

ELECTROLYTIC DECONTAMINATION OF THE 3013 INNER CAN

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ABSTRACT

Disposition of plutonium recovered from nuclear weapons or production residues must be stored in a manner that ensures safety. The criteria that has been established to assure the safety of stored materials for a minimum of 50 years is DOE-STD-3013. This standard specifies both the requirements for containment and furthermore specifies that the inner container be decontaminated to a level of ≤ 20 dpm/100 cm² swipable and ≤ 500 dpm/100 cm² direct alpha such that a failure of the outer containment barrier will have a lower probability of resulting in a spread of contamination.

Los Alamos National Laboratory (LANL) has designed a containment package in accordance with the DOE standard. The package consists of an optional convenience (food pack) can, a welded type 304L stainless steel inner (primary) can, and a welded type 304L stainless steel outer (secondary) can. With or without the food pack can, the material is placed inside the primary can and welded shut under a helium atmosphere. This activity takes place totally within the confinement of the glove box line. Following the welding process, the can is checked for leaks and then sent down the line for decontamination. Once decontaminated, the sealed primary can may be removed from the glove box line. Welding of the secondary container takes place outside the glove box line.

The highly automated decontamination process that has been developed to support the packaging of Special Nuclear Materials is based on an electrolytic process similar to the wide spread industrial technique of electropolishing. The can is placed within a specially designed stainless steel fixture built within a partition of a glove box. This fixture is then filled with a flowing electrolyte solution. A low DC electric current is made to flow between the can, acting as the anode, and the fixture, acting as the cathode.

The passage of current through this electrolytic cell results in a uniform anodic dissolution of the surface metal layers of the can. Iron is oxidized to the ferric ion, nickel to the

nickelous ion, and chromium to the hexavalent form. Under the alkaline conditions of the electrolyte solution, the iron and nickel components precipitate as hydroxides while the chromium remains soluble in solution as the chromate ion. The nature of the precipitate is such that the actinide contaminants, which are freed from the surface during the electro-dissolution of the underlying stainless steel, are insoluble and become entrained in the precipitate. The application of ultrafiltration technology results in a separation of the actinide activity from the flowing solution. This process results in a rapid decontamination of the can. The electrolyte is fully recyclable, and the separation of the chromium from the actinides results in a compact, non RCRA secondary waste product.

Following the decontamination, the system provides a flow of rinse water through the fixture to rinse the can of remaining salt residues. The system then carries out a drying cycle. Finally, the fixture is opened from the opposite side of the partition and the can surface monitored directly and through surface smears to assure that decontamination is adequate.

1. INTRODUCTION

In order to facilitate the disassembly and conversion of nuclear materials from nuclear weapons to a storable form, it is necessary to provide a means for packaging and safe long term (greater than fifty years) storage of the materials. To this end, the United States Department of Energy (DOE) has published a storage standard for these materials (DOE-STD-3013). As part of the Advanced Retirement and Integrated Extraction System (ARIES) demonstration taking place at Los Alamos National Laboratory (LANL), material is being packaged to this standard. (The ARIES process is a pilot line for a planned United States Pit Disassembly and Conversion Facility (PDCF) to be built at a location not yet determined.)

In accordance with the DOE standard, special nuclear materials returned from the stockpile and converted to either

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oxide powder or metal pucks are to be stored in a doubly contained hermetically sealed storage vessel, the inner vessel of which must be free of contamination to the levels specified in the Code of Federal Regulations, 10-CFR-835, that is, levels ≤ 20 dpm/100 cm² of alpha for swipable contamination and ≤ 500 dpm/100 cm² for direct alpha measurements.

For the ARIES process, type 304L stainless steel canisters are utilized as the primary inner container. These cans are introduced into the glove box line where they are loaded with a nominal 4.4 kg of nuclear material (either oxide or metal) and welded closed. A secondary canister then encloses the primary, and this canister also welded closed. Because the primary canister is introduced into and handled within the contaminated glove box system within which the weapons components, plutonium metal, and plutonium oxide are handled, the can must be decontaminated to reach the specified contamination limits. Furthermore, secondary welding occurs outside the primary glove box line making it imperative that the inner can be shown to be decontaminated prior to its removal from the glove box line.

2. THEORETICAL BACKGROUND

The electrolytic decontamination of 304L stainless steel in alkaline electrolyte has been well demonstrated at LANL¹⁻⁴. This method has been successfully applied to the decontamination of stainless steel glove boxes, uranium weapon components, and other items at LANL.

The electrolytic decontamination process is similar in design to the wide-spread industrial practice of electropolishing. The electrolytic decontamination technology utilizes an electric current to dissolve surface layers of the metal and, in the process, cleans away surface contamination. The major differences between this application and commercial electropolish applications are the voltage-current requirements and reduction in electrolyte concentration necessary to produce a desired finish. The finish observed in the electrolytic decontamination process is more of a uniform electrolytic etch, than a polish.

The chemistry of the process is depicted in Figure 1. When current is made to flow between two stainless steel surfaces through an alkaline solution of 0.2 molar sodium sulfate, dissolution of the anode occurs resulting in the generation of iron(3+), nickel(2+) and chromium(6+) ions at the anode-solution interface. At current densities on the order of 40 mA/cm² as are of interest in the current study, on the order of 88% of the current passing through the anode

results in the oxidation of water to protons and oxygen gas. The cathodic process observed is the reduction of water to hydroxide and hydrogen gas.

Once dissolved from the surface, the solvated iron and nickel components precipitate as Fe(OH)₃ and Ni(OH)₂ respectively. This precipitation reaction is key to the success of the technique in that the precipitation of these metals effectively entrains the actinide contamination, restricting contamination to the precipitating solid sludge.

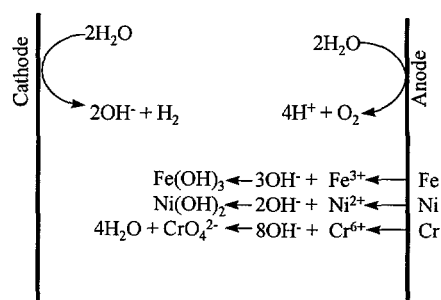


Figure 1: Chemistry of the electrolytic decontamination process on stainless steel.

The chromium component of the metal hydrolyzes to the chromate ion. Periodically, (on the order of once every fifty cans processed) the precipitate is allowed to settle from the electrolyte solution where it is decanted from the bottom of the electrolyte reservoir and filtered. The chromium may then be reduced to chromium(3+) and precipitated out as the hydroxide. This procedure allows for a separation between the actinide and chromium components.

In order to maintain pH balance in the solution, sodium hydroxide is dosed by a pH control subsystem. Left unadjusted, the pH of the solution will fall, due to the hydrolysis reaction of the chromium component. This reduction in pH has results in an increased solubility of the metals. This increase in solubility has a deleterious effect on the decontamination efficiency because of the increased potential for recontamination of the surfaces by solubilized actinides.

The electrolytic decontamination process has been extensively tested on stainless steel. The results of testing on primary storage cans indicates that initial surface contamination levels achieved through nominal handling of the can reach as high as millions to tens of millions of disintegrations per minute (dpm) of swipable transuranic contamination. This contamination level was readily reduced to non detectable swipable contamination levels within just 10 minutes of electrolysis time at a current

density of 40 mA/cm². Non-swipable contamination was reduced to just a few hundred dpm.

The majority of the non-swipable contamination remaining after decontamination was observed to migrate about the can upon successive decontamination cycles. The conclusion reached was that this is a recontamination effect: actinide materials were being re-deposited on the can surface, probably along grain boundaries where it was not susceptible to removal by swiping. During these studies, no filtration was employed and the precipitate generated in the process was recycled through the system. It was this observation which led to the inclusion of ultrafiltration within the decontamination system.

Because neither sulfate nor sodium ions are involved in the electrode or solution reactions, there is no degradation of the electrolyte solution. Continuous reuse of the electrolyte solution is permitted, providing waters lost to electrolysis and evaporation are replenished. This is accomplished by periodically transferring enough of the rinse water solution to the electrolyte reservoir to replenish the lost water. This procedure minimizes the waste from this process to a compact metallic oxide powder. The balance on the water usage has not yet been determined, but aqueous waste is expected to be extremely low (less than ten liters per year of operation).

2A. Design of the ARIES Decontamination System

The ARIES decontamination process was specifically engineered around the described chemistry to enable the efficient and routine decontamination of the primary can while generating as minimal a waste stream as possible. To that end, a decontamination system similar to that shown in Figure 2 was constructed.

The decontamination system for the ARIES line incorporates a high degree of automation. The system is laid out within a multiple compartment glove box with the decontamination fixture built into one of the partition walls which separates a section of high contamination from one of essentially no contamination.

The decontamination fixture is a clam-shell housing constructed of stainless steel. The fixture may be opened from either side of the partition to enable the can to be placed into the fixture from the contaminated side of the partition, and removed from the non-contaminated side. This fixture is designed to closely encase the storage can with a uniform annular space separating the can from the fixture walls. Nylon spacers provide positive spacing to ensure that the two surfaces do not contact one another. Anode leads pass through nylon sleeves at the top and the

bottom of the fixture to make the electrical contact with the storage can. During the decontamination cycle, electrolyte solution flows through the annulus and the can is made anodic, the fixture made cathodic.

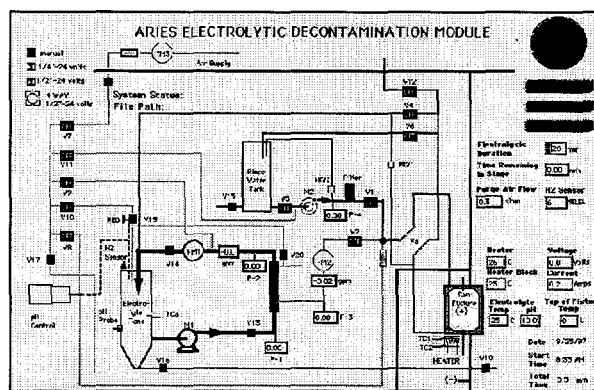
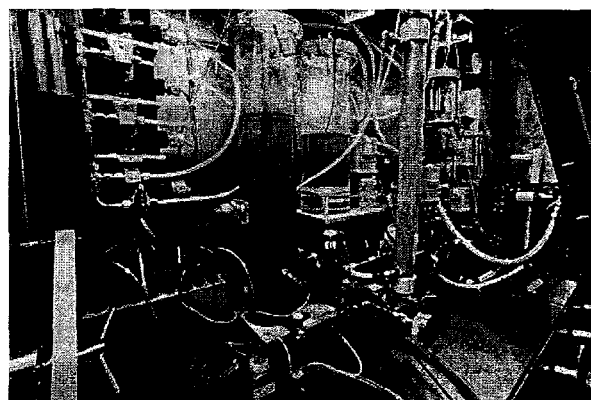
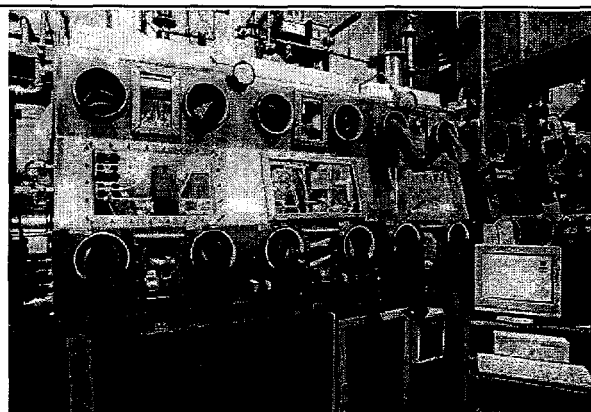


Figure 2: Photograph of an automated primary nuclear material storage can decontamination system. The decontamination fixture is built into the glove box partition at the far end of the glove box in the center photo. The bottom image is the LabView™ operator interface computer display.

The decontamination fixture is fed an electrolyte solution which is provided from the permeate side of a commercial hollow-fiber ultrafiltration module. This permeate contains no precipitate, and, therefore, contains little or no radioactive component. The flow enters from the bottom of

the fixture, displacing evolved gasses and electrolyte through the top of the fixture. The flow then returns to the electrolyte reservoir.

The system is operated via a computer running LabView™ software. The computer controls the actuation of valves, the activation and deactivation of pumps, heaters, and the electrolysis power supply. The computer continuously monitors air and solution flow rates, valve positions, flow pressures, temperatures, electrolyte pH, the concentration of hydrogen gas, both within the glove box and within the head space above the electrolyte reservoir where off-gassing occurs. If an off-normal situation is sensed, the computer is programmed to place the system into a safe condition. Additionally, intermittent operator interaction is required to assure the system is continuously attended during operation.

The full process run can be likened to that of an elaborate dish washer with electrolysis (wash), rinse, and dry cycles. A full run takes roughly an hour to complete, depending slightly on the input electrolysis time. The process begins with the operator placing a can (welded and leak tested) into the fixture from the contaminated side of the glove box partition and closing the door. The operator then actuates the software which takes the operator through a short checklist of items to verify that the system is ready to operate.

The system next establishes a flow of compressed air which aids in the dissipation of the evolving hydrogen gas from the head space of the electrolyte reservoir. The main pump is then activated to establish a flow of electrolyte through the ultrafiltration module. Once this flow is established, the permeate flow (ca. one gal per minute) is made to pass through the decontamination fixture. At this point, the electrolysis current is activated for the time specified (nominally 10 to 20 minutes).

Following the electrolysis stage of the process, the electrolysis current is shut off. The flow of electrolyte through the fixture continues for several minutes to allow dissipation of the hydrogen gas. At the conclusion of this time, the electrolyte is purged from the fixture by compressed air to prepare for rinsing.

The can is rinsed by activation of a secondary pump flowing deionized water through the fixture. This procedure reduces the amount of salt residue left on the can following the drying cycle.

Because the thermal conductivity of the stainless steel fixture is low, rinse water is left within the fixture during the start of the drying cycle. Heaters at the bottom of the fixture are activated and transfer heat across the entire fixture via the heated water. Once the fixture and contents

are sufficiently heated, the rinse water is purged from the fixture by a flow of compressed air.

After purging the rinse water from the fixture, the heaters continue to apply heat and a stream of compressed air continues to pass through the fixture. A few minutes later, vacuum is applied to reduce the boiling point of the water, all the while, continuing to flow air.

After a prescribed time, the heating cycle ends and the can surface is cooled by the flow of air. Once the temperature of the fixture drops below 80°C, the air flow is discontinued, and the process is completed. At this point, the operator opens the door to the chamber on the uncontaminated side of the partition, verifies that the can surface is dry, and performs both an alpha surface survey and an alpha smear survey to verify decontamination.

2B. Test Results

In test runs of the system at an applied current density of 40 mA/cm², the rate of metal removal was found to be uniform over 1000 minutes of electrolysis, achieving a rate of approximately 8 monolayers per second of electrolysis time (see Figure 3). This indicates an expected material removal on the order of 96000 monolayers in a nominal 20 minute decontamination run. Metal removal was observed to be uniform across the surface of the can with no preferential attack at the weld or laser engraved markings. The effect on the surface appeared to be that of a uniform electrolytic etch (see Figure 4). The laser engraved markings remained visible throughout, although the depth of the markings was reduced and the discoloration (presumed oxide) left behind from the laser-marking process was removed, reducing the visual contrast of the markings.

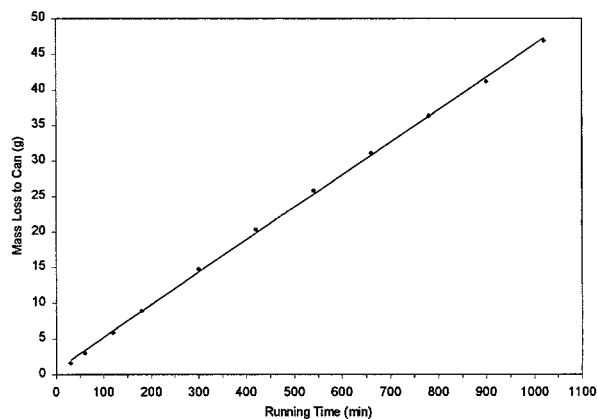


Figure 3: Observed loss of mass to the can as a function of electrolysis time.

A mass balance has been carried out for the data collected during these tests and indicates that current efficiency for metal removal process is on the order of 12.5%, the remainder of the current being consumed by the competing water oxidation reaction. No electrolysis reactions involving sodium or sulfate ions were observed.

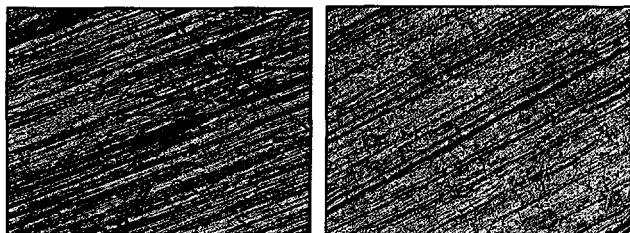


Figure 4: Can surface at 200X magnification prior to electrolysis (left) and same surface after 6 grams of metal have been removed by the electrodecontamination technique (right).

Hydrogen generation during the process can be calculated through Faraday's Law with the assumption that the only process occurring at the cathode is the reduction of water. The mass balance supports this assumption. The resulting generation of hydrogen is then calculated to be 0.30 l/min (0.011 cfm). Oxygen generation at the anode is calculated at 0.14 l/min (0.0048 cfm).

2C. Conclusions

The ARIES decontamination process has been fully installed within the LANL Plutonium Facility. It is being evaluated for effectiveness and waste generation as part of the ARIES demonstration project for eventual inclusion in the PDCF. The electrolytic decontamination technology has a proven track record at LANL and is expected to perform well in this application. Initial testing of a prototype of the process was successful, though recontamination of the can surface by the precipitate was found to be an issue. Ultrafiltration was added to the process system to minimize this effect and has been tested successfully in similar applications.

The process system includes a high level of automation in order to minimize operator error, decrease worker radiation exposure, and to increase productivity. The system has been extensively tested in an uncontaminated state and has been found to perform reliably. The process system is expected to be fully operational and begin processing cans in July of 1998.

NOMENTCLATURE

ARIES: Advanced Retirement and Integrated Extraction System
CFR: Code of Federal Regulations
cm: centimeters
DOE: Department of Energy
dpm: disintegrations per minute
LANL: Los Alamos National Laboratory
mA: milliamperes
PDCF: Pit Dismantelment and Conversion Facility
RCRA: Resource Conservation and Recovery Act
SNM: Special Nuclear Materials

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