L-Gel Decontaminates Better Than Bleach

Scientists have developed a material that is safe for people and the environment but deadly to the agents of biological and chemical warfare.

HE recent cases of anthrax spores deliberately spread through the mail reminded all Americans, and especially managers of federal and state agencies responsible for public health and safety, about potential terrorism with chemical and biological weapons. The anthrax cases have also underscored the need for safer and more efficient methods to decontaminate offices and homes of deadly biological agents.

During the late 1990s, scientists at the Department of Energy national laboratories foresaw the need for a safe, reliable, and easily deployable decontaminating agent that could be used for civilian defense against biological and chemical terrorism. DOE managers agreed with the scientists and asked them to use their expertise in chemistry, biology, and environmental protection to develop new decontamination products and procedures.

Lawrence Livermore responded to this request with a team formed from the Environmental Protection Department and three directorates— Chemistry and Materials Science; Nonproliferation, Arms Control, and International Security; and Biology and Biotechnology Research. The team of diverse experts developed a compound called L-Gel (the L is for Livermore), which combines a mild, commercially available oxidizer with a silica gelling agent to create a substance that coats walls, ceilings, and other materials like a paint, effectively decontaminating the coated surface.

The material is nontoxic, noncorrosive, easy to manufacture, easily deployable, and relatively inexpensive (about \$1 to cover a square meter). Tests at Livermore's laboratories and field trials at both federal and foreign facilities have shown that L-Gel has been extremely effective at decontaminating all classes of chemical warfare agents as well as surrogates for biological warfare agents.

Livermore technology transfer specialists are currently engaged in negotiations with several companies to license the manufacturing and marketing of L-Gel. If negotiations proceed apace, government agencies could have the material by the end of the fiscal year (September 30) to respond to any terrorist incident involving chemical or biological agents.

Different Needs for Civilians

According to L-Gel development leader Ellen Raber, a geochemist and head of Livermore's Environmental Protection Department, several decontaminating agents are effective against either chemical or biological warfare agents. However, these materials, which are mainly strong chemicals, were developed by the military for battlefield use, and they pose environmental and health risks when used in civilian settings. At the minimum, they can damage everyday materials such as furniture and office equipment.

Other methods that have been used in civilian settings have serious drawbacks. For example, solutions of laundry bleach work well as decontaminants but are very corrosive. Incineration and irradiation have obvious practical limitations in office settings or face public resistance. Chlorine dioxide gas, used late last year to decontaminate the Hart Office Building that houses members of the U.S. Senate, is a laborious process and poses a safety risk to workers. It also requires the gassed building to be neutralized before people can reenter.

The Livermore team focused on finding an effective decontaminating agent and application system that is safe to use, does not damage commonly used materials and surfaces, is friendly to the environment, and is effective against both chemical and biological warfare agents. "We wanted something that was less corrosive than bleach, that is easy to apply, and that does not leave workers with a huge cleanup job," Raber says.

Raber points out that speed of decontamination, which is all-important in military applications, is less important in civilian applications, where decontamination times of one to several hours may be adequate. More important in a civilian scenario are ease of application, minimal training required for use, moderate expense, and environmentally acceptable byproducts.

The team also recognizes that the new product needs to be effective in three potential settings of a terrorist incident against civilians: an outdoor location such as a stadium, a semienclosed place such as a subway station, and an enclosed space such as an office building. Using the decontaminating material on interior surfaces can have quite different requirements from those appropriate for outdoor use, where natural attenuation from environmental conditions (for example, ultraviolet radiation from sunlight) might well be adequate for effective decontamination.

Start with the Oxidizer

The development effort began with Livermore scientists Ray McGuire and Don Shepley evaluating several acidic oxidizer solutions that could degrade chemicals into nontoxic, environmentally acceptable components. (Oxidizing solutions do not completely destroy chemical agents but rather break key chemical bonds to render the toxic compound inactive.) The oxidizers considered could be deployed in liquid spray systems or incorporated into compatible gels for clinging to surfaces such as ceilings and walls.

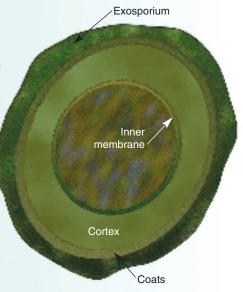
McGuire chose an acidic rather than a basic oxidizer solution, primarily to aid the decontamination of VX, a potent nerve agent. Acidic oxidizer solutions are also known to be effective at decontaminating certain biological warfare agents, including bacterial spores, which are extremely difficult to kill because of their hard, multilayered coats. The coat allows a spore to remain in a dormant state for many years until, under the right environmental conditions, it transforms into a live organism.

"Anthrax is the most difficult biological agent to kill because of its resistant outer coat," says Raber. An oxidizer in acidic solution breaks down the proteins that are found in anthrax coats. Once the oxidizer gets through to the nucleus, its molecules destroy strands of the anthrax DNA or RNA.

The goal was to find the most effective oxidizer at the lowest effective concentration. The oxidizers that were evaluated included potassium permanganate, peroxydisulfate, peroxymonosulfate, hydrogen peroxide, and sodium hypochlorite. The oxidants were evaluated in laboratory tests on chemical warfare surrogates for such agents as VX, sarin (used in the Tokyo subway terrorist incident), and sulfur mustard (used during World War I).

Livermore bioscientist Paula Krauter evaluated the same group of oxidizers on surrogate biological agents and toxins that would likely be used in terrorist attacks. *Bacillus subtilis* was used for spore-forming agents such as anthrax, *Pantoea hericola* was the surrogate for plague, and ovalbumin was the surrogate protein for botulinum toxin.

The initial laboratory tests showed that potassium peroxymonosulfate was more than 99 percent effective at oxidizing both chemical and biological warfare surrogates that were placed on common materials such as carpet, wood, and stainless steel. The results led to the selection of Oxone, a commercial product manufactured by DuPont, which contains potassium peroxymonosulfate-its active ingredient-in a water solution. Previous research at U.S. military laboratories had demonstrated the effectiveness of Oxone in decomposing both VX and mustardtype agents, but the compound had not been previously tested on biological agents.



The cross section of a bacterial spore, such as anthrax, shows its hard, multilayered coats, which both make the spore difficult to kill and allow it to remain dormant for many years.

Gel Adds Staying Power

The team recognized that spraying water-based solutions of Oxone would not be effective in all cases. Consequently, McGuire and Mark Hoffman investigated carrier materials that would thicken the oxidizer so it would better cling to walls, ceilings, and other surfaces to increase contact time with the biological or chemical agent.

Hoffman chose colloidal amorphous silica as the carrier material for several reasons. First, unlike crystalline silica, which is toxic, colloidal amorphous silica is safe to use and is found in many household paint formulations. Also, silicon dioxide colloidal particles are commercially available, don't require manufacturing in a special facility, and, because they are chemically inert, are compatible with oxidant solutions. When mixed with the oxidizer, the gel can be applied with simple delivery systems, such as paint sprayers. After application, it thickens and tends not to sag or flow down walls or drip from

ceilings. Finally, silica gel materials can be easily vacuumed up after they have dried.

Livermore chemists have extensive experience with colloidal silica gel. From the late 1960s to the late 1980s, the chemists developed a series of extrudable high explosives based on the gelling of energetic liquids. Although this research did not advance to the explosives production stage, the development effort provided useful experience for working with silica-gel materials. It was a logical step to adapt this work to the gelling of aqueous oxidizers for candidate decontaminants, says Hoffman. "Our research with high explosives gave us a good feel for working with silica gels."

Hoffman selected Cab-O-Sil EH-5 fumed silica as the gelling agent. The final formulation was named L-Gel 115, which is a formulation of aqueous Oxone solution gelled with 15 percent EH-5 silica gel. The viscosity can be varied, depending on the application. Under development is a

The biocidal effect of peroxymonosulfate, the oxidizer in L-Gel, is seen on this nutrient agar plate of Bacillus subtilis spores (surrogates for anthrax). Three spots of silica gel were added to the plate. Two of the spots contained peroxymonosulfate and one (at right) did not. The peroxymonosulfatecontaining gel inhibited spore germination in the zone surrounding the gel, even leaching into the agar.



second formulation, called L-Gel 200, which contains 10 percent t-butanol cosolvent to promote penetration on surfaces with heavily coated paint or varnish.

Field Tests Prove Effectiveness

The final L-Gel 115 formulation was subjected to a series of tests at Livermore facilities using surrogates of potential terrorist chemical and biological agents. The tests involved placing surrogate chemical and biological agents on various common materials-varnished wood, painted steel, glass, fiberglass, and carpetadding L-Gel to the surface, allowing the gel to dry for 30 minutes to several hours, and then determining the percentage of surrogate that had been decontaminated. L-Gel proved greater than 99 percent effective on all surfaces and for all agents.

The Livermore biological researchers also tested L-Gel on safe strains of the deadly biological agents Bacillus anthracis (anthrax) and Yersinia pestis (plague). These strains-Sterne and Strain D27, respectively-could be safely used in experiments because they are nonvirulent, that is, they do not contain the genes that create the lethal toxins present in the real organisms. (See the article beginning on p. 4 about research on sources and pathways of virulence in organisms.) The researchers used the agar plate resistance test, a standard technique to measure the efficacy of antibiotics. In this test, about one million cells (or spores, in the case of B. anthracis) were combined with liquid agar, then poured onto a petri dish containing nutrients for cell growth. The strains were also tested against dilutions of L-Gel, which proved more than 99.9 percent effective in killing the cells and spores.

L-Gel also was tested against surrogate spore-forming bacteria in two field exercises. In December 1999. researchers Krauter and Tina Carlsen participated in biological warfare field tests that were conducted by the Soldier Biological and Chemical Command at the U.S. Army Dugway Proving Ground, Utah. The tests compared the ability of several decontamination materials to inactivate surrogate organisms placed on six 40-squarecentimeter panels of acoustic ceiling tile, tightly woven carpet, fabric-covered office partition, painted wallboard, concrete slab, and painted metal. Each panel was contaminated with about 10 billion spores per square meter.

After L-Gel was applied, the panels were swabbed about 24 hours later.

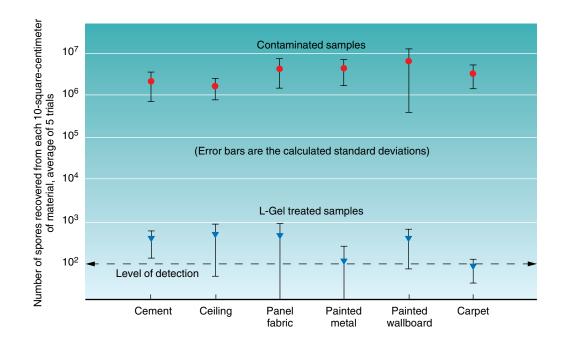
The number of live spores on most test panels was reduced by an average of 99.988 percent.

In October 2000, Krauter and Hoffman participated in a biological warfare agent room-decontamination exercise that was conducted again at the Dugway Proving Ground. The tests used full-scale, mock offices constructed in an abandoned building. Flooring was divided into quarters consisting of carpet, vinyl tile, varnished oak, and painted concrete. Walls consisted of stucco, wood paneling, plasterboard, and carpet, and the ceiling was constructed of suspended ceiling tile. The room was contaminated with 4 grams of spores. After application of L-Gel, about 400 samples were collected from multiple locations in the





Researcher Paula Krauter applies L-Gel to "contaminated" panels of different materials to test the gel's effectiveness.



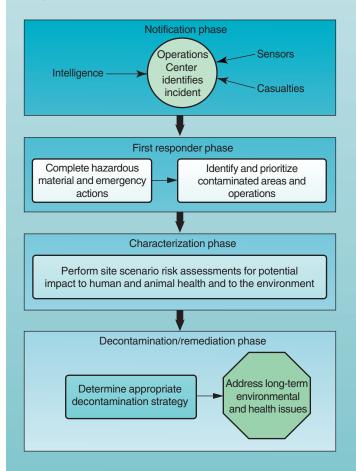
L-Gel was tested against surrogate spore-forming bacteria at the Soldier Biological and Chemical Command at the U.S. Army Dugway Proving Ground, Utah. In one test, surrogate organisms were placed on six 40-square-centimeter panels of acoustic ceiling tile, tightly woven carpet, fabric-covered office partition, painted wallboard, concrete slab, and painted metal. L-Gel reduced the number of live spores on most test panels by an average of 99.988 percent.

How Clean Is Clean Enough?

When a terrorist attack on civilians potentially involves biological or chemical warfare agents, decision makers will need to make fast and informed choices about how to respond. A team of Livermore researchers from the Safety, Security, and Environmental Protection Directorate has developed a process that guides users to make the best emergency response decisions involving notification, identification, characterization, decontamination, and cleanup.

In 1998, at the request of DOE's Office of Nonproliferation and National Security, the team developed a biological agent decontamination plan in the form of a flowchart. It was then used in a recommendation from the Environmental Protection Agency to the National Security Council, the President's principal forum for considering national security and foreign policy issues. In 2001, the Livermore team added chemical warfare agents to the plan, now termed the Chemical and Biological Agent Decision Process.

The process helps users to determine what actions need to be taken at the outset; if an actual or potential impact to health, property, or the environment exists; whether or not decontamination is needed; what steps should be taken and when; and how to verify that cleanup and remediation are complete so that the area can be designated as safe to reenter or reuse.



Under the process, each of four phases (notification, first responder, characterization, and decontamination/remediation) progresses to the next phase as soon as all its issues have been addressed. The format includes numerous yes/no decision points and links to more detailed information on specific topics. The decision process takes into account different environments, such as an outdoor site, and considers individuals in the general population who may be at higher risk for illness and injury.

According Ellen Raber, head of Livermore's Environmental Protection Department, the biological agent decontamination plan addresses a need by several federal agencies for an up-to-date summary of information necessary to evaluate acceptable decontamination levels and procedures. The goal of the plan is to help minimize the number of deaths and illnesses, damage to the natural and built environment, and the extent of economic damage (for example, crop or livestock damage) resulting from a biological terrorism incident.

In developing the plan, Livermore experts did a thorough literature search and consulted with colleagues at the U.S. Army, the U.S. Environmental Protection Agency, and federal health agencies, including the U.S. Public Health Service. The team noted that responding to a civilian event involves different priorities than those for a military setting. For example, during a battle, quick decontamination is critical so soldiers can continue their mission. In a domestic urban scenario, however, considerations of public health and environmental issues are usually more important than immediate decontamination. Also, the decontamination process may need to be staged, with cleanup of gross contamination—for example, of puddles of toxic materials—followed by more localized decontamination, such as cleaning up materials in cracks.

The flowchart is structured so that cleanup criteria are dependent upon the decontamination site. Much stricter criteria are necessary for indoor settings such as offices or homes than for outdoor scenarios where wind, sunlight, temperature, and rain may effectively decontaminate biological agents, toxins, and chemical warfare agents.

Raber says the decision process must include answering the question, "How clean is clean enough?" In this respect, it is more difficult to establish target cleanup levels for biological agents than for chemical agents, in large part because of public acceptance and perception issues. She notes that the public may demand zero living organisms after decontamination, but achieving such a level may not be practical or necessary. In the case of anthrax, for instance, it takes about 6,000 inhaled anthrax spores to cause respiratory anthrax. Furthermore, some biological agents such as anthrax are already indigenous to many farming communities and exist without incident. "Zero concentration of a biological agent and zero risk, in many cases, are clearly not a necessity," she says.

Raber also points out that it is possible to do a poor job of decontamination and to make it look good by doing a poor job of sampling and analysis. "In the end, decontamination must be defensible to regulatory agencies and to the public." room. L-Gel reduced the number of spores by about five orders of magnitude and, in these experiments, did not damage office surfaces, with the exception of bleaching some rust on ceiling supports.

L-Gel was also independently tested on real chemical warfare agents at four locations from October 1998 to October 2000. The tests were conducted at the Military Institute of Protection, Brno, Czech Republic; Edgewood Chemical and Biological Forensic Analytical Center, Maryland; the Defense Evaluation and Research Agency, United Kingdom; and the Soldier Biological and Chemical Command at Dugway. Field tests showed that L-Gel was a more effective decontaminant of real VX. GD (nerve agent), and sulfur mustard than the current military standard, calcium hypochlorite, on such materials as acrylicpainted metal, polyurethane-coated oak flooring, and indoor-outdoor carpet.

Two of the field trials also demonstrated that the L-Gel 200 formulation has improved penetration and thus promotes solution and oxidation in thickened chemical agents. L-Gel 200 was tested on real chemical warfare agents such as thickened distilled mustard and thickened soman (persistent nerve agent) as part of the Restoration of Operations series of experiments at Dugway Proving Ground. The agents were applied on steel test panels, Air Force air–ground equipment paint, and Navy shipboard coating.



A second test at the Dugway Proving Ground in Utah tested L-Gel in a mock office setting.

Meets Safety Standards

With L-Gel's excellent performance demonstrated in both laboratory and field trials, it was time to partner with one or more commercial firms that could manufacture the material quickly and efficiently. Fortunately, says Raber, "L-Gel is simple to manufacture. It's comparable to mixing paint." L-Gel is relatively noncorrosive (its pH is about 4, similar to that of vinegar or lemon juice), and Environmental Protection Agency testing shows its residual materials to be nonhazardous. It also meets the Department of Transportation's nonhazardous and noncorrosive requirements and is stable during shipping.

L-Gel is premixed and then shipped and stored as a semisolid resembling Jello at room temperature. If unopened, its shelf life is expected to exceed a year. It is reliquefied to the consistency of house paint by vigorous shaking by hand or a power stirrer. It can be applied with any type of commercially available spray device, whether airless or compressedair units, with any stainless-steel atomizing nozzle.

Although L-Gel clings to walls and ceilings, it does not harm most painted surfaces or carpets. Decontamination takes about 30 minutes. When dry (in about 1 to 6 hours), the gel residue, unreacted oxidizer, and decontaminated chemical or biological agents can simply be vacuumed up and discarded as nonhazardous waste. For outdoor use, no cleanup is required.

Raber says L-Gel compares favorably to other decontamination methods that have been used recently to kill anthrax spores. The tried-andtrue method is a bleach solution. However, bleach is extremely corrosive to metal surfaces and must be used with care by cleaning crews.

A foam developed at Sandia National Laboratories in New Mexico has also been effective for decontaminating chemical and biological agents. This material is sprayed on surfaces like a firefighting foam. Most of the foam dissipates, and the residual material is then washed off. It has been used to clean offices of Congress and at ABC News. Raber suggests that L-Gel and the Sandia foam could work in tandem, with L-Gel sprayed on walls and ceilings and the Sandia foam applied to large pieces of equipment and floors.

Chlorine dioxide, used to decontaminate U.S. Senate offices, is a gas that kills bacteria but also is



hazardous to human health and thus must be applied by trained personnel. Afterward, its vapors must be sucked out of rooms and then filtered through an ascorbic acid bath to decompose it. Raber notes that gases and aerosols have clear advantages for decontaminating ventilation systems and hidden spores, and research needs to continue to find an environmentally safe gas or aerosol that is effective for these applications.

Irradiation, popular in Europe, kills bacteria and spores and is effective in decontaminating mail, food, and other objects. However, the method requires large machines, which are essentially small accelerators, and is not currently viable for large-scale room decontamination.

In the News

News about L-Gel has spread rapidly, and Raber has been interviewed by several newspapers, television stations, and National Public Radio. She has also received a large number of inquiries from emergency response groups across the country interested in additional information and samples.

The developmental work for L-Gel 115 is complete, and Raber's team has begun to develop a new formulation to decontaminate ventilation systems. "Right now, we don't have an



Livermore chemist Mark Hoffman uses a household paint sprayer to apply L-Gel to a test panel.

easy way to decontaminate air ducts," she says. The team is working on an encapsulation method to aerosolize L-Gel (make it into tiny droplets) so that it could be blown into ventilation systems.

In the meantime, licensing of L-Gel manufacture is well under way, and Raber is hopeful that major organizations will soon have an important yet nontoxic new weapon to counter any biological or chemical attack.

-Arnie Heller

Key Words: anthrax, biological warfare, Chemical and Biological Agent Decision Process, chemical warfare, decontamination, L-Gel, peroxymonosulfate.

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