughout a 38m³ test room. The above results display the ranges of the average measurements. Organism levels varied from 10² to 3 x 10⁸. For all room locations in each experiment, temperature varied over a narrow range of 23.2 to 25.8 °C.

a. Low kill rates due to difficulties in replicating target conditions.

For experiments involving pieces of equipment or smaller surfaces, the organism was typically dispersed in air and allowed to settle, with subsequent testing performed by swabs or similar means. The last column of Table 5.3-4 assists in identifying the procedures used. In all cases, the authors note that “the microorganisms were killed and the toxin was detoxified.” However, while initial levels of the microorganisms were presented (most tests ranged from 10⁴ to 10⁷ spores per mL), numerical results regarding the remaining spores were not available and therefore log-kill data cannot be determined.

Tables 5.3-5 to 5.3-7 show experimental test data of the survival of *B. subtilis* versus variables of time and relative humidity for three different types of stopper closures. These closures are intended to investigate the ease with which formaldehyde can penetrate different materials. The spores were present inside the test tubes. The study, conducted by Hoffman and Spiner (1970) at Fort Detrick, Maryland, provides insight into the penetrating ability of formaldehyde through these materials, rather than the ability of formaldehyde to treat organisms embedded onto these materials. Some conclusions from the authors and from the presented data include the following:

- Higher levels of formaldehyde (10.6 g/m³ versus 3.5 g/m³) result in faster bacteria kill, and higher exposure times result in higher levels of kill. These results are somewhat obvious and expected.
- At a formaldehyde concentration of 3.5 g/m³, intermediate relative humidities (i.e., 33 to 75 percent) are best for penetrating paper, while very high humidity (i.e., 100 percent) is best for glassine penetration and very low humidity (11 percent) is best for cotton penetration. Similar conclusions were found for formaldehyde levels of 10.6 g/m³, with the exception that there was no significant difference in paper penetration for relative humidity between 33 and 100 percent.

Table 5.3-4. Paraformaldehyde Sterilization of Facilities, Materials, and Equipment

Organism	Description of Facility Tested	Facility Volume (m ³)	Paraformaldehyde Conc. (g/m ³)	Temp. (°C)	Relative Humidity (%)	Contact Time (hours)	# Organism Locations in Test; Viable Recoveries/ Total Tests Conducted
<i>B. subtilis</i>	Laboratory room	64	10.7	23.3	60	1	15; 0/5
<i>Serratia marcescens</i>							15; 0/5
<i>B. subtilis</i>	Laboratory room	130	10.7	23.3	60	1	15; 0/5
<i>S. marcescens</i>							15; 0/5
<i>B. subtilis</i>	Mobile laboratory trailer	62	5.4	23.3	60	1	20; 0/5
<i>B. subtilis</i>	Two large connected rooms, of 4 to 5 stories each	1,904	8.6	31	50 to 55	2	200; 0/1
<i>B. subtilis</i>	15 types of surfaces ^a	in 0.71 m ³ chamber	10.7	24	60	1 to 2	(dispersed on each surface); 0/5
<i>B. subtilis</i>	Within filter media of a class I storage cabinet	in 1.3 m ³ cabinet	10.7	24	60	1	24; 0/5
<i>B. subtilis</i>	Vaccine tubes	in 0.06 m ³ chamber	10.7	Not given	60	1	(dispersed on surfaces); 0/2
<i>S. marcescens</i>	Vaccine tubes	in 0.06 m ³ chamber	10.7	Not given	60	1	(dispersed on surfaces); 0/2
<i>B. subtilis</i>	Miscellaneous electronic laboratory equipment	2.8 to 14	10.7	~24	≥50	1 to 2	(dispersed on surfaces); 0/10
Newcastle disease virus	Interior surface of test chamber	0.03	10.7	24	60	1	(dispersed on surface) 0/1
Newcastle disease virus	Class I storage cabinet	1.2	10.7	24	60	0.5	6; 0/1
<i>C. botulinum</i> toxin type A	Air sampler equipment	in 0.08 m ³ chamber	10.7	24	70 to 80	2	(dispersed on surfaces); 0/3

Organism	Description of Facility Tested	Facility Volume (m ³)	Paraformaldehyde Conc. (g/m ³)	Temp. (°C)	Relative Humidity (%)	Contact Time (hours)	# Organism Locations in Test; Viable Recoveries/ Total Tests Conducted
<i>C. botulinum</i> toxin type A	Powder samples (10 mg)	in 0.03 m ³ chamber	10.7	23	60	4	1; 0/3
<i>C. botulinum</i> toxin type A	Powder samples (20 mg)	in 0.03 m ³ chamber	7.1	24	45	48	1; 0/1

Source: Taylor et al., (1969).
a. The surface types tested were glass, rubber, plastic, stainless steel, galvanized metal, wood, paper, sponge, filter paper, painted surface, rigid plastic, copper, aluminum, vinyl sheeting, and mild steel.

Table 5.3-5. Percent Recovery of *B. subtilis* in Test Tubes with Paper Closures

Exposure Time (hr)	RH=11%	RH=33%	RH=53%	RH=75%	RH=100%
1	47.1	35.4	50.3	12.8	52.3
2	10.9	2.6	3.9	2.2	4.2
3	3.9	0.34	0.092	0.005	0.69
4	0.37	0.24	0.008	0.0003	0.15
7	0.0035	0.00015	0.0005	0	0
17	0.0008	0	0	0	0

Source: Hoffman and Spiner, 1970.
Spores were present in test tubes with indicated closure; test tubes were enclosed in a small testing chamber with 3.5 g/m³ formaldehyde gas generated from paraformaldehyde at 25 °C.

Table 5.3-6. Percent Recovery of *B. subtilis* in Test Tubes with Glassine Closures

Exposure Time (hr)	RH=11%	RH=33%	RH=53%	RH=75%	RH=100%
1	80.8	74.2	100	99.0	72.8
2	46.3	64.2	77.5	64.7	27.7
3	27.1	61.3	85.2	34.6	6.6
4	3.2	24.1	35.5	40.3	2.0
7	0.018	4.9	30.3	2.9	0.0005
17	0.0016	0.005	2.3	0	0

Source: Hoffman and Spiner, 1970. Spores were present in test tubes with indicated closure; test tubes were enclosed in a small testing chamber with 3.5 g/m³ formaldehyde gas generated from paraformaldehyde at 25 °C.

Table 5.3-7. Percent Recovery of *B. subtilis* in Test Tubes with Cotton Plug Closures

Exposure Time (hr)	RH=11%	RH=33%	RH=53%	RH=75%	RH=100%
1	62.9	71.6	96.5	82.9	99.1
2	20.4	41.2	57.3	76.3	97.5
3	7.0	27.6	43.6	48.9	100
4	0.6	11.0	57.6	47.7	85.0
7	0.0056	0.061	9.1	9.8	30.8
17	0.0003	0	0	0	0.022

Source: Hoffman and Spiner, 1970. Spores were present in test tubes with indicated closure; test tubes were enclosed in a small testing chamber with 3.5 g/m³ formaldehyde gas generated from paraformaldehyde at 25 °C.

The differences in results by Hoffman and Spiner (1970) regarding penetration ability are likely to cause difficulty in applications of building decontamination. Of the large variety of materials potentially present in such a situation, these results indicate that there is no single ‘ideal’ condition in treating them. The different materials present alternately may be best treated at either low, moderate, or high relative humidity. On the other hand, for general ambient room decontamination results from authors such as Coldiron and Janssen (1984) and Munro et al. (1999), there is agreement that an intermediate relative humidity (e.g., 60 to 70 percent) is effective. In attempting to apply these various results to building decontamination, consideration could be made to the application of a variety of humidity conditions. For example, humidity could be maintained at one level for a period of time followed by a period of time with different humidity.

Reflecting the experience with fumigations utilizing paraformaldehyde, several organizations have issued procedures, guidelines, and regulations pertaining to its use for the treatment of

various enclosed spaces (NIH, 1979), containment areas (USAMRIID, 1999), and biosafety cabinetry (NSF, 2002).

Experience at the Department of Justice mail facility

The mail processing facility within the Department of Justice's Landover Operations Center (LOC) in Landover, MD, became contaminated with *B. anthracis* spores during the October 2001 anthrax mail incident, probably through the processing of cross-contaminated mail. The contamination was discovered through precautionary environmental surface sampling that was undertaken after the contamination at the USPS Brentwood P&DC was detected. This sampling indicated that the *B. anthracis* contamination was limited to the mail facility portion of the LOC, and had not spread to other portions of the LOC warehouse.

Accordingly, the mail facility was isolated from the remainder of the warehouse using barriers consisting of plywood and polyethylene sheeting. The mail facility was exhaust ventilated using three exhaust fans exhausting through a HEPA filter, to keep the mail facility under negative pressure relative to the remainder of the LOC, and to thus prevent the spores from spreading to other parts of the building.

For source reduction, essential items (e.g., certified mail receipts) were packaged and shipped off-site for ethylene oxide fumigation and re-use. Non-essential porous items were cleaned to the extent possible – usually with 0.5% bleach solution or HEPA vacuuming – packaged, and shipped off-site for disposal. Items that were thus removed and sent for disposal included carpeting, upholstered furniture, non-essential paper, personal effects, and workstation cubicles.

Most non-porous surfaces were sprayed with aqueous chlorine dioxide solution or a surfactant solution, and wiped down following a 30-minute contact period. These surfaces included the floor, walls, counters, shelves, and non-porous furniture (desks and file cabinets). Non-porous ceilings and HVAC ductwork were not cleaned.

Paraformaldehyde fumigation was used to treat two pieces of postal equipment, the mail sorter and the stamping machine. Fumigation was selected for this equipment because they contained intricate components and difficult-to-reach areas that would have been impossible to decontaminate using a liquid, except by disassembling the machine. The two pieces of equipment were enclosed within a single tent (approximate volume 8,300 ft³) inside the mail room, constructed using 2- by 4-inch wood framing and a double layer of 6-mil polyethylene sheeting. EPA issued a crisis exemption under FIFRA to allow paraformaldehyde to be used in this application.

Multiple pans containing Hoechst-Celanese paraformaldehyde (95% pure) were placed on hot plates inside the tent. An excess of paraformaldehyde – beyond the minimum 0.3 g of paraformaldehyde per cubic foot of tent volume (NIH, 1979; USAMRIID, 1999; NSF, 2002) – was placed on the hot plates such that the formaldehyde concentration inside the tent would be maintained at the required level (about 8,900 ppm) for the required 12-hour exposure period. An airless sprayer released a water mist into the tent as required to maintain the RH above 50%.

When each stage of the fumigation was over, hot plates inside the tent were activated that contained ammonium bicarbonate (1.5 g of ammonium bicarbonate per gram of paraformaldehyde). After the vaporized NH_4HCO_3 neutralized the formaldehyde inside the tent, the tent was vented to the outdoor air.

The 12-hour fumigation process consisted of two 6-hour treatments. After the first 6-hour fumigation stage was completed, the formaldehyde neutralized, and the tent ventilated, the postal equipment was operated in order to aerosolize any spores remaining within the two machines so that these residual spores would be susceptible to destruction in the second fumigation stage.

Following the remedial activities, the success of the remediation was determined through environmental sampling, mostly surface wipe sampling but also including some vacuum sock sampling. All samples were negative for growth of *B. anthracis*.

After the environmental sampling had proven negative for *B. anthracis*, the fumigated sorting machine was disassembled and further wiped clean prior to re-use.

5.3.5 Concerns for the User

From a practical standpoint, concerns for paraformaldehyde are similar to those for formaldehyde. This is because paraformaldehyde will generate gaseous formaldehyde during storage or use. If it gets in contact with water, paraformaldehyde will similarly break down to formaldehyde. In addition, toxicological data or health concerns regarding paraformaldehyde are not readily available. For these reasons, information in this section will be generally limited to formaldehyde.

Formaldehyde has been identified as a probable human carcinogen by EPA, based on limited evidence of carcinogenicity in humans through inhalation exposure, and sufficient evidence for carcinogenicity in experimental animals. It produces nasal carcinomas in rats (EPA, 2003). Acute effects include respiratory irritation.

Airborne occupational exposure limits for formaldehyde applicable to the United States are as follows (NIOSH, 2003):

- NIOSH REL 8-hour TWA 0.016 ppm (0.02 mg/m³)
- OSHA PEL 8-hour TWA 0.75 ppm (0.92 mg/m³)
- ACGIH TLV 15-minute short term exposure limit (STEL) ceiling 0.3 ppm (0.4 mg/m³)
- Immediately Dangerous to Life or Health (IDLH) Level 20 ppm (25 mg/m³).

These exposure limits are several orders of magnitude below the concentrations used for decontamination as discussed above. Therefore, following decontamination, steps must be taken to completely neutralize excess formaldehyde in the air as well as to similarly remove any chemical which may have condensed onto surfaces. Formaldehyde is a flammable, colorless gas (lower explosive limit of 7 percent) with a pungent odor, all of which reflect additional concerns during use. Crystal paraformaldehyde itself is also combustible, with a flash point of 70 °C.

While the lower explosive limit and the flash point are well above the typical concentration and temperature conditions encountered during use, precautions must be taken for the possibility of extreme localized conditions in a room (e.g., in the immediate vicinity of the gas generation source or in a poorly ventilated area within a room). Formaldehyde gas has a density only slightly higher than that of air (relative vapor density 1.04); because of this similarity no significant difficulties in mixing or partitioning would be expected.

Caution must be taken while handling paraformaldehyde as it decomposes to formaldehyde gas on contact with water or moist air. Personal protection and exposure controls to be employed while handling paraformaldehyde include the use of chemical goggles, full-face shield or a full-face respirator, impervious gloves and boots of chemically resistant material, and body suits, aprons, or coveralls of chemical resistant material. Ventilation requirements for the use of paraformaldehyde include mechanical ventilation, process or personnel enclosure, and control of process conditions. There should also be a sufficient supply of replacement air to make up for air removed by exhaust systems (ClearTech, 2003).

5.3.6 Availability of the Technology for Commercial Applications

This technology is readily available for commercial applications. The heating and dispersion of paraformaldehyde is relatively straightforward. Technology for preparation (e.g., sealing buildings) is routine and similar to what is required for other fumigants. Personal protective equipment requirements are similar to other toxic materials. Monitors for formaldehyde gas (providing real-time data) are commercially available.

As indicated previously, paraformaldehyde can be dispersed using a specially-designed generator or a series of low-cost hotplates. Generator cost varies based on size requirements. The largest available generator by one manufacturer, Certek, is designed to decontaminate a 10,000 ft³ (280 m³) area with a concentration of 10.6 g/m³ (identified as the NIH recommended level). Room volume and concentration are related, so that if a lower concentration is targeted, a larger room could be decontaminated. The cost for this type of generator is approximately \$60,000 and the cost of paraformaldehyde is approximately \$24/ pound for small quantities (bulk chemical quantities are cheaper) (SAIC, 2003). As an example, approximately six pounds of paraformaldehyde would be required in decontaminating a room volume of 280 m³ at a concentration of 10.6 g/m³. In decontaminating a larger area such as a building, either multiple generators could be used or the area can be decontaminated in sections.

5.3.7 Advantages and Disadvantages

Paraformaldehyde and formaldehyde have been used for equipment and room decontamination for many years and therefore benefit from having a 'track record.' Advantages of formaldehyde gas (such as that generated from paraformaldehyde) include that it is a powerful disinfectant, noncorrosive to metals, and relatively easy to generate from either paraformaldehyde or formalin (Coldiron and Janssen, 1984).

A principal disadvantage is that – unlike the other fumigants covered in this report – formaldehyde is a probable human carcinogen. The other fumigants are toxic at fumigation

concentrations, but they have not been adequately studied to determine carcinogenicity, and thus are of lower-level concern.

5.3.8 Potential Areas for Future Research

Although vapor formaldehyde sterilization has been studied for many years, there is some disparity regarding the concentrations needed to achieve effective decontamination. For example, studies by Munro et al. (1999) identified an optimum concentration as 10,500 mg/m³ for organisms such as *B. subtilis*, while other studies such as Lach (1990) identified that concentrations in the range of 100 to 1,000 mg/m³ were effective for *B. globigii*. The combination of gas concentration, relative humidity, temperature, and contact time that is optimally effective for inactivating *B. anthracis* and surrogates needs to be determined.

In addition, most data available are for organisms on spore strips or on nonporous substrates such as metal. The effectiveness of paraformaldehyde appears to vary, depending on the composition and porosity of the surface being treated. There is a need to better quantify the efficacy of this fumigant on a variety of hard, non-porous (e.g., metal, painted surfaces, glass) and porous (e.g., wood, carpeting) surfaces.

Further studies are needed of the effects of formaldehyde on the functioning and lifetime of sensitive electronic equipment.

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5.4 Methyl Bromide

Methyl bromide is a broad spectrum pesticide. It has been registered under FIFRA as a fumigant for termites, insects, and rodents in buildings, and as a fumigant for agricultural applications. It is known to deplete stratospheric ozone, and is being phased out of some of its applications for that reason.

Methyl bromide, like formaldehyde, appears to function by an alkylation mechanism, rather than by oxidation (as ClO_2 and H_2O_2 do). It has never previously been registered as a sporicide, but recent interest in its possible efficacy against *B. anthracis* (BA) spores has been triggered by the 2001 anthrax mail incident.

5.4.1 Description of the Technology

Following the anthrax mail incident, University of Florida researcher Dr. Rudolf Scheffrahn proposed the application of methyl bromide for the building remediation of BA spores. Tests were conducted, with reportedly favorable results, using simulant spore strips in an office-like setting. A patent application has been filed for the use of methyl bromide as a building fumigant for bacterial contamination (Scheffrahn, 2002). The patent application is under evaluation.

5.4.2 Technical Maturity

Methyl bromide is fully mature in the applications for which it has been registered (fumigation of structures for insects and rodents, and soil fumigation). However, it is still in the experimental stage for use against *B. anthracis* spores.

5.4.3 Applications of the Technology

Methyl bromide gas is most frequently used as a gas fumigant against termites, rodents and nematodes. The majority of use in the US (approximately 85 percent) is for pesticide applications involving soil sterilization (EPA, 2004a). Removal of soil organisms enhances crop yields. Of those applications, most is used for the cultivation of tomatoes and strawberries. Methyl bromide is injected into the soil at a depth of 12-24 inches with the presence of a plastic vapor barrier on top of the soil to restrict the entry of the gas into the atmosphere. While the plastic sheeting slows the release of the gas into the atmosphere, it is estimated that the majority of the gas escapes into the air environment.

Ten percent of the remaining use is for commodity and quarantine fumigation. Methyl bromide is also used to decontaminate the exterior of imported produce such as grapes, nuts, cherries, etc. When used as such the materials are placed in a tent and the methyl bromide is released into the tented structure.

Only five percent of the use is for structural fumigation for rodent and termite control. A building is tented and methyl bromide is released into the structure. While the methyl bromide is not very effective against ground resident termites, it is effective against those that reside in the upper portions of the structure.

Methyl bromide is used in almost all parts of the world. Annual consumption figures for soil fumigation are provided in Table 5.4-1 (Champon, 2004). The United States is clearly the largest user of this fumigant. Although these figures are not current (they are from 1996), they do illustrate a global usage for agriculture.

Table 5.4-1. Global Methyl Bromide Pre-Plant Soil Fumigation: Usage of Methyl Bromide for Pre-plant Soil Applications by Country (1996)

Country	Methyl Bromide Consumption (metric tons)	Methyl Bromide Consumption (lbs.)
United States	15,839	34,908,054
Japan	6,345	13,984,380
Italy	6,000	13,224,000
Israel	2,800	6,171,200
Spain	2,670	5,884,680
France	1,428	3,146,342
Brazil	1,260	2,777,040
Turkey	950	2,093,800
Mexico	900	1,983,600
Zimbabwe	765	1,686,060
Morocco	480	1,057,920
Other	8,461	18,648,044
Total Pre-plant	47,897	105,565,120

Sources: UNEP, 1995, ICF, 1997.

5.4.4 Evaluation of Available Data

Methyl bromide was reported to be toxic to *B. anthracis* spores over 50 years ago (Kolb and Schneiter, 1950). Additional literature reports in the late 1970s by Russian scientists also documented the ability of methyl bromide to kill BA spores (Pilipenko, 1976; Polyakov et al., 1976). Chemical methods for spore remediation were well established for laboratory fumigation (paraformaldehyde) and there was not a pressing need to remediate large structures. Thus this work appeared to go relatively unnoticed until the terrorist acts of sending BA spores through the mail. Contamination of buildings with BA spores changed the conventional wisdom and new methods were sought for large-scale remediation operations.

Dr. Rudolf Scheffrahn, at the University of Florida, Ft. Lauderdale Research and Education Center, began evaluation of methyl bromide for bacterial spore inactivation. Dr. Scheffrahn provided documentation of experiments he conducted or contracted to evaluate the effect of methyl bromide on bacterial spores (Scheffrahn and Weinberg, 2003). Excerpts from those documents are included in this section of the report.

Scheffrahn and Weinberg conducted a series of laboratory experiments where they evaluated the effect of methyl bromide on spores from *Bacillus subtilis* var. *niger* (BSN) and *Bacillus stearothermophilus* (BST). Spore strips containing either 10⁵ BST, 10⁶ or 10⁸ BSN were exposed to methyl bromide. Variables included temperature, time, and concentration of methyl bromide. After incubation the spore strips were removed from their protective envelopes and

transferred into tubes containing growth media, and incubated at the appropriate temperatures for growth of the respective organisms. If there was no growth after one-week incubation the data were scored as “pass” if growth was observed, the data were scored as “fail.” Results are illustrated in Table 5.4-2, which shows the germination of *Bacillus stearothermophilus* 10⁵ and *B. subtilis* 10⁶ combination spore strips after exposure to methyl bromide in 9-liter glass chambers under selected concentration, temperature, and time conditions. Each row represents a single chamber exposure, two strips each.

Table 5.4-2. Spore Germination After Methyl Bromide Exposure

Exposure Date	Temp (°C ¹)	MB conc. ² (mg/L)	Time (hours)	Accum. Dose (mg-hr/L)	Spore Germination: Pass/Fail	
					<i>B. stearo.</i>	<i>B. subtilis</i> strip1 strip2
27Nov01	19	48	63	3,000	fail	fail
27Nov01	19	48	104	5,000	fail	fail
27Nov01	19	48	146	7,000	fail	fail
27Nov01	19	80	112	9,000	pass	fail
27Nov01	19	80	134	11,000	pass	fail
27Nov01	19	80	164	13,120	pass	fail
27Nov01	19	160	164	26,240	pass	fail
10Dec01	20	240	48	11,520	nt ³	fail
10Dec01	20	320	72	23,040	nt	fail
10Dec01	20	320	96	30,720	nt	fail
10Dec01	27	240	48	11,520	nt	fail
10Dec01	27	320	72	23,040	nt	fail pass
10Dec01	27	320	96	30,720	nt	pass pass
10Dec01	27	320	96	30,720	nt	pass pass ⁴
18Dec01	27	320	48	15,360	nt	pass pass
18Dec01	27	320	62	19,776	nt	pass pass
18Dec01	32	160	72	11,520	nt	fail fail
18Dec01	32	240	48	11,520	nt	pass pass
18Dec01	32	240	72	17,280	nt	pass pass
18Dec01	32	320	38	12,160	nt	pass pass
18Dec01	32	320	47	15,104	nt	pass pass

¹ Mean ± 0.4°C.

² Theoretical concentration based on MB volume introduced. Actual concentration is lower. Methyl bromide is a colorless and odorless gas at concentrations harmful or lethal to humans and must be handled with extreme caution by certified personnel. The American Conference of Government Industrial Hygienists (ACGIH) threshold limit value (TLV) for human exposure to methyl bromide is 1 ppm (v/v, 8-hour time-weighted average) (equivalent to 0.004 mg/L) (ACGIH, 2002). The concentrations tested here (48 to 320 mg/L) correspond to 12,500 to 80,000 ppm.

³ nt = not tested. In these tests, both strips were tested for *B. subtilis* germination.

⁴ Chamber contained office commodities listed in text.

The results shown in Table 5.4-2 demonstrate temperature dependence for the methyl bromide. The data also suggest that the absolute methyl bromide concentration is more important than the accumulated dose. The data for 18 December for 160 and 240 mg/L (about 40,000 to 60,000 ppm) have the identical accumulated dose but the lower concentration did not kill the spores even though it has a much longer contact time, 72 versus 48 hours. Most importantly these data provide documentation that methyl bromide is toxic to bacterial spores in a laboratory setting.

The authors expanded on the initial results by conducting additional exposures using BSN spore strips containing 10^8 spores per strip. These results also documented the temperature, time and concentration requirements for exhibiting an eight log reduction in spore population. The data are presented in Table 5.4-3, which shows the germination of *Bacillus subtilis* 10^8 spore strips after exposure to methyl bromide in 9-liter glass chambers under selected concentration, temperature, and time conditions. Each row represents a single chamber exposure, two strips each.

The data presented in Table 5.4-3 indicate that methyl bromide has a killing effect on *Bacillus* spores from these two strains. The fact that only two spore strips were used for each condition prevents statistical evaluation of the results. The fact that one has four variables: temperature, concentration, time, and total accumulated dose, dictates that more experimentation is required to critically evaluate the role of these parameters in the effectiveness of the fumigant.

Table 5.4-3. Germination of Spores After Exposure to Methyl Bromide, Second Test

Exposure Date	Temp (°C) ¹	MB conc. (mg/l) ²	Time (hours)	Accum. Dose (mg-hr/l)	Spore Germination: Pass/Fail	
					Strip 1	Strip 2
26Dec01	27.2	320	48	15,360	fail	pass
26Dec01	27.2	320	72	23,040	fail	pass
26Dec01	27.2	240	48	11,520	fail	fail
26Dec01	32.0	320	48	15,360	fail	pass
26Dec01	32.0	200	48	9,600	control strip failure	
26Dec01	32.0	240	48	11,520	fail	pass
26Dec01	32.0	240	72	17,280	fail	pass
07Jan02	32.3	320	48	15,360	pass	pass
07Jan02	32.3	320	72	23,040	pass	pass
07Jan02	32.3	400	48	19,200	pass	pass
07Jan02	32.3	400	24	9,600	pass	pass
07Jan02	38.3	200	48	9,600	fail	pass
07Jan02	38.3	240	48	11,520	pass	pass
07Jan02	38.3	320	48	15,360	pass	pass
07Jan02	38.3	320	24	7,680	pass	pass

¹ Mean \pm 0.4°C.

² Theoretical concentration based on MB volume introduced. Actual concentration is lower. Methyl bromide is a colorless and odorless gas at concentrations harmful or lethal to humans and must be handled with extreme caution by certified personnel. The threshold limit value (TLV) for human exposure to methyl bromide is 3 ppm (v/v).

As a logical extension of this preliminary laboratory work, the authors applied to the U.S. EPA requesting approval to conduct fumigation of a trailer into which spore strips were placed in various locations. The EPA granted a 15-day crisis exemption and the results of the trailer experiment are discussed below.

Authors Scheffrahn and Weinberg conducted a well-documented experiment to evaluate the effectiveness of methyl bromide in a household or office setting. The abstract from the report is presented in Figure 5.4-1.

A partially furnished 10,000 ft³ mobile home was fumigated with methyl bromide (MB) after 80 *Bacillus* spore strips were placed four each in 20 potential spore contamination sites. A total of 306.5 lbs of MB was introduced to yield a mean time-weighted concentration of 303.7 oz MB/1,000 ft³ (about 300 mg/L, or 80,000 ppm) during the 48-hour fumigation. Mean temperatures near spore strips during fumigation ranged between 90-95 °F and relative humidity ranged from 39-69 percent. Of the 40 combined *B. subtilis* 10⁶ and *B. stearothermophilus* 10⁵ spore strips recovered after the fumigation, none showed germination and growth. Of the 40 *B. subtilis* 10⁸ spore strips placed, only 4 (10 percent) produced vegetative cells during incubation. During fumigation, 0-2.5 ppm MB was detected downwind from the structure. During aeration, downwind MB concentrations ranged from 60 ppm at 20 ft to 0 ppm at 150 ft. No damage was detected among the electronic, photographic, cellulosic, fabric, or other commodities fumigated. A transient organic odor was detected up to 7 days after the fumigation.

Figure 5.4-1. Abstract of Scheffrahn and Weinberg Study

Sets of four spore strips were placed in twenty different locations throughout the trailer in an attempt to identify areas that would be hard to reach. Illustrations of some of the placements are shown in Figure 5.4-2.

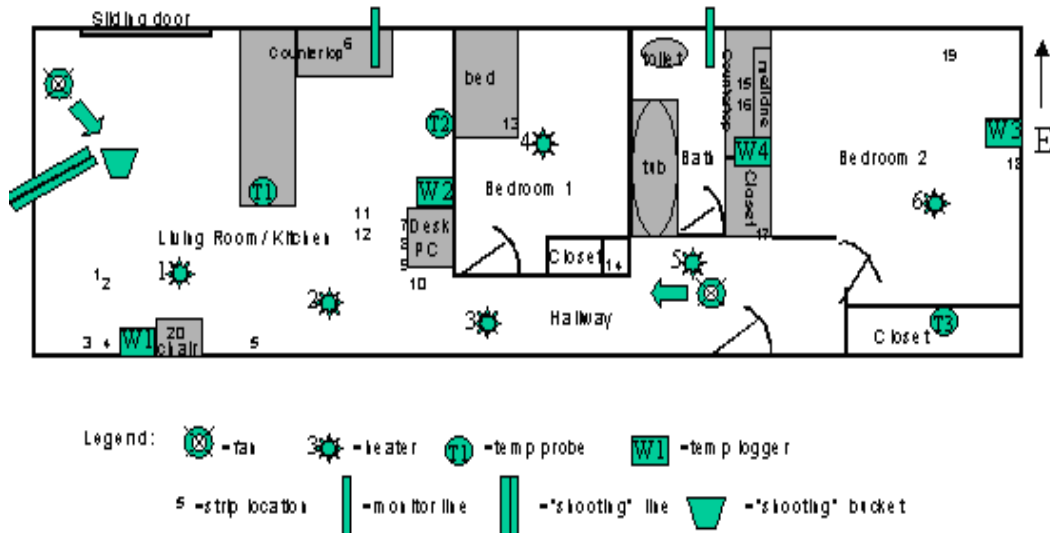


Figure 5.4-2. Trailer configuration

Figures 5.4-3 through 5.4-5 show spore strip placements. The trailer was prepared for methyl bromide fumigation by covering with two tarpaulins that are clamped together and sealed to the ground with sand “snakes” as shown in Figure 5.4-6.



Figure 5.4-3. Spore strip sites 1 and 2 (see Table 1). Clockwise from top left: Strips in sub floor ducting under vent; vent in place. Strips under carpet; carpet in place.



Figure 5.4-4. Spore strip site 13. Left: strips under mattress.



Right: mattress in place.



Figure 5.4-5. Spore strip site 3. Left: strips inside wall insulation. Right: paneling in place.



Figure 5.4-6. The Prepared Trailer

Methyl bromide was introduced into the trailer and circulated with fans. Heaters were utilized to keep temperatures elevated. Methyl bromide concentration was monitored, and additional gas was added when the levels fell below optimal concentration. The profile of methyl bromide concentration is graphed in Figure 5.4-7. As shown, the average MB concentration during fumigation was 303.7 oz per 1,000 ft³ (equivalent to approximately 307 mg/L, or 80,000 ppm).

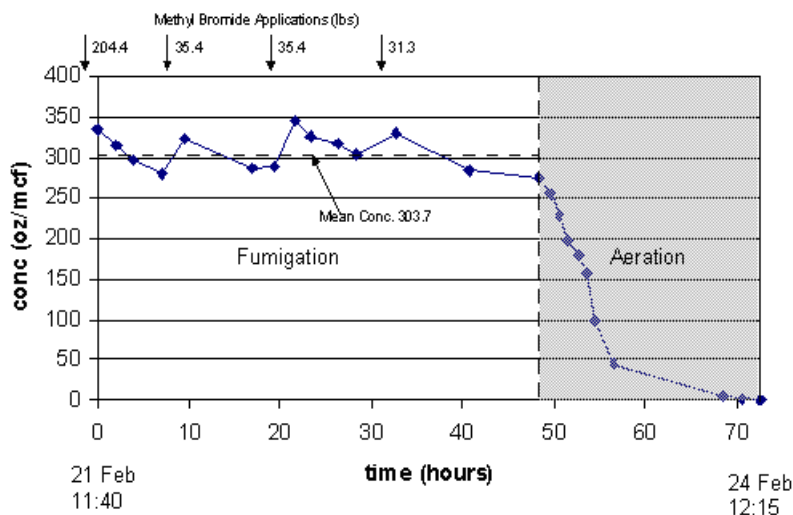


Figure 5.4-7. Methyl Bromide Concentration During Trailer Fumigation and Aeration

Following aeration the spore strips were removed and analyzed for growth. The results are indicated in the table below. Out of 80 spore strips, four demonstrated positive growth. The four strips that resulted in growth contained 10⁸ BSN spores. It is important to note that the higher density spore strips were placed in duplicate. In all cases the duplicate of the spore strip that demonstrated growth had no growth. These results are consistent with a threshold kill in these locations. All four of these locations were in hard to reach locations: inside ducting, in a closed folder on floor, under a mattress, and in a closed closet.

The results of this study suggest that methyl bromide can be an effective fumigant against these surrogate organisms. The apparent ability of methyl bromide to penetrate porous materials without discoloration is a very encouraging observation.

Following these favorable results, the authors requested EPA funding to evaluate methyl bromide against *Bacillus anthracis* spores in a laboratory environment. The resulting report is reprinted in Figure 5.4-8.

Table 5.4-4. Spore Strip Location, Proximal Ambient Temperature Conditions, and Incubation Results for 80 Strips After Exposure for 48 Hours to Methyl Bromide at a Concentration of 303.7 oz/1,000ft³ in Trailer

(Pass = No Spore Germination Occurred; Fail = Spore Germination Occurred)

Trailer Location No. and Description	Exposure Temperatures °F			10 ⁶	10 ⁵	<i>B. subtilis</i> 10 ⁸	
	Mean	Max.	Min.	<i>B. sub.</i>	<i>B. stear.</i>	Strip A	Strip B
1-Floor vent, inside ducting	95.12	98.8	89.6	pass	pass	pass	fail
2-Under carpet fabric	95.12	98.8	89.6	pass	pass	pass	pass
3-Behind wall paneling in insulation	95.12	98.8	89.6	pass	pass	pass	pass
4-Wall plug outlet, covered	95.12	98.8	89.6	pass	pass	pass	pass
5-Wall surface, in closed folder	95.12	98.8	89.6	pass	pass	pass	pass
6-Closed kitchen cabinet	95.07	98.8	89.6	pass	pass	pass	pass
7-PC keyboard, inside back cover	95.07	98.8	89.6	pass	pass	pass	pass
8-PC CD tray, closed	95.07	98.8	89.6	pass	pass	pass	pass
9-Desk drawer, closed	95.07	98.8	89.6	pass	pass	pass	pass
10-Desk drawer, in closed hanging file	95.07	98.8	89.6	pass	pass	pass	pass
11-Ceiling surface, exposed	95.07	98.8	89.6	pass	pass	pass	pass
12-Floor surface, in closed folder	95.07	98.8	89.6	pass	pass	pass	fail
13-Mattress, under box spring	95.07	98.8	89.6	pass	pass	fail	pass
14-Hall closet, closed	90.29	94.1	83.6	pass	pass	fail	pass
15-Medicine cabinet, closed	90.29	94.1	83.6	pass	pass	pass	pass
16-Light fixture, secured globe	90.29	94.1	83.6	pass	pass	pass	pass
17-Central AC inlet, behind filter	90.29	94.1	83.6	pass	pass	pass	pass
18-Window AC, behind filter	93.24	100.2	88.2	pass	pass	pass	pass
19-Under newspapers	93.24	100.2	88.2	pass	pass	pass	pass
20-Recliner chair, under cover fabric	95.12	98.8	89.6	pass	pass	pass	pass

The three sets of experiments by Dr. Scheffrahn summarized above suggest that methyl bromide may be an effective fumigant against Bacillus spores. The data are consistent and supportive of further examination into the possibility of using methyl bromide for the remediation of buildings contaminated with biological materials. (A fourth test in the trailer, utilizing a slightly lower MB concentration, provided more ambiguous results regarding spore kill, which had not been explained at the time of this writing; this underscores the need for further testing.)

Little data were found regarding reactivity of methyl bromide with common building elements such as paints and fabrics. It is reported incompatible with aluminum, dimethyl sulfoxide, strong acids, strong oxidizers, strong bases, nitrates, and alkaline earth metals according to the Materials Safety Data Sheet (MSDS). Thus, methyl bromide may affect some materials found in homes or buildings.

The study, IITRI 2050, investigating the disinfectant capabilities of methyl bromide (MB) against *Bacillus anthracis*, *Bacillus atrophaeus* (ATCC 9372, formerly *Bacillus subtilis*), and *Geobacillus stearothermophilus* (ATCC 7953, formerly *Bacillus stearothermophilus*) spores is complete. The protocol and results are as follows:

Bacillus anthracis ANR-1 was grown on sporulation media, harvested into deionized water, heat-shocked, and stored as a spore suspension. The final concentration of this spore suspension was approximately 1×10^9 spores/ml. Individual glass coverslips were spiked with an aliquot (10 ml - ca. 10^7 spores) of the spore suspension, which was spread evenly over the surface and allowed to dry. Two coverslips were placed into each of the experimental chambers, and three coverslips were placed into the control chamber. In addition, two spore strips containing *G. stearothermophilus* (Raven Biological Laboratories, Inc., Omaha, NE) and one spore strip containing *G. stearothermophilus*/*B. atrophaeus* (Raven Biological Labs) were placed into each chamber. A damp sponge (1 x 1 x 3-cm) was placed into chambers 1, 3, 5, and 7 to increase the relative humidity. Data loggers were placed in chambers 6 and 7 to allow monitoring of internal temperature and relative humidity.

Each chamber was sealed so that a minimum of 1 cm unbroken grease seal was visible for the entire circumference of the chamber. After sealing, the appropriate volume of methyl bromide (MB) gas was injected into the chambers. The gas was injected using a 100 ml syringe, and pressure was equalized after each 100 ml of MB added. A fan was run continually in each chamber during loading, to ensure uniform distribution of the MB over the entire chamber.

Loaded chambers were incubated at 37 °C (99 °F) for 48 hours. The pressure was equalized 2 hours after placement in the incubator, and the temperature and humidity were monitored daily. The relative humidity ranged from 21-22 percent in chamber 6 (no sponge) to 92-100 percent in chamber 7 (with sponge). After the 48-hour fumigation, the chambers were removed from the incubators and vented to allow release of the MB. The *B. atrophaeus*/*G. stearothermophilus* spore strips were removed from their envelopes and placed into Trypticase Soy Broth containing a colorimetric reagent (Raven Biological Labs). Each *B. anthracis* coverslip was placed into a sterile beaker containing 50 ml sterile water and a stir bar. The coverslips were stirred vigorously for 60 minutes to remove any remaining spores from the surface. Serial dilutions of the water were made and plated onto Trypticase Soy Agar. All plates and the *B. atrophaeus* tubes were incubated for 48 hours at 37 °C, and counted (plates) or scored for growth/no growth (tubes). The *G. stearothermophilus* tubes were incubated for 5 days at 55°C and scored for growth/no growth. The results are seen in Table 1.

Figure 5.4-8. Summary of IITRI Research Findings

Recovery of viable spores after exposure to methyl bromide.

Chamber	Accumulated Dosage	Glass Carriers Spiked With	Commercial Spore Strips		
	mg-hour/L MB	<i>B. anthracis</i>	<i>B. atrophaeus</i>	<i>G. stearothermophilus</i> A	<i>G. stearothermophilus</i> B
1 ^a	3840	0	growth	no growth	no growth
2	5760	0	growth	no growth	no growth
3 ^a	7680	0	no growth	no growth	no growth
4	9600	0	no growth	no growth	no growth
5 ^a	11520	0	no growth	no growth	no growth
6 ^b	13440	0	growth	no growth	growth
7 ^{a,b}	15360	0	no growth	no growth	no growth
10 (control)	0	1.41 x 10 ⁷	growth	growth	growth

^a Chambers contain damp sponge.

^b Chambers contain humidity and temperature logger.

All concentrations of MB tested induced a 6-log or greater reduction in *B. anthracis* spores. The limit of detection on this assay is 50 spores per coverslip. The lowest two concentrations of MB were insufficient to kill all *B. atrophaeus* spores on a spore strip, but were capable of killing all *G. stearothermophilus* spores on a spore strip. Chamber 6 showed some anomalous results. While lower concentrations of MB were sufficient to disinfect both *B. atrophaeus* and *G. stearothermophilus* in the other chambers, this chamber showed growth for two of the three spore strips despite the high CT. The reason for this is unclear. Concentrations of MB in the chambers are computed, not measured during the tests, so perhaps an experimental problem resulted in lower than expected MB concentrations in Chamber 6. No leaks in the grease seal were observed at the time of unloading. It is of interest to note that the *B. anthracis* spores in Chamber 6 were completely killed.

Figure 5.4-8. Summary of ITRI Research Findings (concluded)

5.4.5 Concerns for the User

Methyl bromide is highly acutely toxic with a TLV of 1 ppm, resulting in degenerative effects of the nasal cavity and membranes affecting the sense of smell (ACGHI, 2002). The concentrations of up to 80,000 ppm that must be maintained in a building for 48 hr to fumigate for *B. anthracis* are dramatically higher than the TLV. The toxicity is a major consideration at the release points because it is odorless and colorless at dangerous levels. Accordingly, in building fumigations using methyl bromide for pest control, about 1% chloropicrin (tear gas) is added as a warning agent.

The current EPA IRIS classification for methyl bromide is 'D- not classifiable as to human carcinogenicity' (EPA, 2004b). In two-year inhalational carcinogenicity and toxicity studies conducted in mice by the National Toxicology Program, methyl bromide did not induce tumors

in either male or female mice. However, significant neurological effects were noted in mice at the highest dose (NTP, 1992).

It is estimated that between 50 and 95 percent of the methyl bromide used to fumigate structures to rid rodents and insects ends up in the atmosphere (EPA, 2004a). Methyl bromide release to the atmosphere is a serious consideration. Due to the effect of methyl bromide on ozone depletion, the gas will be phased out for U.S. operations by 2005 as a result of the Clean Air Act and Montreal Protocol. In spite of the phase out for most commercial applications, the chemical will still be available for critical agricultural and emergency uses in the U.S. The use of methyl bromide as a fumigant for biological warfare contamination of a building is considered an emergency application.

Methyl bromide is a stable gas and is dispersed into the atmosphere following pesticidal fumigations. This property is a distinguishing factor from paraformaldehyde, vapor-phase hydrogen peroxide, and chlorine dioxide, all of which either self decompose or are neutralized by the introduction of another chemical at the completion of the fumigation.

Venting of highly toxic methyl bromide to the atmosphere is currently legal under current EPA-registered pesticide applications of this product. However, given the large amounts of very high-concentration gas (about 80,000 ppm) that could be present in a building being fumigated for *B. anthracis* sterilization, the venting of this building air may raise concerns, especially in densely populated areas. Given the TLV value of 1 ppm, and given prior experience with the oxidizing fumigants discussed in the previous chapters, a methyl bromide concentration at the building's fence-line would probably need to be maintained at a value below 1 ppm. Unless a reliable technology is demonstrated for removing methyl bromide from the building air being vented, and if dilution alone is to be relied upon to protect neighboring populations, a substantial dilution of the exhaust air would be required to meet the desired fence-line concentrations.

A method of removing methyl bromide from the building air that is vented outdoors is thus crucial, not only from the standpoint of its ozone-depleting characteristics, but from the standpoint of the health issues raised above. The absence of a demonstrated approach for sorbing or otherwise destroying methyl bromide prior to release is a major issue that needs to be addressed.

5.4.6 Availability of the Technology for Commercial Applications

Methyl bromide is registered by EPA as a pesticide, and is available for commercial applications as a pesticidal fumigant in buildings and agricultural applications. However, the compound is not registered as a sporicide. A patent application has been filed in the U.S. for the use of methyl bromide against bacterial spore contamination in buildings. A final decision regarding the patent application has not been made. And, as discussed above, additional data appear to be required before this fumigant could be safely utilized for bacterial sterilization of large buildings.

The application of methyl bromide is relatively straightforward. Monitors for the gas levels, both inside and outside buildings are commercially available.

Methyl bromide is a stable gas. As demonstrated in the trailer test, gas must be added periodically to structure in order to make up for leakage, demonstrating the need for highly effective sealing of the enclosure being fumigated. Three additions of approximately fifteen percent of the original load were required over a forty-eight hour period to compensate for leakage through and under the tarps over the trailer. The cost of methyl bromide gas is projected by the developers to be low compared to the cost of generating and distributing chlorine dioxide or hydrogen peroxide vapor into a structure.

The common practice when using methyl bromide for building fumigation for pest control is to let the gas vent into the atmosphere. However, if the gas is to be used at concentrations on the order of 80,000 ppm for treatment of large buildings that must be kept at negative pressure, an effective means for scrubbing the methyl bromide from the building air before release is critical, to remove concerns about damage to the ozone layer and potential exposure of humans in the vicinity.

5.4.7 Advantages and Disadvantages

The main advantage of this technology is that it appears to be effective against *Bacillus anthracis* and surrogate *bacillus* species under conditions that are achievable at a small building scale. The log kill obtained in laboratory and field trials meets or exceeds the EPA sterilization requirement. The ability of the gas to penetrate porous surfaces and any cracks or crevices demonstrates that the gas will reach all locations that a spore could reach. The gas does not appear to discolor photographs or printed material.

The main disadvantage of methyl bromide is the potential for human exposure to the highly toxic gas and the potential for ozone layer damage, unless a method can be developed to neutralize or scrub the methyl bromide from the air that is vented from a structure during and following fumigation. In addition, 50 to almost 400 time higher concentrations of methyl bromide must be used to fumigate for *B. anthracis*, compared to the required concentrations for the other three fumigants covered in this report, and 4 to 12 times longer contact times are needed.

Methyl bromide is scheduled for phase-out in some of the applications for which it is currently registered by 2005. However, research is currently continuing into its applicability for anthrax decontamination in buildings, to determine whether it offers potential (e.g., due to its penetrability) such that perhaps it should remain available for such emergency applications.

5.4.8 Potential areas for future research

The preliminary data for methyl bromide killing of *Bacillus* spores suggests potential, but significant additional efficacy data are required over a range of conditions. In addition, there is a compelling need for development and demonstration of a means for removal of methyl bromide from the air exhausted from a building during and after fumigation, to protect people from its toxic effects and to prevent depletion of the stratospheric ozone layer. Furthermore, rigorous engineering analysis is required to evaluate the issues involved in scaling up the methyl bromide fumigation technology, from residential pest-control applications to large-building biological decontamination applications.

Because methyl bromide is a strong alkylating agent, it may be interesting to perform preliminary studies to evaluate its effect on chemical warfare agents. If methyl bromide is effective against chemical warfare agents, it might be a candidate for broad spectrum remediation (addressing both chemical and biological agents).

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