IMPROVED TECHNOLOGIES FOR DECONTAMINATION OF CRATED LARGE METAL OBJECTS

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John McFee, Kevin Barbour
Shaw Environmental

Ellen Stallings
Los Alamos National Laboratory

ABSTRACT

The Los Alamos Large Scale Demonstration and Deployment Project (LSDDP) in support of the US Department of Energy (DOE) Deactivation and Decommissioning Focus Area (DDFA) has been identifying and demonstrating technologies to reduce the cost and risk of management of transuranic element contaminated large metal objects, i.e. gloveboxes. DOE must dispose of hundreds of gloveboxes from Rocky Flats Environmental Technology Site (RFETS), Los Alamos National Laboratory (LANL), and other DOE sites.

This paper reports on the results of four technology demonstrations on decontamination of plutonium-contaminated gloveboxes with each technology compared to a common baseline technology, wipedown with nitric acid. The general objective of the demonstrations was decontamination to an alpha-emitting nuclide rate of less than 50,000 dpm/100 cm^2. The technologies demonstrated include:

- A LANL-developed electrochemical decontamination system (EDS) technique utilizing a recycled electrolyte solution to contact the glovebox surface via a small fixture, which is moved from location to location until the entire metal surface is decontaminated.
- A commercial three-step decontamination technology marketed by Environmental Alternatives Inc. (EAI), also deployed at RFETS, was demonstrated to quantify its performance relative to the baseline technology.
- Cerium (IV) nitrate decontamination, previously utilized at other DOE sites and developed for application to gloveboxes at RFETS, was demonstrated to quantify its performance in this application.
- A Russian-developed electrochemical decontamination (ECD) technology was monitored by the Los Alamos LSDDP for potential application in DOE. Although this decontamination activity was not an LSDDP "demonstration," it was planned, monitored, and reported using LSDDP methodologies.

Generally, the experience from these demonstrations shows that all innovative technologies perform better than the baseline, nitric acid wipedown. The goal of meeting 50,000 dpm/100 cm^2 was not achieved by the baseline technology or cerium nitrate decontamination at all measured locations. However, the decontamination achieved may be acceptable for LLW status at some facilities. Both electrochemical techniques are capable of decontaminating surfaces to the targeted contamination level and, if desired, can decontaminate to very low levels. The EAI technology is the best performing of the wipedown techniques, but is more costly.

INTRODUCTION

The Los Alamos LSDDP in support of the DOE DDFA has been identifying and demonstrating technologies to reduce the cost and risk of management of transuranic element contaminated large metal objects, specifically gloveboxes.

The LANL waste inventory includes approximately 200 “legacy” gloveboxes in temporary storage. These gloveboxes will be processed through the LANL Decontamination and Volume Reduction System (DVRS) and separated into low level waste (LLW) and transuranic (TRU) waste components. The LLW fraction will be disposed of at LANL, and the TRU fraction will be packaged and certified for ultimate disposal at the Waste Isolation Pilot Plant in Carlsbad, New Mexico. A majority of the gloveboxes to be processed by the DVRS has been classified as TRU.

It is costly to dispose of items in the TRU category. For LANL, the estimated cost is approximately $140,000 per average sized TRU glovebox. By decontaminating to the LANL-prescribed LLW activity level (50,000 dpm/100 cm^2), which is acceptable at the LANL LLW disposal site, disposal cost is reduced to an estimated $6,500 per glovebox. In addition to cost savings, reduction in waste category provides an immediate path forward for disposition as opposed to storage and extensive characterization.

Traditionally at LANL, gloveboxes were manually decontaminated by repeated scrubbing, using nitric acid and polypropylene rags. This method exposed workers to hazardous materials and was inefficient, as several iterations were needed to adequately decontaminate the glovebox surfaces. Most significantly, a large volume of contaminated rags was generated. The demonstrations reported here were conducted in a manner that allows one-to-one comparison of the decontamination technologies to this baseline technology on plutonium-contaminated gloveboxes.

- Electrochemical decontamination of plutonium contaminated gloveboxes has been utilized at LANL in production operations for glovebox cleanup and re-use. This demonstration documented the technology cost and risk impacts when compared side-by-side with the baseline technology, nitric acid wipedown.
- A commercial decontamination technology marketed by EAI was developed for plutonium-contaminated glovebox application at RFETS. This three-step decontamination process was used extensively in Building 776 and was reported to reduce the building closure costs considerably. This technology was demonstrated in this LSDDP to quantify its performance relative to the baseline technology.
- The RFETS Closure Project developed a specialized application for acidic cerium nitrate decontamination of plutonium-contaminated tanks. This technology was reconfigured for application to gloveboxes and used extensively in Building 771. The LANL LSDDP demonstration of this technology quantified the performance realized by this technology, again in comparison to nitric acid wipedown.
- A Russian-developed electrochemical decontamination technology was monitored by the Los Alamos LSDDP for potential application at LANL and DOE. Under DOE sponsorship, Russian investigators developed a specialized electrochemical decontamination technology. Although this decontamination activity was not an LSDDP “demonstration,” it was planned, monitored, and reported using LSDDP methodologies.

Results – LANL Electrochemical Decontamination System

The LANL-developed EDS has been used on gloveboxes in some areas of LANL. The system relies on a closed-loop electrolyte recirculation system that pumps the electrolyte through the process system and back to the surfaces to be decontaminated. A uniform electrolytic etch is achieved at low voltages and currents in combination with controlled solution chemistry to rapidly strip a few microns from the metal surface, resulting in the removal of surface contamination. The electrolyte solution is monitored and automatically adjusted to keep the pH at a high level, promoting the formation of metal hydroxides, which precipitate from solution. Solution recycle utilizes ultrafiltration with in-line separation of these hydroxides (including the radiological contaminants). This recycle and filtration technique minimizes aqueous process waste and results in minimal solid/radioactive wastes trapped in the disposable filter cartridges. This process has been shown to reduce plutonium and americium contamination by more than six orders of magnitude in some LANL applications, permitting the gloveboxes to be reused on location.

Figure 1 shows the system, including the electrolyte recycle system and the decontamination head that is vacuum attached to a vertical metal surface.

Figure 1. LANL Electrochemical Decontamination System

The purpose of the demonstration was to compare the decontamination efficiencies and the implementation costs of the LANL EDS to the baseline (nitric acid wipedown) in a one-to-one manner using LSDDP techniques for monitoring costs and wastes. The LSDDP team recorded operations time from start to finish, total work hours, waste generation, and expenditures for materials during all phases of the demonstration. (1)

In this demonstration, the innovative and baseline technologies were used to decontaminate a highly contaminated glovebox in the TA-55 area at LANL. The overall goal was to decontaminate the glovebox for reuse. An intermediate LSDDP goal was to decontaminate the glovebox to the LANL-prescribed LLW activity of < 50,000 dpm/100 cm^2.

The LANL EDS was successfully demonstrated with the following key results:

- Since the actinides were recovered and reprocessed, no liquid waste was generated.
- Contamination levels were reduced to below 50,000 dpm/100 cm^2 after two applications of the EDS.
- After two applications using the nitric acid wipedown process, a portion of the glovebox was still above 50,000 dpm/100 cm^2.
- A second application of the EDS reduced contamination levels in the glovebox to levels suitable for reuse.
- The cost of the electrolytic decontamination was \$2900/m^2, and the baseline cost was \$2900/m^2.

Results – Environmental Alternatives Inc. Technology

A second demonstration utilized a commercial decontamination technology developed and marketed by EAI. The EAI decontamination technology requires application and removal of three separate chemical formulations in a specified sequence. Each formulation is customized based on the metal to be decontaminated and the contaminants present. Each formulation is applied in low volumes, usually as a spray, left to set for a defined time, rinsed clean, and then removed. The technology is not dependent on scrubbing to be effective. The application and removal of all three formulations (and associated rinsing) to the contaminated surfaces consists of one cycle of the process, and typically requires one day (24 hours) to complete. This cycle is repeated as needed until the desired residual decontamination levels are achieved. (2)

The demonstration included the application of the EAI solution formulations (as directed by EAI technical representatives) to all of the interior surfaces of an approximately 11.1 m^2 plutonium-contaminated glovebox. Prior to conducting the demonstration, the inner surfaces of the glovebox were cleaned and wiped down with Fantastik™. All points measured on the glovebox surfaces showed an activity above one million counts per minute (cpm). Detector calibrations translate the one million cpm value to an alpha nuclide emission level of 2,857 thousand dpm/100 cm^2.

To be successful, the demonstration had to show a reduction of free and fixed contamination on all contacted surfaces to below 50,000 dpm/100 cm^2. The operation times from start to finish of each task, alpha survey measurements for surface activity, and waste volumes generated during the demonstration were recorded. Figure 2 shows the glovebox floor during decontamination.

Figure 2. Decontamination of a LANL glovebox using EAI Technology

The EAI decontamination demonstration results were:

- Two workers decontaminated the inner surfaces of a 2.4 m x 1.1 m x 0.76 m glovebox in approximately 13 labor hours.
- Three cycles of decontamination were conducted using the EAI technology, reducing the average contamination levels to less than 50,000 dpm/100 cm^2.
- The same baseline decontamination data was used for this technology as the LANL EDS system. Since ½ of an entire glovebox was decontaminated during theEDS demonstration, and the contamination types and levels were similar, the same baseline is used.
- The demonstration produced approximately 0.0281 m^3 of waste.
- The cost for each technology on a unit basis is \$3100/m^2 for the EAI technology and \$2900/m^2 for the nitric acid wipedown. A significant element of the EAI technology cost is related to the cost of the service provided by EAI for decontamination.

Results – Cerium IV Nitrate Decontamination

A third decontamination technology demonstrated at LANL involved the use of cerium IV nitrate. This technology has been used in other applications in DOE, including RFETS. It was demonstrated in this LSDDP to allow one-to-one comparison on plutonium-contaminated gloveboxes. Cerium nitrate (in acid) is a strong oxidizer capable of oxidizing and solubilizing plutonium and stainless steel components such as nickel, chrome, and iron. The solution is sprayed onto the surfaces, scrubbed with polypropylene rags, allowed to react, and then rinsed with water. While reacting, the solution strips a few microns from the metal surface of the glovebox, which results in the removal of fixed radiological surface contamination. Figure 3 shows the glovebox that was used in the demonstration. (3)

Figure 3. Glovebox used in LANL Cerium (IV) Nitrate demonstration

The cerium nitrate technique was demonstrated on a 17-year old, plutonium-contaminated glovebox. The demonstration included decontamination of the glovebox floor by applying the cerium nitrate solution to one half and dilute nitric acid solution to the other half. Prior to conducting the demonstration, the inner surfaces of the glovebox were cleaned and wiped down with Fantastik™. All points measured on the glovebox surface initially registered more than one million counts per minute, which indicates surface activity higher than 2,857 thousand dpm/100cm^2.

As in the previously mentioned demonstration, success would be reduction of free and fixed contamination on all contacted surfaces to below 50,000 dpm/100 cm^2. The operation times from start to finish of each task, alpha survey measurements for surface activity, and waste volumes generated during the demonstration were recorded.

The demonstration provided the following results:

- Two workers conducted the decontamination demonstration for the floor of a 1.4 m x 1.1 m x 0.76 m glovebox.
- Five cycles of decontamination using cerium nitrate solution were required to reduce the contamination to 50,000 dpm/100 cm^2, except for two spots located in glovebox floor. An average drop in surface activity over the entire surface for each decontamination cycle was calculated and resulted in a drop from 2857 thousand dpm/100 cm^2 to 90,000 dpm/100 cm^2.
- Five applications of nitric acid solution reduced the overall actvitiy of the glovebox floor, but failed to achieve a contamination level to below 50,000 dpm/100 cm^2 at any single survey

location. An average drop in surface activity over the entire surface for each decontamination cycle was calculated and resulted in a drop to 104,000 dpm/100 cm^2.
- The demonstration produced approximately 0.012 m^3 of waste for each technique (i.e., spray bottles, damp polypropylene rags, Scotchbrite pads) to decontaminate 0.52 m^2 each.
- Since only a glovebox floor was decontaminated in this demonstration, and the floor is the most difficult task, the conclusion of this demonstration is that cerium nitrate accomplished the task at 2/3 the cost of the baseline. This ratio is applied to the baseline for the LANL EDS demonstration.

Results – Russian electrochemical decontamination

A second electrochemical decontamination process was evaluated using LSDDP procedures. This process was developed by the All-Russian Design and Scientific Research Institute for Complex Power Technology (VNIPIET). The VNIPIET technology differs from the LANL electrochemical method in several areas. The VNIPIET approach uses low-ohm electrodes incorporating an electrically conductive brush. Each fiber behaves as a microelectrode, closely approaching the surface and at the same time, separated from the surface with a thin film of electrolyte. Alternating current is utilized to remove the interfering oxide layer created on stainless steel during the electrolysis process. In addition, alternating current allows chromium from stainless steel to go into solution as a Cr^{+3}, simplifying treatment of the liquid radioactive waste. Hydrogen gas release is significantly decreased, especially at lower current densities. (4)

The VNIPIET system is also configured for electrolyte recycle. An in-line sorption technology is used to remove the radionuclides and metals from the solution and recycle the electrolyte solution (in this case, formic acid). The process uses an inorganic sorbent, which can be then solidified into a non-leachable waste form.

In this demonstration, the technology was used to decontaminate a plutonium-contaminated glovebox located at the V.G. Khlopin Radium Institute in St. Petersburg, Russia. The overall goal was to decontaminate the glovebox to very low levels, to meet free release criteria. An intermediate goal was to decontaminate the glovebox to LLW activity of <50,000 dpm/100 cm^2. The LSDDP Team recorded operations time from start to finish, total work hours, and expenditures for materials during all phases of the demonstration.

The VNIPIET system was successfully demonstrated with the following key results:
- Contamination levels were reduced to below 50,000 dpm/100 cm^2 after two runs.
- A third application reduced contamination levels in the glovebox by an additional factor of two.
- The system provided decontamination factors that met the demonstration requirements with an extremely easy-to-use decontamination probe.
- Since the decontamination solution was recovered and the actinide waste solidified, no liquid waste was generated.
- The cost for each technology on a unit basis when extrapolated to an entire glovebox is estimated to be \$1,636/m^2

Conclusion

The Los Alamos LSDDP continues to provide substantial cost savings to the DVRS process in this third year of demonstrations. Cost and performance of the decontamination demonstrations were developed to provide LANL management information for decontamination technology selection and are summarized in Table 1, below:

Table 1. Summary of Decontamination Technology Performance

Process	Cycles	DF*	Initial Activity (dpm/100 cm^2)	Final Activity (dpm/100cm^2)	Cost ($/$m^2$)
LANL EDS	2	177	100k – 1M	0.5k – 5k	2,900
Baseline	4	17	100k – 1M	10k – 50k	2,900
EAI	3	99	2.4M	24k	3,100
Baseline	4	17	>2.9M	10k – 50k	2,900
$CeNO_3$	5	32	>2.9M	90k	1,900
Baseline	5	27	>2.9M	10k – 50k	2,900
Russian ECD	3	18	140k	8k	1,636
Baseline	None				

* DF = Decontamination Factor or Initial Activity divided by Final Activity

Generally, the experience from these demonstrations shows that all innovative technologies perform better than the baseline, nitric acid wipedown. The goal of meeting 50,000 dpm/100cm^2 was not achieved by the baseline technology or cerium nitrate decontamination at all measured locations. However, the decontamination achieved may be acceptable for LLW status at some facilities. Both electrochemical techniques are capable of decontaminating surfaces to the targeted contamination level and, if desired, can decontaminate to very low levels. The EAI technology is the best performing of the wipedown techniques, but is more costly. This additional cost is related to the cost of using the EAI decontamination service, as opposed to in-house labor.

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