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RCRA DELISTING OF AGENT-DECONTAMINATED WASTE AND REMEDIATION WASTE AT DUGWAY PROVING GROUND

- A PROGRAM UPDATE -

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by

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Introduction

In July 1988, the state of Utah issued regulations that declared residues resulting from the demilitarization, treatment, and testing of military chemical agents to be hazardous wastes. These residues were designated as corrosive, reactive, toxic, and acute hazardous (Hazardous Waste No. F999). These residues are not listed by the U.S. Environmental Protection Agency (EPA) as hazardous waste under the Resource Conservation and Recovery Act (RCRA), which is the primary law governing management of hazardous waste in the United States.

The RCRA regulations (40 CFR 260-280), the Utah Administrative Code (R-315), and other state hazardous waste programs list specific wastes as hazardous but allow generators to petition the regulator to "delist" if it can be demonstrated that such wastes are not hazardous. In 1994, the U.S. Army Test and Evaluation Command (TECOM) initiated a project with the Argonne National Laboratory (Argonne) to demonstrate that certain categories of F999 residues are not hazardous waste and to achieve delisting. The initial focus is on delisting agent-decontaminated residues and soil with a history of contamination at the U.S. Army Dugway Proving Ground (DPG), Utah.

An overview of the DPG delisting program was presented at the 1995 American Defense Preparedness Association Environmental Symposium. Since that time, much progress has been made. The purpose of this paper is to review the DPG delisting program and discuss overall progress. Emphasis is placed on progress with regard to analytical methods that will be used to demonstrate that the target residues do not contain hazardous amounts of chemical agent.

Background

An important mission of DPG is to test the effects of chemical agents and agent-decontamination procedures on military equipment that could become exposed to chemical agents during an actual armed conflict. Equipment that may be tested includes many different materials, ranging from helmets to actual combat vehicles. This test mission has been carried out at DPG since it was initially established in the 1940s and remains an important mission today.

The F999 listing pertains to both the materials that are tested (referred to as substrates) that become waste, as well as to the spent decontamination fluids that are used to decontaminate the substrate after the tests are completed. Many of DPG's tests result in the production of waste materials that, because of their association with agents, are listed as F999 even though they have been decontaminated. In addition, the F999 listing includes media with a history of contamination

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(e.g., soil) that may be generated as DPG proceeds with its Installation Restoration Program (IRP).

Decontamination is designed to remove the agent from the substrate and to rapidly decompose the agent into relatively nontoxic components. For example, many of the agents are rapidly degraded by the addition of strong caustics such as sodium hydroxide. In addition, much of the soil that may have been contaminated by agents in the past (and hence designated F999) has been exposed to the elements for years. Any agent that was initially present would be expected to have degraded into relatively nontoxic components long ago. The Army, therefore, believes that many F999 wastes do not contain residual amounts of chemical agents and do not otherwise pose a significant health hazard. Consequently, the Army is pursuing delisting.

From 1991 to 1992, Southern Research Institute (SRI) conducted an initial program for the Army to gather, evaluate, and document all pertinent agent waste stream and other information to support the delisting effort. In addition, limited research into analytical methods that could be used to support the agent analyses was performed. These actions resulted in the preparation of a series of background documents and delisting test plans describing a proposed delisting demonstration testing program. In June of 1993, the Army met with the Utah Department of Solid and Hazardous Waste (DSHW) and presented its approach to meeting delisting requirements and filing a formal delisting petition. DSHW comments have since been incorporated into the delisting program.

Overview of the Phase I Delisting Program

To delist F999 residues, the Army must demonstrate that the residues do not 1) contain hazardous quantities of the listed agents, 2) contain hazardous quantities of constituents listed in 40 CFR Part 261, Appendix VIII, 3) exhibit characteristics that could otherwise define the residues as hazardous, and 4) fail a series of acute toxicity tests. This last requirement is not typically required for delisting demonstrations but has been requested by the state of Utah.

The Phase I effort will be a test case for subsequent delistings. Hence, the process established in Phase I may be applied to other waste streams and other installations (including those outside Utah) in subsequent phases at a significantly lower cost. The agents being addressed in Phase I are GB (Soman), GD (Sarin), HD (Mustard), and VX. Specific waste streams selected include nonporous, nonpermeable solids, represented by metal test substrate; spent hypochlorite-containing decontamination solutions, represented by high test hypochlorite (HTH); and soil with a history of contamination from a solid waste management unit (SWMU) at DPG. The delisting program is being conducted in three phases, as shown in Figure 1.

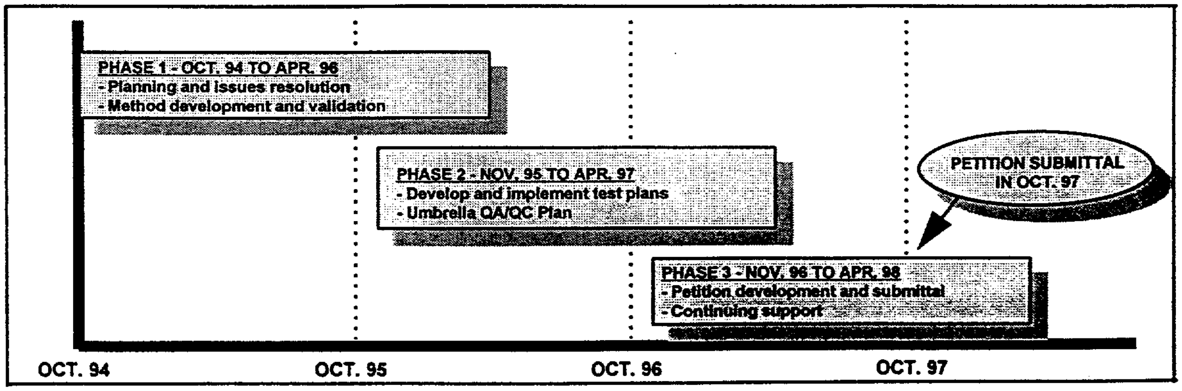

Figure 1. Schedule for Phase I Delisting Program

The first phase of the program, initiated in October 1994, includes planning and issues resolution, as well as analytical method validation studies for the agents on the waste matrices that will be delisted. Method validation is not typically required for delisting, because the EPA has validated numerous analytical methods for use under RCRA. However, because the delisting is focused on agents for which EPA has not validated methods, the state of Utah has requested that the Army demonstrate that the analytical methods to be used will produce data of acceptable quality.

The second phase of the delisting program is demonstration testing. This testing includes agent analyses, RCRA constituent testing, RCRA characteristics testing, and toxicity testing, all in accordance with a Quality Assurance/Quality Control (QA/QC) Plan. The demonstration test plans and QA/QC Plan will be implemented, and a Delisting Test Report will be prepared. These and other documents will form the basis of the delisting petition.

Preparation of the delisting petition and postpetition submittal support to the Army constitutes the third phase of the program. The petition is targeted for submittal to DSHW in October 1997.

Progress to Date

A great deal of progress has been made since the delisting program was initiated. First, a core group of Army agencies was assembled to oversee the program and coordinate with Argonne scientists. This group includes TECOM and DPG as well as the Army Environmental Center (AEC), the Center for Health Promotion and Preventive Medicine (CHPPM), the Chemical and Biological Defense Command (CBDCOM), the Program Manager for Chemical Demilitarization (PMCD), and the West Desert Test Command (WDTC).

In addition, several meetings were held with the Utah DSHW to discuss issues and agree on their resolution and to present plans and discuss progress. Also, considering the level of public concern that presently exists regarding military agents, a significant public interaction activity has been planned. Delisting decisions are first issued by the regulator as a proposed rule, where comments from the public and other interested parties are solicited. Following evaluation of these comments, the regulator issues a final rule. Ultimately, it is the regulator who determines whether listed waste qualifies for delisting, and the public has significant input into this decision. Hence, it is important that the regulator be involved in key decisions and that the public have a role as well.

In addition, Argonne has developed a series of technical reports and planning documents intended to support the delisting program. Included among these is a background document describing agent chemistry, decontamination chemistry, and fate and transport in the environment. This document, *Agent/Decontamination Chemistry Technical Report* (Final, October 19, 1995), is key to the delisting program. It provides the regulator and the public with a strong technical understanding upon which to evaluate the hazard posed by chemical agent-associated wastes.

One of the most significant accomplishments to date relates to the analytical methods that will be used to demonstrate that the wastes of concern do not contain chemical agents above levels that may be considered to pose a hazard to human health and the environment. One of the Utah DSHW's comments at the June 1993 meeting was that "the most important requirement of the analytical method is that it be able to detect the agent at or below the adopted safe concentration level." The Army was faced with the challenge of demonstrating that the analytical methods to be used for the agents will achieve the required level of sensitivity and produce data of acceptable quality. Argonne was charged with the task of refining and validating the Army's existing chemical agent analytical methods for application to the appropriate waste materials. The delisting program agent analytical method validation effort is described below.

Toxics Testing Performance Evaluation

On November 29, 1995, Argonne issued its *Third Draft Toxics Testing Performance Evaluation (TTPE) Plan*. This plan is currently being implemented at DPG laboratories under Argonne direction and oversight. It focuses on Gas chromatography (GC), which SRI evaluated during the initial phase of the program (*Waste Sampling Test Report*, July 31, 1992). However, the Army's GC methods need to be refined to increase sensitivity to allow measurement of the agents in the parts per billion range. In addition, matrix interferences exist that need to be overcome, particularly with regard to decontamination fluid. Also, a means of accounting for sources of imprecision in agent spiking and extraction steps and for addressing decontamination-time variability, which may also contribute to imprecision, is needed. Finally, a means of confirming the presence of agent must be developed because GC has been know to produce false positive results. The general approach to method refinement and validation is described below, with particular attention to these areas.

General Approach -- The studies described in the TTPE plan involve methods for analyzing each of the four chemical agents in three waste matrices (metal substrate, soil, and spent decontamination fluid), resulting in twelve methods. Each of these twelve methods consists of a single-step extraction of the matrix with chloroform and preconcentration of the analyte in the extract onto a cartridge containing a sorbent resin. Agents are quantitated by thermal desorption of the analyte into the gas chromatograph with flame photometric detection (GC/FPD). The method validation study includes spiking the matrix with the agent over a range of concentrations, followed by extracting the matrix and analyzing the extract. These experiments are being replicated a minimum of four times at each spiking level. The method validation studies have been planned so as to conform, as much as possible, with quality assurance requirements specified by both AEC and EPA.

Increased Sensitivity -- As indicated above, preconcentration of the analyte in the extract onto a cartridge containing a sorbent resin is being employed. The sole purpose of this measure is to increase sensitivity of the method such that it will be capable of accurately measuring the agents in the parts per billion range. All extracts will be processed using sorbent tube preconcentration, followed by thermal desorption into the GC instrument. The basic sorbent tube preconcentration technique is illustrated schematically in Figure 2.

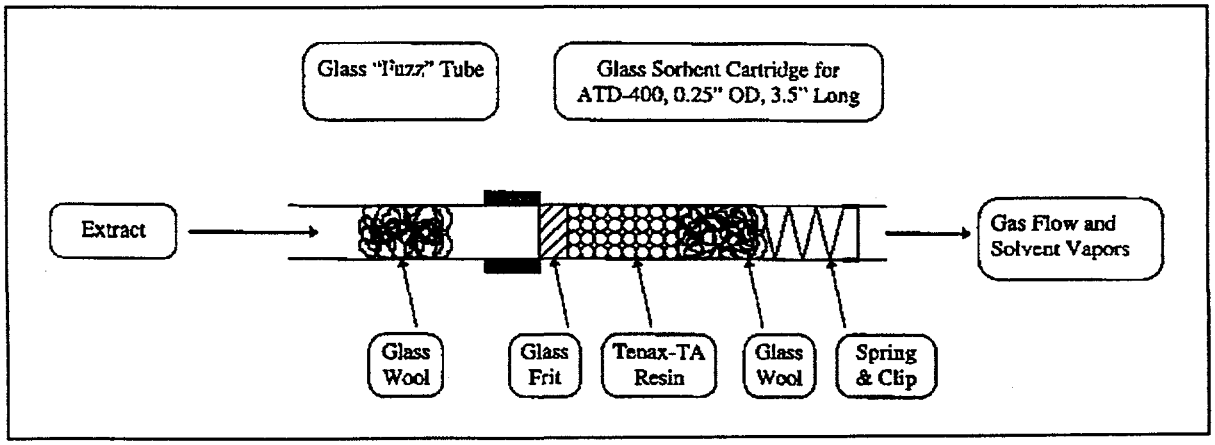

Figure 2. Basic Set-Up for Sorbent Tube Preconcentration

As shown in Figure 2, the sorbent resin upon which the agents will be preconcentrated is in the downstream tube, while the upstream tube, called the "fuzz" tube, contains silanized glass wool. The "fuzz tube" is used to minimize solvent damage to or solvent washing of the sorbent resin and to permit volatilization of the solvent and analyte prior to entering the sorbent cartridge. The sorbent tubes are available in stainless steel or glass; glass cartridges will be used for this project and will be supplied prepacked with Tenax TA resin. The newest cartridge design provides for retention of the resin between a glass frit retainer on the upstream end and a glass wool plug and glass spring on the downstream end. It is anticipated that Tenax TA will be used for all agent preconcentration procedures.

The two tubes will be connected using either Teflon tubing or a standard Swagelok fitting. After assembly, air is passed through the system at a rate of up to 250 mL/min by applying a vacuum to the downstream end. Alternatively, an inert gas can be supplied through the upstream end. Then an aliquot of the agent-containing extract is dosed onto the silanized glass wool in the "fuzz tube." The gas stream evaporates the solvent and the agent from the glass wool and transfers the vapors to the cartridge, where the agent is retained within the pores of the polymeric Tenax TA resin. The degree to which the agent and solvent are retained within the resin is a function of volatility and molecular polarity and is reflected by the specific retention volumes of the various compounds on the resin at a given temperature per unit weight of resin. After a period of time sufficient to allow for transfer of the agent onto the cartridge (ca. 5 min.), the gas stream is discontinued, and the cartridge is then capped on both ends and held for GC analysis.

<u>Matrix Interference</u> -- Validation of the analytical methods for the metal substrate and the soil for the agents of concern is expected to pose few problems. However, method validation for the spent decontamination fluid for agents is problematic simply because the decontamination fluid is designed to destroy chemical agent on contact. Standard chemical analyses of the spent decontamination fluid would therefore be expected to show nondetect values for any agent that was initially present, as well as the agents that were spiked into the solution as part of typical method validation experiments. Standard method validation practices in this case would provide little useful data.

It is nevertheless important to demonstrate that the analytical methods that will be used to analyze for the presence of agents would detect any agent that, for whatever reason, is present in the spent decontamination fluid. The EPA ran into this type of problem during a delisting action dealing with cyanide. Specifically, the waste matrix of concern contained strong oxidizers (e.g., bromine) that destroyed any cyanide that might have been present in the waste, or that was spiked into a solution for quality control purposes. In recognition of this, EPA determined that the waste could be delisted if the petitioner was able, among other things, to show that cyanide could be quantitatively recovered from the waste if the oxidizing agent were removed from the waste matrix (by adding a reducing agent). A similar approach for the analysis of agents in the spent decontamination fluid is being taken as part of the TTPE. Specifically, a reducing agent will be introduced into the sample matrix prior to agent spiking to reduce the hypochlorite. In addition, the pH of the decontamination fluid will be adjusted to optimize agent stability. By reducing the hypochlorite and adjusting pH, the Army hopes to show that if agent were present in the sample, it would have been detected. Several different reducing agents are being examined. While sodium arsenite is probably the better reducing agent, alternatives are being evaluated because sodium arsenite is a hazardous material and would create another hazardous laboratory waste stream.

<u>Sources of Imprecision</u> -- Several sources of imprecision can be traced to the spiking and extraction steps; the most probable are errors in pipeting. Contact-time variability may also contribute to imprecision, in proportion to the rate of agent hydrolysis. The use of recovery surrogates provides the means to monitor for gross errors of these types and will aid in distinguishing among the

various sources of imprecision. Surrogates are chemicals that are chemically inert, but similar in structure and behavior to a "target" analyte. Surrogates are commonly used in sophisticated chemical analysis to provide an internal quality control check for unusual matrix effects (such as might be expected with the decontamination fluid) and gross errors in the extraction step of the analytical process. Multiple surrogates will be examined for each of the chemical agents being evaluated in the Phase I delisting program.

Confirmation Methods -- The Army does not expect that agent will be found when the materials to be delisted are analyzed. However, because of both the sensitivity of the methods to be validated and the possible presence of interfering substances, positive results are sometimes found even when agent is absent. Erroneous positive results are referred to as false positives. Thus, methods are needed to confirm or deny the presence of agent when positive results are found. The confirmation methods to be employed will be GC using a mass selective detector (GC/MSD). These procedures will also be developed and validated as part of the TTPE.

Review and Conclusions

The Army believes that many of its chemical agent-associated wastes are truly nonhazardous and that millions of dollars are being spent unnecessarily to manages these wastes as hazardous. This paper summarizes progress to date on a complex technical program that has been initiated by the Argonne National Laboratory for the U.S. Army Test and Evaluation Command to support delisting of chemical agent decontaminated residues and contaminated soil at the U.S. Army Dugway Proving Ground, Utah.

Significant progress has been made to date, especially with respect to plans for conducting analytical method refinement and validation for the chemical agents. The Toxics Testing Performance Evaluation is underway at Dugway Proving Ground Laboratories and is expected to be completed sometime this summer. The authors hope to be able to report on progress as the program advances.

Acknowledgements

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