

DECONTAMINATING THE DOE-STD-3013-96 INNER CONTAINER TO MEET 10 CFR 835 APPENDIX D REQUIREMENTS

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ABSTRACT

The United States Department of Energy (DOE) has published a standard that specifies the criteria for preparation and packaging of plutonium metals and oxides for safe long-term storage (DOE-STD-3013-96). This standard is followed for the packaging of materials resulting from the disassembly of nuclear weapons at Los Alamos National Laboratory under the Advanced Retirement and Integrated Extraction System (ARIES) project. Declassified plutonium metal or oxide material from the ARIES project is packaged into doubly contained and welded type 304L stainless steel containers that comply with the DOE standard.

The 3013-96 standard describes requirements for maximum contamination limits on the outer surface of the sealed inner container. These limits are 500 dpm per 100 cm² for direct measurements and 20 dpm per 100 cm² for removable contamination. For containers filled, welded, and handled inside a highly contaminated glovebox line, these limits are difficult to obtain. Simple handling within the line is demonstrated to contaminate surfaces from 10,000 to 10,000,000 dpm alpha per 100 cm².

To routinely achieve contamination levels below the maximum contamination levels specified by the 3013-96 standard within a processing operation, a decontamination step must be included. In the ARIES line, this decontamination step is an electrolytic process that produces a controlled uniform etch of the container surfaces. Decontamination of the 3013-96 compliant ARIES inner container is well demonstrated. Within 30 to 50 minutes electrolysis time, fixed contamination is reduced to hundreds of dpm generally occurring only at electrode contact points and welds. Removable contamination is routinely brought to non-detectable levels. The total process time for the cycle (includes electrolysis, rinse, and dry stages) is on the order of 1.5 to 2 hours per container.

The ARIES inner container decontamination system highly automated and consists of a plumbing loop, electronic controls and process monitors, and a decontamination chamber or "fixture". The fixture is situated like an air lock between a contaminated and an uncontaminated section of a processing glovebox. The welded and leak tested container is placed into the fixture through a door on the contaminated side and the electrolysis process is run, including rinse and dry cycles. The container is then removed through a second door into the uncontaminated side where it is monitored for surface alpha contamination, leak checked, and reweighed.

INTRODUCTION

The Advanced Recovery and Integrated Extraction System (ARIES) Project at Los Alamos National Laboratory is a demonstration and testing line for weapon disassembly and fissile material conversion to unclassified form. The technology of ARIES becomes the baseline technology that will be applied to a future Pit Disassembly and Conversion Facility (PDCF). The ARIES process takes the heart of a nuclear weapon (the "pit"), disassembles the components, extracts the plutonium, converting it from classified to unclassified form, and places this material into a container designed for long-term (>50 years) storage. The final product is in a form suitable for inspection by international treaty inspectors such as the International Atomic Energy Agency (IAEA).

One of the more challenging steps of this process is to containerize the plutonium. Plutonium is a material that is hazardous, even at the nanogram quantity. Handling of this material is normally done remotely or through the gloves of a glovebox. Because the material recovered from weapons will not be stored within a glovebox, but within rooms where personnel have access, the container must be leak tight. Furthermore, this package must remain intact even if storage or shipping conditions become severe, such as in a fire or vehicular accident. This requires that the material being stored be in a stable form and that the packaging be resilient. Ideally, the containment should be double-walled, decreasing the chances of a breach. In addition to being leak tight, the outside surfaces of this container must be free of plutonium and its decay products. In fact, to further decrease the chances of a plutonium release, the external surfaces of both the internal and external vessels of a doubly contained package should be contamination free.

This is the rationale behind the DOE's long term packaging standard for plutonium as specified in DOE-STD-3013-96 (currently under revision). The standard specifies acceptable forms of the material for this long-term storage and the minimum requirements of the containment vessel.

The containment vessel specified in '3013-96 is a vessel within a vessel. These vessels must be leak tight and be made of materials that will not degrade under normal storage conditions. The external surfaces of both of these vessels (and presumably the inner surfaces of the outer container) must be contamination free to the limits specified in the Code of Federal Regulations (CFR), Chapter 10, Section 835, Appendix D. For alpha emitting materials (e.g., plutonium), these contamination limits are 20 dpm/100 cm² for removable contamination and 500 dpm/100 cm² for non-removable contamination. There is an allowance for higher levels (up to 3×) of contamination so long as the average contamination on an item does not exceed the prescribed levels.

Scientists on the ARIES team have developed a stainless steel container package meeting or exceeding all aspects of the '3013-96 standard, and a process by which the inner container may be filled, welded shut, verified to be leak tight, and decontaminated to the strict requirements of 10-CFR-835. The inner container is then removed from the glovebox line for placement into the outer container and subsequent analysis and surveillance.

The canning and decontamination segment of the ARIES demonstration line consists of two gloveboxes. In the first of these gloveboxes, the plutonium (as an oxide or metal puck) is placed within the primary (inner) container and welded shut under a helium atmosphere. The weld is accomplished using a tungsten inert gas (TIG) weld designed for 100% penetration. The helium atmosphere of the glovebox provides an inert atmosphere over the material while at the same time providing a means of leak testing the container later in the process. The welded primary container is then moved down the process line to the decontamination glovebox by means of an interconnecting conveyor. Leak testing and decontamination of the inner container are performed within the decontamination glovebox.

The decontamination glovebox is segregated into three sections (Figure 1). The first of these sections, Section A, is radiologically contaminated or "hot". Section B is also "hot" and is where the solution handling process equipment is housed. The dividing wall between these sections serves to segregate solutions from the containers of plutonium to minimize the hazard of a breach of solution containment. Both Sections A and B are connected to the facility Zone 1 air handling system. Section C is radiologically uncontaminated or "cold" and is open to the room, maintaining an inward airflow through connection to the facility Zone 2 air handling system, much like an open-front hood.

Section A is where the initial leak testing (before electrolytic decontamination) is carried out. If the container is found to meet the requirements for leak tightness (leak rate $< 1 \times 10^{-7}$ std. cc/sec), the container is placed into the decontamination chamber built within the wall separating Sections A and C of the glovebox. Decontamination is achieved within this chamber as detailed in the following section of this paper.

Following the decontamination process, the container is removed from the chamber into Section C. In this location, the container is radiologically surveyed to verify successful decontamination and a secondary leak check performed to verify that the can remains leak tight. Once certified leak tight and contamination free, the container is removed from the process line and brought into the room. The secondary containment is applied within a helium chamber in the same manner as the primary container, but without the radiological controls.

ELECTROLYTIC DECONTAMINATION

The decontamination process utilized in the ARIES demonstration is an electrolytic process. The stainless steel primary container is placed inside a chamber mounted directly within the partition separating the "hot" and "cold" sections of the decontamination glovebox. Electrodes

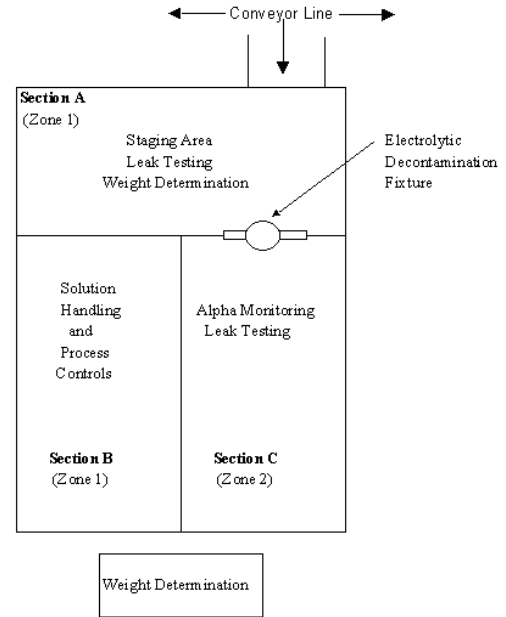


Figure 1: Layout of the ARIES electrolytic decontamination glovebox and process equipment..

passing through insulators in the stainless steel chamber make contact to both the top and bottom of the container.

Once the can is inside the chamber and the "hot" side door closed, the decontamination process is started. The decontamination process itself is similar to the widespread commercial surface preparation process of electropolishing, but with properties of electrolytic cleaning.

Electropolishing is a metal surface preparation technology that produces a microscopically smooth and brightened surface without abrasives. The resulting surface has many desirable characteristics including enhanced corrosion resistance and a high luster. In electropolishing, the metal to be polished is made the anode (positive electrode) of an electrolytic cell. As current is made to flow through this cell, a relatively thick viscous layer of reaction products is generated at the surface of the metal. Diffusion of the dissolved metal ions through this film becomes rate limiting, resulting in a smoothing of surface features. Figure 3 depicts a typical cold worked stainless steel surface before and after electropolishing in a solution of concentrated phosphoric and sulfuric acids.

Electrolytic cleaning is a preparation technology used to clean contaminants from metal surfaces prior to electroplating or other surface treatment where adhered oils or other films could result in a degraded final product. In contrast to electropolishing, the surface to be cleansed is generally made the cathode (negative electrode) of an electrolytic cell. When current is passed through the cell, copious volumes of hydrogen gas are evolved and a highly caustic environment is created at the metal-solution interface. The caustic interface conditions loose the bonds between the surface and surface grime and the evolving gas that nucleates beneath and around surface dirt and grime aids to break it free of the surface, generally without changing the surface of the metal.



Figure 2. Inner container decontamination fixture and decontaminated storage container as viewed from the "cold" segment of the glovebox.

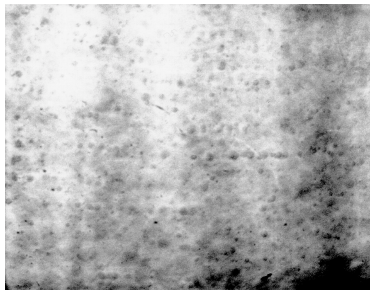
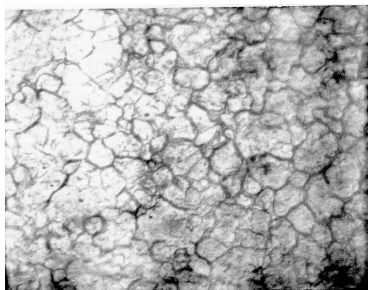


Figure 3. Typical type 304L stainless steel cold worked surface before (left) and after (right) electropolishing. Approximate magnification 200X.

The methodology developed at LANL for decontamination of stainless steel surfaces has features of both electropolishing and electrolytic cleaning. In the LANL technology, the

electrolyte solution is not a concentrated acid as in most commercial applications of electropolishing. Instead, the electrolyte contains a moderate concentration of a sulfate salt at an elevated pH of 10 to 12. The part to be cleaned is made the anode. As current is driven through the cell, the process of water oxidation consumes a large fraction, greater than 80% of the total current. Figure 4 depicts the chemistry of the decontamination process on stainless steel.

The evolution of oxygen gas serves to lift particulates from the surface, while the generation of hydronium ions lowers the local solution pH, allowing the metallic cations to remain soluble near the interfacial region, which improves the uniformity of the metal dissolution. Stainless steel surfaces treated in this manner are uniformly etched and decontaminated.

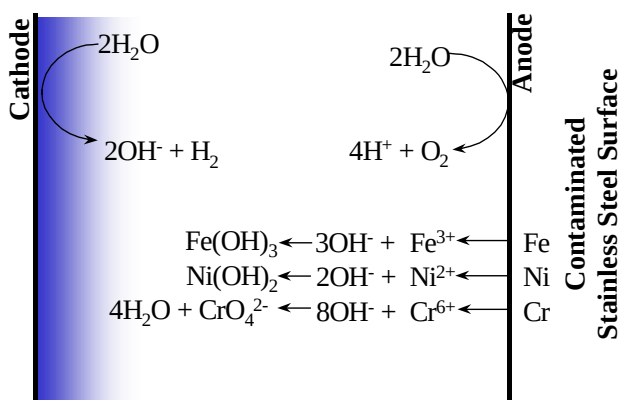


Figure 4. The chemistry of the anodic dissolution of stainless steel in alkaline sodium sulfate solution. Actinides freed from the surface during the process are entrained in the metal hydroxide precipitate.

RECYCLE OF ELECTROLYTE

In order to recycle the electrolyte solution, the radioactive components and metal cations must be removed. Because both iron and nickel are insoluble in modest alkali, the sodium sulfate electrolyte is maintained at a constant, high pH through the continuous addition of small quantities of sodium hydroxide solution. The formation of the metal hydroxide precipitates is key to the process. Not only does the precipitation facilitate the removal of these elements from solution, but also the precipitate entrains or "captures" the actinide particles that have been released from the metal surface. A mechanical filtration of the electrolyte solution results in a decontamination of the electrolyte.

In the ARIES process, separation of the precipitated metal hydroxides and the entrained actinides is accomplished through the use of ultrafiltration. Electrolyte is cycled through a commercial ultrafiltration module producing a precipitation free (read "contamination free") permeate stream which provides the electrolyte flow to the decontamination fixture. This results in an accumulation of these precipitates within the electrolyte reservoir. This accumulation of precipitate is then removed through a more conventional batch filtration. The detailed application of ultrafiltration in this and other electrolytic decontamination systems will be detailed elsewhere¹.

Unlike iron and nickel, the hexavalent chromium ion does not precipitate. Instead, it reacts with hydroxide ions to form a soluble chromate (CrO_4^{2-}) species. Chromate is removed from solution by a secondary process in which the hexavalent chromium is chemically reduced to a trivalent oxidation state by addition of a reducing agent (e.g., ferrous sulfate). The trivalent chromium then precipitates as chromium hydroxide ($\text{Cr}(\text{OH})_3$). Filtration of the electrolyte solution provides a compact metal hydroxide residue for discard while the filtrate is returned to the process for continued usage.

AUTOMATION OF THE PROCESS

Operation of a complex system within an actinide-processing environment presents many unique constraints on system design. The system must be robust and modular because replacement of failed components is challenging within a glovebox system. Individual components must be sized to be replaceable, i.e., replacement parts must fit through door or window openings of the glovebox. Negativity of the glovebox system must be ensured while at the same time safe hydrogen levels must be maintained through introduction of a gas purge. And, all waste produced in the process will be radioactive and therefore must be minimized.

The complexity of the ARIES container decontamination system requires a high level of automation to remove the potential for human error. Valves, pumps, heaters, pH control, and data collection are computer controlled. A computer running a LabVIEW program continuously monitors and displays the operating state of the system and responds to any off-normal conditions by shutting down the system in a predetermined manner. Process stages are sequentially stepped through by the computer to ensure a proper operational sequence is always followed, though an operator is always present to oversee system operation. The system periodically requests operator acknowledgment to prompts. Failure of the system to receive acknowledgment forces system shutdown. In this way, the operator need not take any special actions if a facility emergency is sounded.

A decontamination cycle proceeds in the logical sequence of electrolysis, electrolyte purge, rinse, fixture preheat for drying, rinse water purge, drying, and cool down stages.

RESULTS

Testing of the decontamination system was broken down into four logical stages. In the first stage, containers were welded outside the contaminated glovebox line, then processed through the system without being contaminated. This stage occurred prior to connection of the glovebox to the facility and allowed the operators and system engineers to determine the expected performance parameters for the system prior to introduction of radiological hazards.

The second stage of testing occurred following connection of the glovebox to the facility. Containers welded outside the glovebox were introduced to the glovebox line, contaminated, were verified to be contaminated by direct survey with alpha probes, and then decontaminated. This stage of testing allowed for verification of the system parameters required to achieve decontamination of the container. Containers with laser-engraved markings were also decontaminated to verify that container marking would not be detrimental to the decontamination process.

The third stage of testing involved welding of the containers within the contaminated glovebox line. In this stage, evaluation of the quantity of fixed contamination within the weld could be evaluated.

The fourth and final stage of testing involved the processing of a container holding a quantity of special nuclear material destined for storage. This stage permitted the verification of the direct assay procedures (gamma interference from the contained materials). It also provided an opportunity to study the effect of the thermal loading on the drying cycle temperatures.

As a result of the testing, it was determined that a minimum of 40 minutes of electrolysis at 40 amps (53 mA/cm²) was required to adequately decontaminate a container to meet the specifications of 10-CFR-835. A nominal time of 50 minutes was settled on for the routine processing of containers. In 50 minutes of electrolysis, a removal of approximately 2 grams of material from the container – about 3.5 microns – is routinely observed. This material removal is uniform and results in decontamination.

Non-removable contamination was found at the electrode contact points on top and bottom of the container. These locations showed evidence of oxide formation consistent with electrolysis at elevated temperatures. The effect is repeatable. It is expected that these regions locally heated during the passage of current, a phenomenon determined in bench scale tests to result in the formation of oxide and a decrease in the rate of metal dissolution. This contamination is non-removable, and remains non-removable over time.

Deep laser engraving with a pulsed laser resulted in contaminated regions that were difficult to decontaminate. Lighter engraving with a continuous wave laser was more amenable to decontamination, presenting no observed impact on the decontamination process. These markings remain legible, though with reduced visual contrast (oxidized material left within the marked areas by the laser is removed), following the decontamination process. Contamination in welds fabricated within the glovebox line was not observed to be an issue. No measurable non-removable contamination was observed in the welds.

Some removable contamination was found on the top and bottom surfaces of the container following the decontamination process, but was readily wiped off with a damp piece of cloth, allowing packages to meet the storage criteria. It is presumed that contamination is transferred to the rinse water over many cycles of processing.

The dry cycle temperature program was not influenced by the thermal loading of significant quantities of fissile material within the containers, nor was the direct surface assay of the containers affected by the gamma radiation emitted by this containerized material.

The full decontamination cycle requires nearly 2 hours to complete, the majority of this time is related to the drying of the container. A dry container surface is necessary for obtaining an accurate counting of any residual surface alpha activity immediately upon completion of the decontamination process.

FUTURE

An integrated demonstration of the ARIES process line is intended to occur early to midyear calendar 1999. The goal of the demonstration is to validate processes and collect data for use in the future full scale Pit Disassembly and Conversion Facility (PDCF). This decontamination system will be fully tested during that time. Additional upgrades are, however, currently planned. These upgrades include the installation of a distillation unit to produce clean rinse water from the electrolyte solution for each process run, introduction of robotic systems for container handling, and an integration of the canning and decontamination process into a single glovebox. Migration of the system controls from LabVIEW to programmable logic controllers is also planned.

The ARIES demonstration line is currently packaging material into a nominal 6-inch tall package. The 3013 standard allows for a 10-inch tall package to accommodate a greater volume of plutonium oxide. The 10-inch container will be the standard for the PDCF. As a result, the decontamination system will be upgraded to allow for decontamination of the 10-inch tall package.

Additionally, studies to determine how to alleviate the small quantity of fixed contamination at the electrode contact points are ongoing, as is a study to determine the effect of electrolyte chromium concentration on the decontamination process efficiency.

ENDNOTES

1. K. R. Weisbrod, H. E. Martinez, D. E. Wedman, "Evaluation of Ultrafiltration Membranes for Decontamination Applications", LA-13450-MS, in editing.