Global Environmental Operations, Inc.

Minimizing Adverse Effects of
Military Decontamination

by

David L. Russell, P.E.

Synopsis:

In the event of a chemical accident or a deliberate release of agent materials, all equipment must be decontaminated before it can be used, and before injured personnel can be transported to medical facilities. This is true of both civilian and military operations.

Decontamination of military agents can be more complex than may be apparent. This paper will examine the environmental fate of selected military agents, and will 1) suggest ways in which decontamination procedures can be made more effective for the ultimate re-inhabitation of the land by a civilian population; 2) suggest minor modifications to the decontamination process which will reduce the overall environmental damage; 3) examine some current disposal technologies for decon solutions, and 4) examine some of the problems associated with large scale decontamination activities.

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In the event of an accidental or deliberate deployment of chemical agents, the military must fulfill its role and mission. It must act quickly. There may not be time to assess all the possible consequences of these actions. Under field conditions, exhaustive study of the most effective decontamination methods is nearly impossible.

In order to cut through the theoretical and discuss the practical, we will focus applications of some simple civilian technology which may be of assistance in developing a decontamination plan for equipment. We will discuss some additional treatment methods for decontamination products, and the cost of some of the technologies.

The information for this paper has been developed from public sources. The sources are listed at the end of this paper.

The Agents

We will examine **Sarin, Soman,** and **VX,** and the chlorine bleach decontamination system used on these materials. Then we'll also consider some information developed on the cleanup of the Chernobyl site as it may pertain to land restoration.

VX

VX, or O-ethyl-S-(2iisopropylaminoethyl) methyl phosphonothioate is a very effective chemical agent. VX degrades extremely slowly in the environment. The degradation pathway is complex and pH dependent. The degradation pathways are shown in Figure 1. The principal degradation products appear to be EMPA (ethyl methyl phosphonic acid), EA2192 (S-[2-diisopropylaminoethyl] ethyl methylphosphonic acid), and MPA. VX, EMPA and EA2192 are quite toxic, and MPA is extremely stable in the environment but substantially less toxic. Fortunately, the degradation pathway which forms EA2192 takes place at pH ranges outside many of those found naturally in the environment.

The principal bond cleavage in the C-O bond produces EA2192 in solutions of pH greater than 10 or less than 6. The other compounds of EMPA and MPA are also quite toxic but somewhat more biodegradable in the environment. The half life of VX in the environment is estimated at about 2500 h.
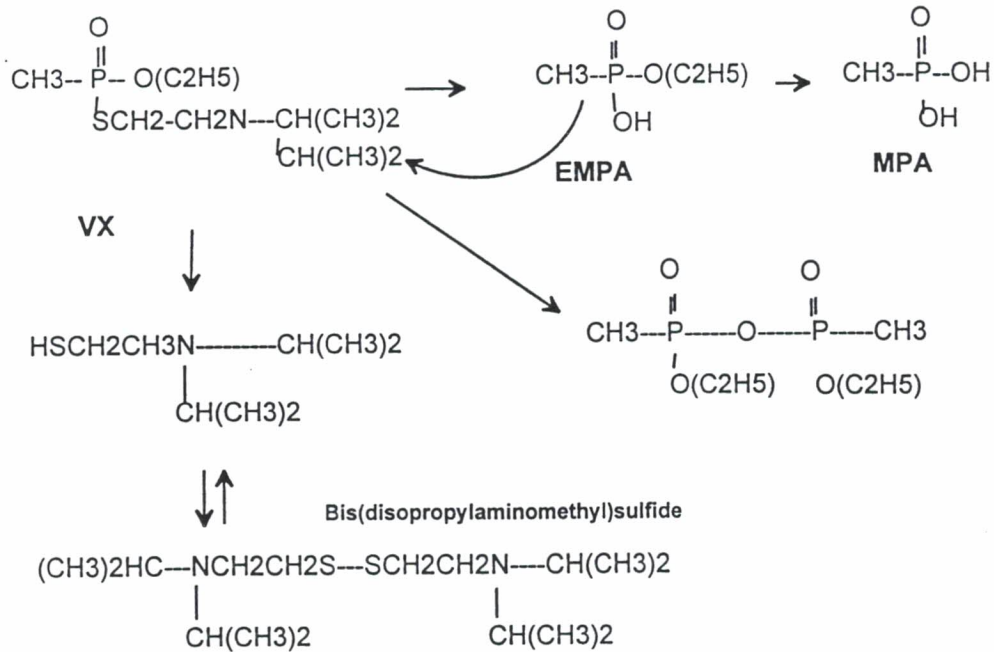
$$CH3-- \overset{\overset{O}{\|}}{P}- O(C2H5) \atop \underset{\underset{CH(CH3)2}{|}}{SCH2\text{-}CH2N\text{---}CH(CH3)2} \longrightarrow CH3\text{--}\overset{\overset{O}{\|}}{P}\text{--}O(C2H5) \atop OH \quad (EMPA) \longrightarrow CH3\text{--}\overset{\overset{O}{\|}}{P}\text{--}OH \atop OH \quad (MPA)$$

VX

$$HSCH2CH3N\text{---------}CH(CH3)2 \atop \underset{CH(CH3)2}{|}$$

$$CH3\text{---}\overset{\overset{O}{\|}}{P}\text{------}O\text{------}\overset{\overset{O}{\|}}{P}\text{-----}CH3 \atop O(C2H5) \quad O(C2H5)$$

Bis(disopropylaminomethyl)sulfide

$$(CH3)2HC\text{---}NCH2CH2S\text{---}SCH2CH2N\text{----}CH(CH3)2 \atop \underset{CH(CH3)2}{|} \qquad \underset{CH(CH3)2}{|}$$

Figure 1. VX hydrolysis from P-S bond cleavage
From: Kingery and Allen

$$CH3\text{----}\overset{\overset{O}{\|}}{P}\text{----}O(C2H5) \atop \underset{\underset{CH(CH3)2}{|}}{SCH2CH2N\text{----}CH(CH3)2} \longrightarrow CH3\text{--}\overset{\overset{O}{\|}}{|}\text{-}P\text{----}OH \atop \underset{\underset{CH(CH3)2}{|}}{SCH2CH2N\text{---}CH(CH3)2}$$

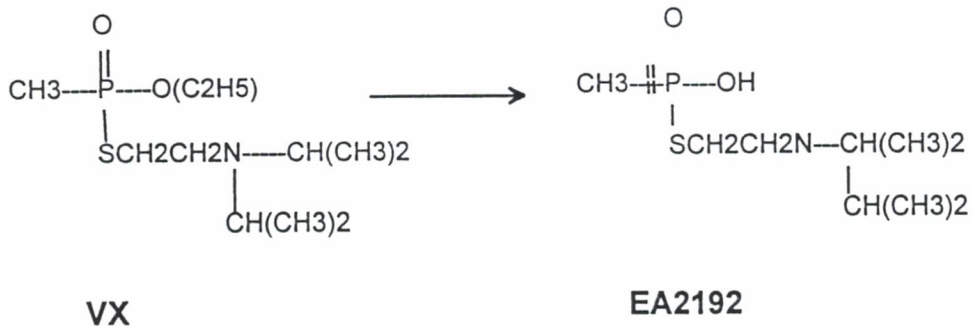**VX**   **EA2192**

Figure 2. VX hydrolysis from C-O bond cleavage
Kingery and Allen

The principal route of degradation is by hydrolysis, which is strongly pH depend-ent.   At elevated pH, and in the presence of chlorine, such as in the decontamination process, the hydrolysis is principally through the P-S bond cleavage.

The decontamination if carried through to completion, provides complete breakdown of the VX to methyl phosphonic acid (MPA).   MPA is a compound commercially available. Though extremely corrosive to unprotected skin and mucous

membranes, the commercial literature (MSDS's) indicates little, or no toxicity[1] for this compound.

Sarin (GB)

Sarin is isopropyl methylphosphoflouridate. Physically, it degrades through hydrolysis of the fluorine bond and is converted to isopropyl methyl phosphonic acid and then to MPA. This is shown in Figure 3.
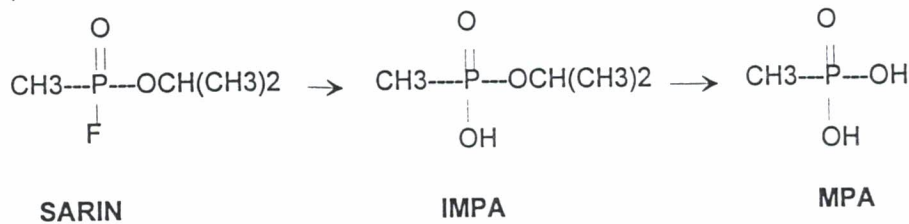
$$O \qquad\qquad O \qquad\qquad O$$
$$\parallel \qquad\qquad \parallel \qquad\qquad \parallel$$

CH3---P---OCH(CH3)2 $\rightarrow$ CH3----P---OCH(CH3)2 $\longrightarrow$ CH3---P---OH

     F   OH   OH

  SARIN   **IMPA**   **MPA**

Figure 3. Hydrolysis of Sarin
From Kingery and Allen

The estimated half life of Sarin in the environment is approximately 250 hours. The conversion to methylphosphoric acid is also highly pH dependent; in a highly alkaline pH and in the presence of hypochlorite compounds, the estimated life of Sarin is about 3 seconds at pH~ 12. The degradation end product is the same end product as VX.

GD (Soman)

Soman or pinacoyl methylphosphonoflouridate is another of the nerve agents in the MPA family. The degradation pathways have not been as extensively researched, but the basic chemistry of the degradation pathway is known.

Soman hydrolyzes to pinacolyl methylphosphonic acid (PMPA) which further hydrolyzes to MPA. The chemistry and structure of the hydrolysis is shown in Figure 4.

The hydrolysis of Soman in the natural environment is approximately 4 times faster than that of Sarin, and about 400 times faster than that of VX. Soman has a half life of approximately 60 hours in the environment. Like the other agent compounds, the hydrolysis is highly pH dependent.

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[1]   The 1994 Edition of Sax's Dangerous Properties of Industrial Materials, 8th Ed. Lists the oral toxicity of methyl Phosphonic Acid at 1740mg/kg for rats, and 500 mg for a dermal exposure on Rabbits. There is no information on toxicity for humans.
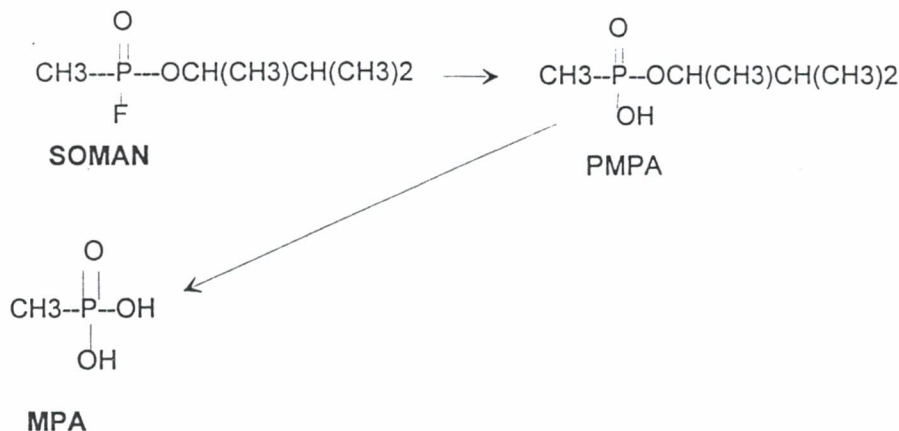
$$CH3---\underset{\underset{F}{|}}{\overset{\overset{O}{||}}{P}}---OCH(CH3)CH(CH3)2 \longrightarrow CH3--\underset{\underset{OH}{|}}{\overset{\overset{O}{||}}{P}}--OCH(CH3)CH(CH3)2$$

SOMAN   PMPA

$$CH3--\underset{\underset{OH}{|}}{\overset{\overset{O}{||}}{P}}--OH$$

MPA

Figure 4. Hydrolysis Pathway for soman

Source: Kingery and Allen

Decontamination and Environmental Effects

The recommended protocols for decontamination are excellent for military uses. These products and byproducts may still cause adverse environmental impact. The principal decontamination products include a highly alkaline solution which has high levels of the OCl radical and "other" compounds. The other compounds in the decon solutions will include small amounts of fuels, lubricants, paints, solvents, and other materials washed off in the decontamination process. Because of the decontamination environment, many of these "other" compounds will also be reacted with the decon solution, and chlorinated. The decon solution will also contain MPA.

Field decontamination operations are not always neat or tidy. Standard precautions should include a method to contain the decontamination fluids to prevent them from entering the groundwater. Containing the decon solutions will make the ultimate cleanup of the site substantially easier.

One method of containing the decon solutions is by polymers sprayed on the soil to make a permeation barrier. A number of polymers are resistant to strong alkaline solutions. These polymers can be sprayed on the ground form a soil barrier sufficiently tough enough to drive a tank across, and maintain their chemical resistance properties. These compounds have a low viscosity, can penetrate and seal the soils, and are formulated to set up in minutes upon contact with the moisture in the soil.

Acrylamide polymers don't work well for this application. Urethane compounds are suitable. Grout chemistry can be controlled to form an impermeable chemical barrier with the soils in as little as one minute or as long as several days.

Alternatively, a site with lots of clay or silt may work as well. The clays or silts should be at least 0.5 meter thickness, well compacted, and without sands or gravel lenses.

The decontamination area should also be drained to a lined pit or pond where the wash and rinse waters can be collected and retained for later treatment prior to disposal. The field decontamination station collection lagoon should have sufficient freeboard to allow the accumulation of at least 1 meter of precipitation over the planned volume of decontamination fluids it will receive. However, the containment pond or lagoon should not be located where it will drain a large area, nor should it be located upstream from a drinking water supply.

bermed and lined Decon Area

Lined Containment Area

Decon Area sloped to central collection
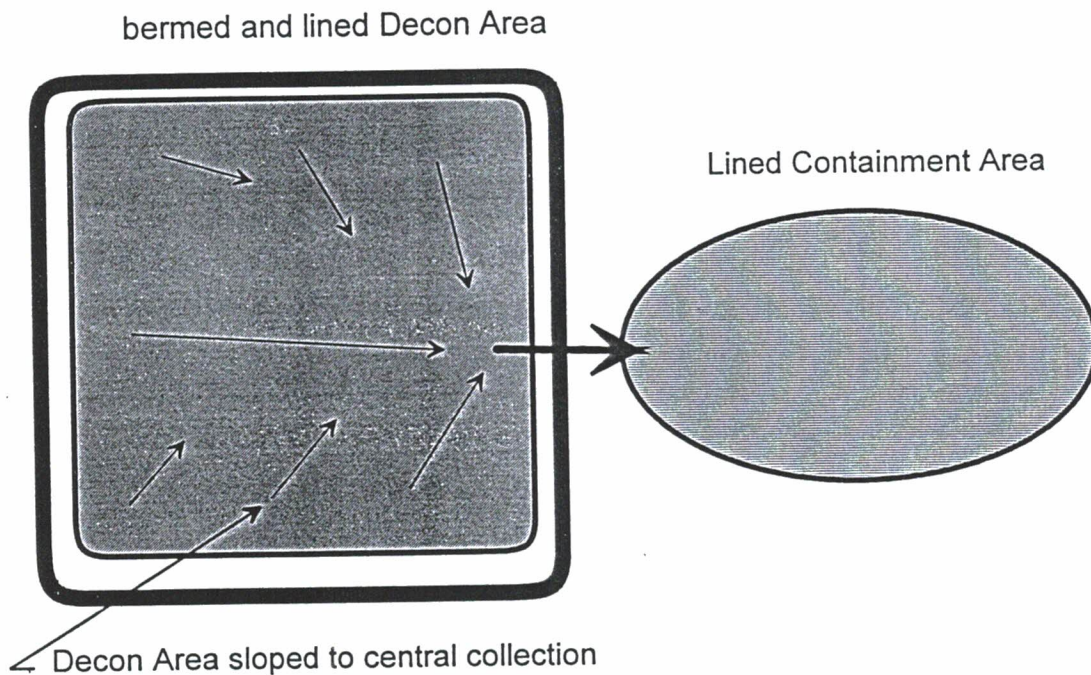
Figure 5. Schemctic of Decon Configuration

This is not as difficult as it may first appear. A site which is hollowed out of a plateau or a plain may serve adequately. Reasonable precautions should be taken to insure that the lagoon will: 1) protect the groundwater, 2) hold the fluids until they can be collected and sent off for treatment, 3) be designed so that it will not be overtopped or overfilled from rain or runoff, and 4) be located where the consequences of a breach in the dike or the liner will not contaminate the surface water. The consequences of treatment lagoon failure may not be as bad as an agent release, but will be environmentally significant.

A soil liner should be selected with regard to the permeability of the material. Standard clay liners used on US landfills have permeabilities between 10^{-6} and 10^{-9} cm/sec. (A dense clay or a bentonite clay liner has a permeability of 10^{-9} cm/sec.) In an emergency, the requirements may be relaxed somewhat, but permeabilities should never be less than 10^{-5} cm/second; sand and gravels have permeabilities of approximately 10^{-3} cm/second, and are unsuited for this purpose.

The need for groundwater protection is substantial. If we can for a moment consider the problem arising from the need to clean up spilled or leaked petroleum, there are a number of lessons which may prove valuable and illustrate the need for the ground water protection liner.

The first is the partitioning of the various materials. For that we'll look at a simple model from the US environmental data base. The following figure may be helpful.
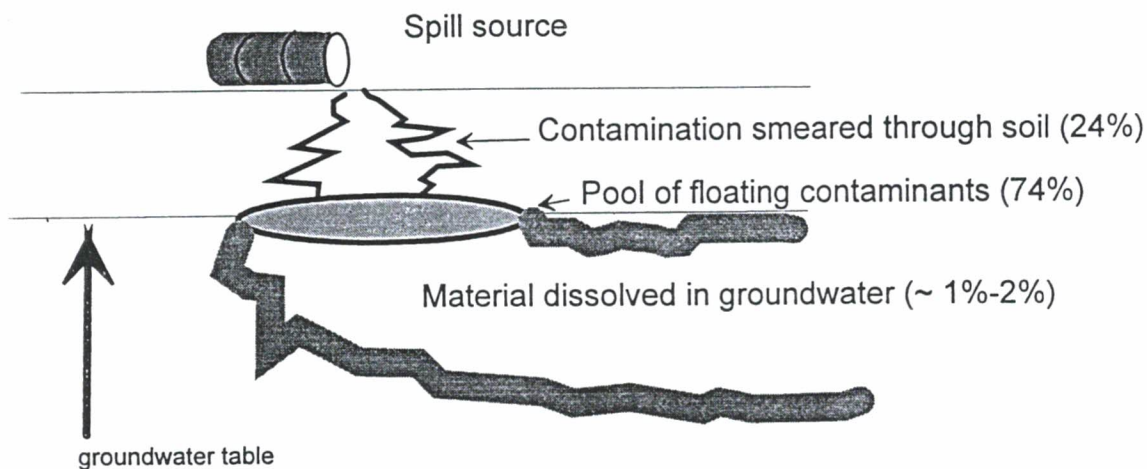

Figure 6. Groundwater contamination example

If we assume that there has been a spill of 1000 l of gasoline or diesel fuel on to the ground, we would find the approximate partition of the materials. About 24% or 240 l of the materials would be trapped and smeared through the soil. Another 740 l or about 74% would be pooled on the surface of the groundwater, or at the bottom of the aquifer if the material is heavier than water. The balance or about 1%, 20 liters, will be dissolved in the aqueous medium. It is these 20 liters are the most expensive to cleanup and recover, and which may do the most severe and long term environmental damage[2].

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[2]   If the material spilled is heavier than water, the material may sink to the bottom of the aquifer where it is much more difficult to remove, and the materials have been known to emulsify, increasing both their mobility and the amount of material dissolved in water.

On a relative cost scale, we can excavate and dispose of the soils for about $70-$100 per metric ton (by incineration) where each cubic meter represents between 1.4 and 2.0 metric tons. We can remove the floating pool on the groundwater for about 8 times as much as the excavation, and we can pump, treat, and cleanup the groundwater for about 20 to 50 times as much as the excavation. In the US, where we are being forced to cleanup leaking underground petroleum storage tanks, a simple remedial project may cost in excess of $125,000 for a gasoline leak. Seventy-five percent (75%) f the total cost may be spent on cleaning up the groundwater! If the leak is for diesel fuel, the costs may double.

The physical and chemical properties of the various residual and degradation materials are important. In the case of the partitioning constant of a substance like gasoline or diesel fuel, the materials have an partitioning coefficient of several hundred to several thousand. The relative partitioning coefficient of MPA and many of the agent materials is less than 20. This indicates that the MPA, residual agents, and other decontamination products will not be retained in the soil but will be released to precisely the area where it is most difficult to remove-- the groundwater.

While Sarin, Soman, and VX have some hydrolysis in water and some apparent biodegredation in soils and water, it is apparent that the most common endpoint of the decontamination reactions MPA, and EA2192 have biodegredation rates of near zero. IMPA and PMPA have degradation rates which are on the order of 10^{-4} to 10^{-9} /hour, and Kingery and Allen caution that the biodegredation (hydrolysis) rates for the agent compounds and their decomposition daughters may be on the order of 1/1000 of that observed in the laboratory. Given the uncertain nature of the toxicity data regarding MPA and the high toxicity of EA2192, and the other agent compounds, it is imperative that the groundwater be protected where possible[3].

What to do with decontamination solutions

Now that we have looked at containment, we'll examine potential methods of handling the decontamination solutions, to prevent further damage and reduce, as far as practical, the costs for treatment and disposal.

Additional pretreatment

If the field decontamination has been successful, the spent decontamination solutions will have a pH of 12-14 SU, and contain a superabundance of chlorine in the OCl form. When this solution has been contained, the pH needs to be lowered to somewhere in the range of pH 8-10; and some of the chlorine needs to be stripped out of the solution. The act of lowering the pH will help, because it will shift the HOCl-OCl balance in solution and make the chlorine more readily removable and more active.

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[3] The natural pH of groundwater is frequently well above 6 SU, but often below 8 SU. However, groundwater can, if conditions are right, have a pH well below 6 and well above 10 if the soil chemistry is right.

One of the ways of lowering the pH is by the addition of various acids. Sulfuric acid is a good choice because at pH less than 10 it forms a precipitate with calcium which leaves about 3000 mg/l of $CaSO_4$ in solution. The optimum point for the precipitation of calcium sulfate is approximately pH =7.2

The high levels of chlorine in the water preclude the use of biological treatment. Biological treatment may be an option for various types of wastes, including decontamination wash waters, but the chlorine levels must be reduced before the biological treatment is initiated.

The excess chlorine can be removed three ways: 1) by thiosulfate, 2) by neutralizing and aerating the water, and 3) and by adding some reactive organic substrate such as starches or sugars.

Aeration is the preferred route of chlorine removal. It can be accomplished with a perforated pipe and a large pressure blower or commercial compressor, or even with a pump and spray system to aerate the water. The reason the aeration is preferred is that it doesn't add more salts to a liquid already rich in salts. The amount of aeration can be easily and precisely controlled with minimal support and manpower.

Incineration

Some protocols for disposal of decontamination fluids call for their incineration. In the field that's just not practical. For agents, it may be necessary, but not for an aqueous solution which contains high levels of salts and chlorides. Decontamination waste waters will contain lots of things which an incinerator does not like. Unless the waste is classified as "highly hazardous" and needs incineration for a specific reason, it shouldn't go anywhere near an incinerator.

The cost of disposal of "highly hazardous" wastes in the US is measured in terms of dollars per liter of solution destroyed. Part of that high cost is the USEPA's externally imposed environmental regulation program which dictates how the wastes are classified and handled. While the US wastes are destroyed safely, there is a substantially higher cost associated with the regulatory burden of insuring that destruction.

The other cost component for an incinerator is the wear and tear on the incinerator. Wastes containing chloride ions and chlorine form hydrochloric acid and sodium deposits in the incinerator. The HCl attacks the refractory and supporting steel, eating away the metal components of the incinerator. Sodium forms deposits on the walls. These deposits bond tightly to the refractory and have to be removed by chipping them off. This degrades the refractory as well.

If one has to incinerate wastes which have high levels of chloride and sodium, consider blending them for disposal in a cement plant. Cement plants have a large demand for chlorine and can and do accept a variety of chlorinated waste materials for incineration. Some cement plants can even accept and destroy PCB's.

While many of the people from Edgewood can speak more about the costs of disposal of liquids, I believe that the current disposal of a highly chlorinated waste material which also contains high levels of sodium and chlorine will be on the order of

about $350-$500 USD per 55 gallon drum of wastes. That works out to between $1.68 and $2.40 per liter.

The incinerators suited for large scale destruction or decontamination of tons per hour of contaminated materials are large stationary units. However, there are some large transportable units available on the market as well. One unit is a rotary kiln which can be transported in 20 trucks. When assembled, the footprint of the unit is about 35 meters by 60 meters, and will process 20 MT of soils per hour and provide an acceptable environmental product with the destruction of all the hazardous components to their elemental forms. The destruction efficiently of this unit is well within RCRA guidelines for PCB's and exceeds 99.9999% destruction efficiency. This is a rear echelon unit, not a field unit. It requires approximately three weeks to assemble, 12 people to operate it (including front end loaders, mechanics, and operators), and about 4 people to maintain the equipment. The unit is transportable, not portable.

Encapsulation

Let me first clarify some terms. Encapsulation is not a treatment process per se. It will not destroy or render the waste less toxic. All that encapsulation does is surround the waste with other relatively inert materials immobilizing the objectionable compounds where they can be indefinitely stored. If the equipment decontamination has been successful, encapsulation may provide a low cost alternative to disposal by incineration. With careful selection of properties and materials, the waste can be incorporated into commercial roadways or sent off for disposal at a commercial landfill. Commercial landfill disposal is substantially cheaper than incineration[4].

If the decontamination process has performed satisfactorily, the waste solutions from it should be suitable for stabilization. If the encapsulation of the wastes has been successful, the lechate from the encapsulation should not contain any harmful substances. However, the characteristics of the stabilized material should be carefully investigated prior to its final disposition, paying particular attention to the lechate from the encapsulated material.

Some laboratory confirmation of the success of the stabilized material may be required. The short time for laboratory evaluation won't compromise the stabilized wastes. With some planning, it should be possible to develop a range of formulas and mixes which are successful for encapsulating most waste materials, and from that, a operational "cookbook" of encapsulation recipes can be developed.

There are a number of successful encapsulation systems. Most are suitable for inorganic compounds, liquids, and metallic wastes. Inorganic encapsulation systems generally do not work in streams which contain a high concentration of organic materials, especially where the organic waste stream contains lube oils and solvents.

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[4]   The cost of landfill disposal can range from $100/ ton down to $20 per ton depending upon the nature of the waste material and the associated hazard. More hazardous materials should be disposed of in a lined landfill which has lechate monitoring and treatment systems.

Encapsulation of organic wastes is dependent upon the composition of the waste, the quantities of solvents, and interactions with the stabilizing materials. There are very few wide spectrum organic encapsulant materials which will perform satisfactorily, and the costs are competitive with incineration.

Where the waste contains a mix of fuels, oils, and solvents in concentrations less than 5%, an inorganic encapsulation system can be used to stabilize the waste stream. Cleaning solvents such as methylene chloride and other low weight chlorinated organic solvents can be extremely difficult to capture and retain in any encapsulation system. In some instances, waste streams with chlorinated compounds can be stabilized effectively by a highly alkaline cement type stabilization system. The strong alkali in the cements reacts with the chlorine in the compound, either de-chlorinating it, or binding into the encapsulant matrix.

Where lube oils and solvents are greater than 15%-20% alternative methods should be considered. One of the most effective organic encapsulent systems employs HDPE drums with heat sealed lids

Many of the inorganic encapsulants rely upon cementation reactions with lime, clay, silicates, or a combination of those materials added to cement and cement admixtures like latex. The mixes and formulae for these encapsulants vary widely as do their properties and their success rates in containing specific compounds. The structural integrity of the materials also varies widely. Depending upon the amount of silicates and cement in the mixtures, the final product can be hard enough to incorporate into concrete foundations or use in pavements, or it can be as soft as chalk.

Clays are alumino-silicate compounds of very small size and very large surface area. The compounds are polar and reactive. Clays contain a variety of other metals including sodium, calcium, magnesium, manganese, iron, etc. Many of these cations have been demonstrated to be effective in absorbing agent compounds, and in catalyzing their degradation. Clay has been successfully used in slightly alkaline medium combined with sodium silicate as an encapsulating agent.

Bentonite clay is often a material of choice for use in encapsulation systems because it is inexpensive and readily available. The bentonite has an accordion-like physical structure which causes it to swell when it is wetted, and it can transform a lagoon full of liquid into a viscous slurry or solid in very short time (days). Bentonite can also be mixed with a wide variety of other commercial compounds and incorporated into concrete.

When clay is combined with silicates, using between 4% and 10% by volume of sodium metasilicate to the clay mixture, it forms an excellent inorganic encapsulent material. The metasilicate is quite caustic and needs sulfuric or hydrochloric acid to lower the pH of the mixture. The lowering of the pH of the mixture causes the sodium metasilicate to precipitate, and to react with the aluminum in the clay. This forms a highly stable soil-like material which can be handled with conventional earth moving equipment. This material is inert, and can be buried in a landfill or even directly, if the lechate is shown to be innocuous.

US companies such as Chemfix, Inc. (New Orleans, Louisiana) and others have been successful in stabilizing many types of hazardous wastes containing predominantly inorganic chemical compounds. There are a number of other companies worldwide who use this type of inorganic stabilization system.

Another inorganic encapsulent in commercial use is sodium metasilicate plus Portland cement. The end product can be controlled to be as hard cement, or soft like soil. The amount of cement applied to the mixture will control the hardness. Both sodium metasilicate and cement have excellent properties for working in alkaline solutions and both are outstanding for their ability to bind a number of non-organic chemicals into their matrix. Compounds like sugars, and high levels of soft metals like lead and copper tend to inhibit the stabilization, and cause the final end product to be much softer.

If the waste stream is organic in nature, but does not contain substantial quantities (greater than 10%) of low molecular weight organics and solvents, an asphaltic base compound may be applicable. Depending upon the volume of the waste and the composition, it may be possible to use the decontamination residues and wastes as an admixture into an asphalt plant. In certain cases, even when the waste does contain substantial quantities of the solvents, they can be incorporated into asphalts provided the potential for volatilization of the wastes and a soft end product are recognized.

If the waste has an organic phase layer which is separable that material may be destroyed by combining it in with a fuel and incinerating it in an asphalt plant, a cement kiln, or commercial boiler. Many countries outside the US use cement kilns to destroy highly chlorinated hazardous wastes including Polychlorinated Biphenyls (PCB's). The temperature of the kiln and the highly alkaline conditions in the kiln are ideal for waste destruction. The kilns also have a voracious appetite for energy and burn a wide variety of fuels, and also have a high demand for chlorides to balance the alkalis in the cement.

Asphalts have been used as encapsulation systems for a number of compatible organics and some nuclear waste materials, but the equipment is a heated extrusion unit which is not suited for field conditions, or large scale applications. If the waste is granular or solidified, or if additional treatment is necessary to reduce the leaching of the wastes from the stabilized mixture, incorporation of the waste into the fillers of an asphalt plant may be an ideal solution. Even in the environment, leaching from asphalt aggregates can be effectively stopped by application of a surface or second course of asphalt. .

Biological Treatment

From the chemical literature and information on fate of decontamination compounds, it appears that it may be possible to treat field decontamination wastes in a biological treatment plant and reduce the materials to CO_2, water, Phosphates, and other innocuous compounds. While the information about the degradation of agents is extremely limited, the literature does indicate that the degradation products from the decontamination process are biodegradable.

Biological treatment systems have a low tolerance for many toxins, including agent materials, and strong oxidants, unless they have had the opportunity to acclimatize to them first[5]. Care must be used in reducing the chlorine and oxidation potential of the various decontamination fluids before sending them to a waste water treatment plant (WWTP). The amount of free chlorine and strong oxidants in a solution for biotreatment should ideally approach zero. Practically, if the waste to be treated is a small portion of the total WWTP flow (less than 5%) the chlorine content should generally not exceed 10-20 mg/l as free chlorine. The salts, especially the soluble salts matter less if at all unless they contain identified toxins such as copper, mercury, lead, etc.

In researching this paper, we looked at the structure of MPA. MPA is extremely stable, but under the right conditions it can be degraded by a strain of e. coli which is enteric to man and animals. The "right conditions" appear to be the key. The tests with MPA were limited to those trials where the MPA was the sole source of phosphorous, and the bacteria was grown on culture plates. In the laboratory it is possible to limit the availability of sources of P. Waste water treatment plants have been attempting to control the amount of P discharged to the environment for years. Excess P in a discharge causes algal blooms.

A few years ago, many WWTP's were operated in a "luxury P uptake" mode. This means that the biopopulation was first starved for P and then fed a waste stream where the P was available. The bacteria acted much like a starving man at a banquet. They stored up extra P to accommodate themselves for a while -- enough to make a significant reduction in the amount of available P going out of the plant.

It should be possible to take bacteria, such as that coming from the clarifier on an activated sludge system and feed small quantities of wastes containing MPA to the mix. It may require some additional separate tankage and holding times, but the degradation should be possible in a waste water treatment plant. If the MPA is the principal nutrient source of P in the system, the addition of additional sources of carbon and sugars so that the overall balance for the system achieves a C:N:P ratio of between 100:20:1, and 20:5:1 should, with adequate time, enable the complete mineralization of the MPA.

Anaerobic decomposition of the MPA may also be a distinct possibility. A number of recent experiments in the US have indicated that chlorinated solvents including Trichloroethane, Carbon Tetrachloride, and a number of chlorinated aromatic compounds have been successfully treated under anaerobic conditions by co-metabolizing the materials with methane. It may be possible to use the anaerobic digester on a sewage treatment plant to reduce MPA and perhaps some of the agent compounds. No information is available on this point in the literature.

However, the hypotheses about degradation of MPA and agents under aerobic and anaerobic conditions in waste water treatment plants are educated guesses require further evaluation.

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[5] Carbon Tetrachloride, chlorinated compounds and phenolics, all considered toxic to waste water treatment plants are successfully biologically degraded.

The equipment for examination is relatively simple, some tankage, a few chemicals, an air source, and access to a waste water treatment plant with a good chemical laboratory. It may in fact be possible to collect, treat, and destroy decontamination waste waters at a conventional waste water treatment plant at extremely low costs.

Large Area Decontamination

In a military sense decontamination of large areas may be outside the mission parameters or practicality. Decontamination of large areas is neither easy or quick. In areas where agents have been deployed, decontamination may be even more difficult than when the area has been contaminated with nuclear compounds. The nuclear accident at Chernobyl serves as an interesting object lesson about operations in this scale.

The Chernobyl disaster contaminated several thousand square kilometers with low to moderate levels of α and β radioactive materials, as well as low levels of heavier radioactive compounds in the Thorium-Uranium-Radium series. These compounds all had surface active components which accumulated in the extremely fine soil fractions, with silts and clays.

In 1993-94, there was a serious proposal under consideration for funding a massive cleanup effort in Belarus. The proposed scope included collecting the top 0.5 meters of several thousand hectares of farmland in Belarus and processing it by soil washing. Soil washing is a combination of wet screening and flotation processes which would remove about 3%-6% of the total weight of the soil, including most of the more active radioactive materials. The project appeared attractive and was under serious consideration by the US Trade and Development Agency for funding of a Feasibility Study in an amount of almost $2 million dollars.

The problems with the concept were monumental. While soil washing would remove many of the nuclear contaminants in the soils, it would not remove all of them. The soil washing processing would remove the fines and the organic materials in the soil. These the organic material and humus is necessary to support plant growth. In effect, this process, like incineration, would sterilize the soils and remove and destroy the organic fraction in the soils. Finally, there was no consideration of the changes and displacements required, nor the impact and requirements of a soil restoration program.

The proposal also did not detail how or what it would do with groups of large contaminated objects-- such as forests and rock outcroppings, and buildings. As many of you already know, decontamination of a porous solid can be extremely difficult. Demolition and massive excavation seemed indicated, but there was nothing to address this point in the proposal.

A final consideration was that the logistical and infrastructure resources required for the execution of the proposal were not available. At the processing rate proposed, Belarus would have been scraping off topsoil, and processing it at the rate of over 300,000 tons of soil per day for the next hundred years. After processing, the soils would be returned to its original location[6].

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[6]   At the rate of 30 tons per truckload, this would amount to 10,000 round trip truck

The initial proposal suggested examination of the feasibility of washing approximately 100 billion tons of soil. This processing would generate a waste pile of approximately 5 billion tons (3.6 billion cubic meters) which would contain all of the radioactive materials removed from the Belarus soils. This is a very large waste pile!

The requirements for manpower and transportation were so massive that an entirely new transportation infrastructure would also have been required. The proposal would have spent $110,000 USD per acre ($271,700 USD per hectare processed). The average value of the crops grown in Belarus were approximately $200 per hectare per year. The project was to be supported by a 20% tax on all industry within Belarus.

Overall, the idea was not politically, economically, nor technically feasible, nor a good return on investment. The World Bank and the USTDA declined the opportunity to fund the feasibility study, causing the project to die. This project, however ill conceived, illustrates the scope and magnitude of a wide large scale cleanup.

The decontamination of large volumes of contaminated soils by physical means is not practical. Biological degradation of agent contaminated materials is one of the few options practical for a large area, only because other options may not be affordable.

The environmental fate of nerve agents has been discussed by Kingery and Allen, and is summarized below[7]. Sarin in contact with soils has a half life of approximately 240 days. An older study at Edgewood estimates that the half life of Sarin in soils is between 12 and 24 hours, and averages about 12.4 hours. The degradation rate of VX has been estimated at between 8% and 12% per day, or a half life of approximately 6.5 days. All the rate information, especially on VX is highly variable and the information provided by Kingery and Allen is probably the best available in a public forum.

It is interesting to note that the studies produced by the US Army in 1990 indicate that some of the residence times for some of the degradation products which include EMPA, IMPA, and PMPA may exceed 35 years, and as cited earlier, the respective half lives of the three agents examined are between 105 days for VX to less than 6 days for Soman.

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movements per day. One hundred processing sites were proposed.

[7] Kingery and Allen, p. 175. See references for citation.

Compound	Media	Rate Constant (h^{-1})	Notes
Sarin	Water	2.8×10^{-2} - 7.1×10^{-1}	Epstein Study, Second constant on Seawater which contains high levels of salts.
	Soil	9.0×10^{-2}-2.2×10^{-4}	Principally volatilization from soils
Soman	Water	1.2×10^{-4}-6.1×10^{-3}	Near Neutral pH
	Soil	1.4×10^{-2}	
VX	Water	2.0×10^{-4}	
	Soil	2.9×10^{-3}	
EA 2192	Water	Near Zero	
Breakdown Compounds[1]			
MPA	Water	Near Zero	
IMPA	Water	8.7×10^{-9}-8.7×10^{-7}	
EMPA	Water	2.4×10^{-10}	tests at pH 4, extrapolated to 25°C
PMPA	Water	2.9×10^{-6}	One data point

[1]   Bis (diisopropylaminoethyl)disulfide was not included because it generally occurs by S bond cleavage at pH<6 or pH>10, and because the degradation rate is near zero in soils.

Note that most if not all the agents have a relatively short life in the environment - except EA2192. The reason for including EA2192 in the list of agents rather than the breakdown compounds is because of its toxicity and relative ease of formation under some natural conditions. Effectively the agents are going to be around for quite a while- measured in terms of weeks and months. Their breakdown compounds will be around for substantially longer.

I believe that the only practical solution for decontamination of large areas is in biological decontamination of the agent materials.

Summary

We have looked at some of the challenges associated with treatment of decontamination solutions. The most effective means appear to be collection and neutralization, encapsulation or biological treatment. However, before biological treatment can be successfully employed, there are still some studies to be performed.

For large scale cleanup, about the only practical solution will be biological degradation and restoration.

References:

There are a number of references in the public domain. Several are from the Internet and are listed separately:

Kingery, Andrew F., and Allen, Herbert E. *"The environmental Fate of Organophosphorous Nerve Agents: A review,"* Toxicological and Environmental Chemistry, vol 47,pp 155-184, Gordon and Breach Science Publishers, S.A., Amsterdam, Netherlands.

Yang, Yu-Chu, Baker, James A., and Ward, Richard, *"Decontamination of Chemical Warfare Agents"*, Chemical Reviews, Vol 92, pp: 1729-1743, 1992

Sigma Chemical Corporation, St. Louis, MO, *"MSDS for Methylphosphonic Acid"*
Epstein, Joseph, Bauer, Virginia E., Saxe, Melvin, and Demek, Mary M., *"Chlorine Catalyzed Hydrolysis of Isopropyl Methylphosphonofloridate (Sarin) in Aqueous Solution"*, Journal of American Chemical Society, Vol 78, pp:4069-4071

Internet resources

A surprising amount of information is available on the Internet. A search of the Internet World Wide Web using **www.dogpile.com**, "chemical warfare agents" provided over 10,000 hits and cross links. Most of the listings were on *Altavista* (9500+ hits) and *Excite* (1290+ hits) search engines. Many of these listings are unimportant and trivial, but some of the more important sites are listed below:

http://www.Geocities.com/CapeCanaveral/Lab/7050/
This site contains information on manufacture of various types of agents as well as decontamination information. The decontamination information is much less detailed than the synthesis information.

http://www.apgea.army.mil/safety/msds/index.html
site run by the US Army and contains Material Safety Data Sheets on the Agents.

http://www.outbreak.org/cgi-unreg/dynaserve.exe/cb
contains structural information and medical information on agents.

http://www.mitretek.org/offer/energy/cw_page/cwagent.html
contains information in support of CWC agent treaty

http://www.calpoly.edu/~drjones/chemwarf.html
California Polytechnic Institute's page on CBW agents and CWC treaty. Contains some information on agent manufacture.

http://www.opcw.nl/chemhaz/nerve.htm

A site run from the Netherlands which has some good general information on agents, medical and their properties and effects. Also shows some photos of various injectors used in treating agent exposures.

http://www.cbiac.apgea.army.mil/

Site run by Battelle Institute but sponsored by the US Army and lists documents, exposure models, and other sources of information.

http://www.whatuseek.com/cgi-bin/redirect.go?url=http://www.outbreak.org/cgi-unreg/dynaserve.exe/cb/bionews.html

This site contains a listing of threats and rumors from various sources . Technically unimportant.

The Author:

David L. Russell is a Registered Professional Engineer, and President of Global Environmental Operations, Inc. He has over 30 years of professional practice in the environmental field and has provided cleanup consulting services to a number of clients in various parts of the world, including Romania, Venezuela, and Puerto Rico. He is a member of a number of technical societies, including the American Institute of Chemical Engineers, and is listed in Who's Who in Engineering. He also has written a book, " Cleanup of Petroleum Contaminated Sites," published by Technomic Press, Lancaster, Pennsylvania, and has authored a number of articles on environmental practice and cleanup. He also serves on a number of technical committees for the Water Environment Federation, has contributed to their manuals of practice, and is vice chair of the Pollution Prevention Subcommittee for the WEF.