Supporting Safe Storage of Plutonium-Bearing Materials through Science, Engineering and Surveillance

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Abstract

Reductions in the size of the U. S. nuclear weapons arsenal resulted in the need to store large quantities of plutonium-bearing metals and oxides for prolonged periods of time. To assure that the excess plutonium from the U. S. Department of Energy (DOE) sites was stored in a safe and environmentally friendly manner the plutonium-bearing materials are stabilized and packaged according to well developed criteria published as a DOE Standard. The packaged materials are stored in secure facilities and regular surveillance activities are conducted to assure continuing package integrity. The stabilization, packaging, storage and surveillance requirements were developed through extensive science and engineering activities including those related to: plutonium-environment interactions and container pressurization, corrosion and stress corrosion cracking, plutonium-container material interactions, loss of sealing capability and changes in heat transfer characteristics. This paper summarizes some of those activities and outlines ongoing science and engineering programs that assure continued safe and secure storage of the plutonium-bearing metals and oxides.

Introduction

The end of the Cold War caused dramatic reductions in the size of the U. S. nuclear arsenal and has resulted in large quantities of excess special nuclear materials. This excess includes plutonium-bearing metals and oxides that require safe and secure containment for prolonged periods of time. Plutonium is a transuranium, actinide metal that is of practical importance because various isotopes, principally ${}_{94}Pu^{239}$, have attractive properties for energy production and nuclear weapons. Although trace quantities of plutonium occur naturally in uranium ore deposits, the vast majority of plutonium on earth today has been produced in nuclear reactors. Operating nuclear power reactors are currently producing approximately 20,000 kg of plutonium per year, worldwide, as a by product of reactor operations. This power reactor produced plutonium is either reprocessed to produce mixed plutonium and uranium oxide fuel or remains contained in spent fuel elements. The spent fuel is stored in a variety of ways including storage pools, dry storage canisters, and geologic repositories. The plutonium produced in power reactors is typically either fuel grade (~80-93% Pu^{239}) or reactor grade (generally <80% Pu^{239}).

On the other hand, the excess plutonium in the U. S. nuclear arsenal was produced in nuclear materials production reactors primarily located at the Hanford and Savannah River Sites, and was extracted from fuel elements designed specifically to produce plutonium for nuclear weapon applications. This plutonium is considered weapons grade because it contains generally >93% Pu239. The breakup of the Soviet Union and the associated reduction in nuclear weapons in the U. S. stockpiles created an excess of plutonium at various U. S. Department Of Energy (DOE) sites including, Hanford, Los Alamos, Rocky Flats, Savannah River, Lawrence Livermore and Idaho. To assure that the excess plutonium from the DOE sites is stored in a safe, environmentally friendly manner the plutonium-bearing metals and oxides are stabilized and packaged according to criteria provided in DOE-STD-3013 (1).

The DOE Standard applies to plutonium-bearing metals and oxides that contain at least 30 wt% actinides and is designed to assure that storage containers maintain integrity for at least 50 years. Significant research and development was required to provide the technical basis for the Standard. This research has generated the data and analyses required to predict that the plutonium-bearing materials will be safe and stable for long-term storage at DOE facilities and that the containers will maintain integrity and require only minimal surveillance under anticipated handling, shipping, and storage conditions. The stored containers will ultimately be accepted by the DOE's Materials Disposition Program for disposition [2] or converted to a mixed plutonium-uranium oxide for use as a fuel in nuclear reactors.

Assuring against failure is a difficult concept especially when the storage conditions may change with time. Providing such assurance for the plutonium storage containers involves proving that age related degradation processes cannot occur if certain conditions are established prior to storage and if certain conditions are maintained throughout the storage period. This paper summarizes a continuing multi-year multi-laboratory program conducted to assure that the excess plutonium in the DOE inventory is safely handled and maintained under conditions conducive to future deposition or conversion. Basically, the program described is a failure prevention program that involves the application of science, engineering and surveillance to assure the continuing integrity of stored containers containing plutonium-bearing materials.

The 3013 Standard

The DOE Standard for stabilization, packaging and storage of plutonium-bearing materials is a living document that may be revised based on emergent information including beneficial comments and pertinent data sent to the Technical Standards Project

Office [1]. Since its inception, the Standard has been revised several times. The 2004 version of the Standard notes that a significant portion of the DOE plutonium oxide inventory contains chlorides and recommends that storage containers be fabricated from ductile, corrosion resistant materials such as the 300 series stainless steels. These two notations almost immediately imply that a potential exists for stress corrosion cracking in the container material and attention must be given to assuring that, even if such cracking occurs, the container system will not be compromised. This assurance is addressed by concluding that "the Standard does not impose a limit on chloride contamination because the extent of corrosion is limited by the available moisture, rather than the available chloride. The moisture content limitation in this Standard (0.5 wt%) is considered sufficient to avoid significant corrosion". The Standard also imposes criteria for the stabilization of the plutonium-bearing materials, design of the containers for the materials and places limits on the container contents. The criteria for plutonium metal and plutonium oxide differ significantly because of the differences between these two types of material.

Plutonium Metal

Plutonium metal may exist in six different allotropic forms, depending on temperature as shown in Table 1.

Table 1. Allotropic Forms of Pu metal as a Function of Temperature.

Crystal Structure, Density and Range of Stability for Plutonium Allotropes			
Phase	**Crystal Structure**	**Density, g/cm^3**	**Range of Stability, °C**
Alpha, α	Simple Monoclinic	19.86	Below 112
Beta, β	Body-Centered Monoclinic	17.70	112-185
Gamma, γ	Face-Centered Orthorhombic	17.14	185-310
Delta, δ	Face-Centered Cubic	15.92	310-452
Delta Prime, δ'	Body-Centered Tetragonal	16.00	452-480
Epsilon, ε	Body Centered Cubic	16.51	480-640
Liquid		16.65	Above 640

The low temperature allotropes, α, β and γ, have low symmetry and consequently low ductility. In fact the α -phase is so brittle that α -phase alloys are fabricated primarily by casting and machining. However, the face-centered cubic allotrope, δ, which, in pure plutonium is only stable at temperatures above 310 C, is quite ductile and amiable to wrought processing technologies. The δ-phase can be stabilized to room temperature by alloying with small amounts (1 to 2 at%) aluminum or gallium.

The heat generated by radioactive decay of the various plutonium isotopes may raise the temperature of the plutonium in the storage container. The equilibrium temperature will depend on the mass and isotopic content of the stored plutonium as well as the heat transfer characteristics of the storage system. However, because of the heat generation by radioactive decay of the plutonium and associated fissile materials, the potential for phase instability must be considered and because plutonium is a reactive metal, corrosion and oxidation may occur, depending on the exposure atmosphere. Additionally, a storage temperature of only 184°C places the plutonium metal at one-half its absolute melting temperature and virtually assures vacancy migration and diffusion within the stored metal. Diffusion across metal-to-metal interfaces could support solid state interactions between the stored plutonium and the container material and these interactions must also be considered.

Plutonium Oxide

Plutonium oxide, PuO_2, has excellent chemical stability, a high melting temperature (<2450°C), and undergoes no phase transformations. Pellets of this face-centered cubic oxide made with the isotope $_{94}Pu^{238}$ have provided the heat sources for electrical production in virtually all of NASA’s deep space missions. These heat sources operate at about 1350 C and, because of the oxide stability do not react with the container material, an iridium alloy. However, the oxide is hydroscopic and will adsorb moisture from the surrounding environment if the relative humidity is not very low. Therefore, the 3013 packaging requirements require that the amount of moisture in the oxide not exceed 0.5wt% at the time of packaging. This moisture specification is considered critical for the prevention of corrosion of the container materials because many of the oxide mixtures at the various DOE sites are impure and contain chlorides. The chlorides are also hydroscopic and the combination of chlorides and moisture is a well known corrosion causing environment.

There are explicit requirements for stabilizing the oxides prior to packaging. These requirements include heating the oxide material in an oxidizing environment at a temperature of at least 950 C for not less than 2 hours with a resulting moisture content of <0.5wt%. Properly stabilized oxides should not interact with either the container or the surrounding environment. The DOE-STD-3013 requires that the headspace of each container be inerted to remove all but 5% O_2 to limit the amount of reactive gases present. However, any adsorbed moisture could experience transfer from the stabilized oxides to the container wall or storage environment and under go corrosion reactions with the container material or radiation induced decomposition to hydrogen and water.

The Containers

The 3013 container includes properly prepared plutonium-bearing materials stored in a nested set of welded austenitic stainless steel containers (Figure 1). Type 316L and 304L stainless steel containers have been used in the packaging process, although the standard does not explicitly require the use of these alloys. The multi-barrier storage container system is essentially designed to be maintenance free over a storage period that may stretch to fifty years. The 3013 standard requires a minimum of two nested containers with weld closure but most packaging sites have also provided a third container, or convenience container, as the innermost container of the assembly. The minimum design pressure for the outer container is 699 psi which is about seven times the maximum pressure that could develop based on known credible mechanisms in properly packaged systems.

The outer pressure vessel in the container system is designed and fabricated to meet ASME code requirements but is not stamped as being compliant with the ASME pressure vessel code. The fact that the final seal weld cannot be pressure tested precludes an ASME code stamp. However, because the final weld cannot be pressure tested, the weld qualification process was quite extensive

The design, fabrication, packaging, and sealing processes for the 3013 container systems have been developed to assure the long term safe storage of the plutonium-bearing materials. To accomplish the storage mission the containers of plutonium-bearing materials must be handled and transferred from location to location and the transfer may include cross country shipment. Shipments involve loading the plutonium bearing 3013 containers into Department of Transportation Type B packages certified for interstate shipping of radioactive materials and transfer of the containers between DOE sites. Additionally, many of the plutonium-bearing 3013 containers are stored in shipping packages at the Savannah River Site. Therefore a series of drop tests were conducted to assure that the 3013 containers could withstand an accidental drop of 9 meters (the maximum anticipated storage height) and remain leak tight (maximum leak rate less than 1×10^{-7} cm^3/sec). Additionally, the inner containers were dropped from a height of 1.33 meters to assure that an accidental drop during packaging would not cause a leak in the 3013 inner container. These drop tests were part of the qualification program to support the handling necessary for placement of plutonium-bearing 3013 containers inside shipping packages. A schematic of a 9975 shipping container is shown in Figure 2.

The engineering design and testing necessary to qualify a container for shipping radioactive materials is extensive and well developed [3,4]. However, the use of a 9975 shipping package for the long term storage of plutonium-bearing 3013 containers required a basic knowledge of the long term behavior of the shipping 9975 package materials. Among the variety of materials used to manufacture the 9975 are fiberboard for insulation (Figure 3) and Viton O-rings to seal the plutonium packages inside stainless steel containment vessels (Figure 4). The effects of long term exposure to low level radiation at anticipated storage temperatures on these two materials were determined to assure that the heat transfer characteristics of fiberboard and the sealing capabilities of the O-rings will not be compromised during the storage period at SRS.

The Contents

The nuclear characteristics that make plutonium useful in weapons and reactors limit the amount of plutonium that can be safely stored in any container or group of containers. Nuclear physics calculations made to assure that, even under the worst possible accident scenario (flooding; for example), a nuclear criticality event cannot occur, demonstrate that a 4.53 kg sphere of ^{239}Pu is not a critical mass even when fully water reflected. The k_{eff} of such a sphere is 0.95 and a k_{eff} of 1.0 is required for nuclear criticality. Therefore, the absence of a criticality event is assured by limiting the fissile material content in any container to 4.4 kg. The margin of safety under these conditions is high because there is not enough plutonium to support a criticality, the plutonium is not a sphere (the geometry that best supports a criticality) and the reflectivity of the container is nowhere near that of water. Photographs of plutonium metal samples and stabilized plutonium oxide are shown in Figure 5.

Properly packaged plutonium metal is considered relatively easy to store. To minimize the potential for ignition, the 3013 standard requires that the specific surface area of the metal be less than 200 mm^2/g and that the metal be free of non-adherent surface oxides and organic materials. Turnings from machining processes, wires and foils are specifically excluded and tramp materials are removed, if practical. The oxide materials are stabilized, as previously described, and the moisture content of the stabilized materials is determined by testing.

The radioactive decay of plutonium (and any other fissile material) generates heat which is removed by heat transfer through the storage system. The heat transfer processes are modeled and the models verified by experiment. The maximum amount of heat generated in any plutonium container is limited to 19 watts by the DOE-STD-3013. Although this value is less than the wattage of a typical room light, the equilibrium maximum temperature inside a 19 watt package may exceed 200°C. The maximum metal-container interface temperature is calculated to be 189°C (above one-half the absolute melting temperature of plutonium). Analytical evaluation of the impact of long term storage at this temperature on potential interactions between the stored plutonium and the storage container show that diffusion-induced material exchange across the plutonium-container interface is very unlikely because of the low elemental diffusivities and the protective qualities of the surface films formed on both the plutonium and the container surfaces.

Thermal gradients inside the container may cause moisture, especially water vapor, relocation to the colder portions of the container. Such relocation may impact the potential for corrosion of the container. For example, moisture condensation coupled with the presence of chlorides can lead to stress corrosion cracking of austenitic stainless steels. An experimental program to evaluate the potential for corrosion and stress corrosion cracking in properly packaged 3013 containers has been ongoing for well over a decade.

Stress corrosion cracking is an electrochemical process and, as such, requires the presence of an electrolyte such as moisture on the container material. The tendency for moisture adsorption will depend on the relative humidity of the environment inside the container and the relative humidity will depend on the moisture content of the container, the amount and type of salts present in the container and the temperature or temperature gradients within the container. Analytical and experimental studies to establish the role of relative humidity in influencing the potential for stress corrosion cracking are also ongoing.

The Environment

The fill gas atmosphere over the plutonium-bearing material in the 3013 containers, including a convenience container, if used, is not specified but must not react adversely with the container or the plutonium-bearing materials. Additionally, the environment must allow for leak testing of the sealed containers. Helium gas is generally used to meet these requirements. The gas pressure inside the container may change during storage as a result of helium generation by the radioactive decay of the stored fissile materials, because of gasses generated by evaporation and/or hydrolysis of contained moisture, and because of gas generation by moisture induced corrosion. The gas pressure inside the container at any given time will be determined by the temperature of the system, the free volume in the container and the total gas present at the time of interest. Extensive studies to determine the pressure in a container as a function of packaging and storage variables (volume of plutonium-bearing material stored, moisture content, gas fill pressure, alpha decay rates, storage time, etc.) have shown that the maximum conceivable pressure (~100 psig) is significantly less than design pressure (699 psig) of the container.

Surveillance

The design, materials selection, container fabrication and material requirements for the packaging and storage of plutonium-bearing materials were carefully established to minimize the probability that the integrity of any container will be compromised during the storage period. The overall goal of the storage program is that none of the thousands of containers processed will contain significant defects and that no defects adverse to storage will develop. However, engineering experience and conventional wisdom suggest that destructive and non-destructive surveillance programs are necessary to support a safe, efficient, and environmentally friendly storage program. For example, the three conditions necessary for stress corrosion cracking, 1) a susceptible material, 2) applied or residual tensile stresses and 3) an electrolyte containing chloride may exist in properly packaged containers. The goal of the surveillance program is to use destructive and non-destructive inspections of a small fraction of the storage inventory to provide a statistically justifiable conclusion that the integrity of the overall inventory of stored plutonium materials is not compromised during prolonged storage. To accomplish this goal, regular, routine surveillances of selected samples from the storage inventory must continue over the lifetime of the storage program. The container selection and evaluation processes are based on statistical methods to assure that known differences in container contents and storage temperatures are evaluated.

Examples of Science and Engineering Support

The science and engineering activities supporting the storage of plutonium-bearing materials in 3013 container systems are continuing and include work that has been conducted over the past several decades. This R&D has been conducted, reviewed and/or evaluated by well established technical experts at numerous DOE sites, including members of the Materials Identification and Surveillance (MIS) Working Group. The MIS working group is an organization made up of highly qualified engineers and scientists who were selected because their expertise was relevant to the safe handling and storage of plutonium-bearing materials. A significant portion of the work that supports the standard has been published in the peer reviewed literature. For example, the references in the DOE-STD-3013 include papers authored by over sixty five different researchers from within the DOE complex and numerous other individuals from university and international laboratories. This paper describes a small fraction of the science and engineering activities that support the basis for the safe storage of plutonium-bearing materials. The activities are divided into six basic categories:

1) ties between the containers and the 3013 standard requirements,
2) temperature related issues,
3) material characterization,
4) statistical approaches to 3013 container surveillance,
5) corrosion and corrosion prevention,
6) gas generation and pressure buildup, and
7) validating safe storage.

The following sections provide selected examples of work from each category to demonstrate the types and variety of work associated with developing a safe storage strategy for plutonium-bearing materials. This overview provides a flavor for the R&D required to support the safe storage of plutonium-bearing materials. The compendium of papers in the Winter 2009 and Spring 2010 special issues of JNMM also, highlights a significant portion of the program.

Weld Qualification: A tie between containers and the 3013 Standard

The outer 3013 containers are fabricated from Type 316L stainless steel and conform to the ASME Section IX Pressure Vessel Code except that the filled container cannot be hydrostatically tested and the closure weld is not made by the container fabricator. The DOE Standard does not specify the welding process but states that container safety should be equal or superior to the intent of the Code. Different weld processes are used for container closure. These processes create an autogenous closure by either laser or gas tungsten arc welding. The laser welding process was developed in England and transferred to the US by analysis and duplication of the weld system and qualification processes. However, both Hanford and Savannah River close the outer container by autogenous GTAW using an automated welder designed, qualified and assembled by the Savannah River Technology Center (now the Savannah River National Laboratory).

The weld joint, illustrated in Figure 6, seals the outer container top to the 0.118 inch thick container side wall. The lip on the container top is 0.157 inches thick and the full penetration weld fusion zone must be confined between the top and the side wall. The rigor required to qualify the welding process is demonstrated by the volume of data presented during a qualification review for the welder that SRTC assembled and shipped to Hanford. A summary of the data is provided in the next several paragraphs.

The acceptance criteria for the qualification welds were that the welds must be: 1) leak tight (leak rate < 2 x 10^{-7}cc/sec He), full penetration, sound (meet ASME VIII radiographic acceptance), meet strength criteria (burst strength, for example) and meet the ASME VIII weld bead geometry shown in Figure 7. Tests were conducted to evaluate controllable parameters affecting arc density, including the tungsten alloy used for the tip, tip geometry, weld shield gas and pulsed currents. Additionally, weld travel speeds, tacking prior to seal welding and the use of chill blocks were also evaluated. These evaluations led to the target welding parameters shown in Table 2.

Table 2. Target Welding Parameters for GTA Seal Welding of 3013 Containers

Target Welding Parameters	
Weld Tip Material	Tungsten with 2% Th,
Weld Tip Geometry	60° angle, 0.030 inch flat, 6-8 Ra finish
Gas	97% Ar – 3% H_2 shield gas
Tack Welds	Seven small, equi-spaced tack welds
Amperage	185 Amps primary welding current@ 0.45 s with 40 Amps background @ 0.02 s
Arc Gap	0.072”
Travel Speed	0.62 RPM
Additional	Modified weld start, chill block used to control temperature

After the target welding parameters were developed, one hundred production certified containers were welded and evaluated. The welds were made with an ASME Section IX qualified welding procedure specification (WPS) by an ASME qualified welding operator. All welds passed the leak test requirements. Seventy five of the welds were made at the nominal target parameters and twenty five were made under upset conditions for process evaluation. Metallographic evaluations of selected containers were made at the weld start/stop position and at 90, 180, and 270^o from the start/stop position. Five consecutive welds made under nominal welding conditions were evaluated to assure that the ASME weld geometry requirements were met and then a statistical parameter study was made to evaluate three primary variables. The welding current was varied from 160 to 200 amps, the travel speed varied from 0.58 to 0.66 RPM, and the arc gap varied from 0.062 to 0.082 inch. The variables were controlled so that heat input extremes were evaluated. All these welds met leak and weld bead geometry acceptance criteria.

Selected welded containers were burst tested and none failed in the closure welds (Figure 7). The burst pressures (essentially 4600 psig) met the ASME Section VIII requirement of exceeding 3920 psig. The weld metallography (Figure 8) and radiography revealed sound, essentially pore-free welds that met the ASME Section VIII requirements.

Fiberboard and O-ring Behavior: A Temperature Related Topic

Fiberboard and Viton O-rings are two essential non-metallic materials in the 9975 shipping containers. The Viton O-rings provide the seals that separate the external environment from the 9975 containment volume. This separation is required to assure that, regardless of the behavior of the 3013 container, plutonium-bearing materials cannot contaminate the environment outside the 9975 containment vessels. The fiberboard provides the impact resistance, insulation, and criticality spacing necessary for the 9975 shipping container to meet DOT and other regulatory requirements. Additionally, the thermal behavior of the 3013 containers inside the 9975 will depend on the time dependent behavior of the Fiberboard. The radiation levels and temperatures inside the 9975 could, with time, affect the behavior of both the O-rings and the fiberboard and thereby impact the behavior of the storage system.

The effect of irradiation, time and temperature on the sealing capacity of the Viton O-rings was evaluated by exposing O-rings to gamma irradiation while the material was compressed in the apparatus shown in Figure 9. The time, temperature and irradiation dose were controlled so that the individual and combined effects of these exposure variables on the sealing capacity of the O-ring could be determined. Sealing capacity was determined by measuring the compression stress relaxation (CSR) in the O-rings after the various exposures and as the CSR increased the sealing capacity decreased. Examples of O-ring sections having various compression sets are shown in Figure 10. Data obtained in laboratory testing suggest that the O-rings at nominal service conditions should remain functional throughout an extended storage period greater than twelve years. Ongoing laboratory and surveillance tests will provide predictive capabilities of O-ring lifetime for storage periods greater than twelve years.

The effects of irradiation, time, and temperature on the density and heat transfer characteristics of fiberboard were also measured. These studies demonstrate that the behavior of fiberboard has not been compromised by the storage conditions

Plutonium/Stainless Steel Interactions: A Material Topic

The thermal analysis of the plutonium/container interface in a 3013 filed with plutonium shows that the interface temperature can exceed 200°C if the plutonium is producing 19 watts and the 3013 container system is in a 9975 shipping container. At this temperature vacancies in the plutonium should be mobile and the potential exists for solid state reactions between the plutonium and iron, chromium and nickel in the stainless steel container. The phase diagrams for Fe-Pu and Ni-Pu show plutonium rich eutectics that melt at 413°C and 465°C respectively. The Fe-Pu phase diagram is reproduced in Figure 11. The addition of about 1% gallium (gallium may be an alloy element in some plutonium metal pieces) to the iron eutectic can lower the melting temperature to about 400°C. This temperature represents the lowest temperature liquid that could develop by solid state reactions between the plutonium and the container wall. Thus the lowest temperature where liquid metal could form in the container system is over 150°C above the bounding interface temperature during the transport and storage of plutonium. This temperature difference is certainly sufficient to assure the absence of interfacial liquids, even if the plutonium metal makes intimate contact with the stainless steel. However, intimate contact is highly unlikely because of the surface films that will be present on both the plutonium and the stainless steel.

Stainless steel is corrosion resistant because of the chromium rich film that naturally forms and protects the underlying metal from further reaction with the surrounding environment. Plutonium metal surfaces are also covered with a naturally occurring protective film. The surface film, on either or both materials, will prevent or at least limit metal-to-metal contact between the stored plutonium and the container. In the absence of such contact, diffusion of iron, chromium, or nickel from the container into the plutonium is highly unlikely even though vacancy movement may occur in the plutonium. The films will also mitigate any tendency for plutonium to diffuse into the container material. Additionally, even if intimate contact was established between the plutonium and container material, diffusion into the container is not anticipated because the temperatures are too low for significant vacancy migration in the austenitic stainless steel. For example, sensitization of austenitic stainless steel does not generally occur at temperatures below 300°C because of the inability of chromium to diffuse from the austenitic grains into the grain boundaries. This analysis suggests that there will be no solid state reactions between the plutonium and the storage container, a conclusion consistent with observations made for plutonium metals stored in steel containers for decades.

Corrosion and Corrosion Prevention Topics

a) Stress Corrosion Cracking

The potential for stress corrosion cracking exists whenever a susceptible material is simultaneously exposed to tensile stresses and an environment that promotes stress corrosion in the exposed material. Chloride environments have the potential to promote stress corrosion cracking in austenitic stainless steels. The plutonium oxide residues within the DOE complex frequently contain chlorides and forming processes used to fabricate the 3013 containers produce high residual stresses in the as-fabricated containers. The presence of high residual stresses was demonstrated by exposing container sections to $MgCl_2 - H_2O$ solutions boiling at approximately 150 C. These tests caused extensive cracking in the containers, Figure 12. The crack patterns revealed the regions of high residual tensile stresses and outlined the regions in the container expected to be most susceptible to stress corrosion cracking. Knowledge of these locations provided the technical basis to focus the stress corrosion cracking surveillance activities in the susceptible regions.

The amount of water in any storage container is severely limited (<0.5wt%) and stress corrosion cracking of the container walls was not anticipated. However, to demonstrate the lack of stress corrosion cracking under simulated storage conditions a series of tests were conducted. One group of Type 304 stainless steel tear drop (U-bend) samples cracked within 166 days during exposure to plutonium oxide mixtures containing $CaCl_2$ salts at room temperature, Figure 13. The moisture content of this test group, 0.6wt%, was slightly larger than permitted by the 3013 Standard but the results demonstrate that the potential for cracking in properly packaged 3013 containers may exist. Companion samples of Type 316 stainless steel did not crack after similar exposures. Type 316 stainless steel is known to be more resistant to stress corrosion cracking than Type 304 but the increase in resistance is often simply a delay in the time to crack initiation and/or a decrease in crack propagation rates rather than immunity vs. susceptibility. Since the exposure times for these tests were less than a year, the absence of cracking in the Type 316 stainless steel samples may not be relevant to a fifty year storage life. The observations of stress corrosion cracking under unanticipated but storage relevant conditions caused the initiation of a test program designed to elucidate the results of this group of tests. Those tests are in progress and will be evaluated as results become available.

b) Relative Humidity

Stress corrosion cracking is generally thought to be an electrochemical process and as such, an electrolyte is required for cracking to occur. The electrolyte may simply be a monolayer or two of moisture on the surface of the stainless steel but regardless of the amount required, an electrolyte is necessary. Under equilibrium conditions, the distribution of moisture among the various components inside the 3013 container will depend on the relative humidity that is present inside the container. The relative humidity will depend on the amount of moisture contained in the container, the amount of corrosion and irradiation induced hydrolysis that has occurred, the temperature distribution in the container and the amount and types of chloride salts present. The occurrence of stress corrosion cracking in seemingly dry environments has been known for decades and well known since the discovery of hot salt stress corrosion cracking in titanium alloys. However, the knowledge that chloride induced stress corrosion cracking occurs in austenitic stainless steels in fairly dry environments is relatively new.

Recent studies have shown that $MgCl_2$ and $CaCl_2$ deposits on austenitic stainless steels will cause stress corrosion cracking at temperatures below 50 C when the relative humidity is barely above the deliquescence relative humidity for the salt. Under these conditions, the tendency for cracking increases as the temperature increases and decreases as the relative humidity decreases. This effect is illustrated in Figure 14. The observations in this published study are consistent with the observation of stress corrosion cracking in the Type 304 stainless steel U-bend samples exposed to plutonium oxide/chloride salt environments, as observed in the 3013 corrosion program. Because of the importance of relative humidity to stress corrosion cracking susceptibility, and because the relative humidity inside a 3013 container may be estimated by considering the amount of moisture present in the container along with the container contents and temperature distributions, a program has been initiated to assess the role of relative humidity and packaging conditions in determining the potential susceptibility of a container of plutonium-bearing material to stress corrosion cracking.

Pressure Development: A Gas Generation and Pressure Buildup Topic

The environment inside sealed 3013 containers storing plutonium-bearing materials will change with time because of the alpha radiation and interactions between adsorbed moisture and the stored materials. For example, alpha irradiation may cause radiolysis of adsorbed water to produce hydrogen and oxygen and may also cause radiolytic recombination of hydrogen and oxygen to water. Adsorbed moisture can evaporate, react with plutonium to form plutonium oxide and hydrogen or with stoichiometric plutonium oxide to form super-stoichiometric plutonium oxide and hydrogen. Gasses such as HCl may be generated in containers having impure, salt containing plutonium oxides and helium is generated by the plutonium decay processes. The DOE-STD-3013 requires that the headspace of each container be inerted to remove all but 5% O_2 to limit the amount of reactive gases present. Therefore, there are basically three sources for gas pressure inside the container:

1) the container fill gas,
2) the gas mixture created by vaporization, radiolysis, desorption and chemical reactions, and
3) helium produced by alpha decay.

The pressures generated by these gasses will depend on the temperature and free volume of the sealed container as well as the number of moles of each gas present in the container. The amount of container fill gas should not change during storage and the alpha decay helium will increase in a predicable fashion. However, the gas mixture created by radiolysis, desorption and chemical reaction is not readily predictable from first principals but can modeled based on the results of laboratory testing and analytical assessments.

The free volume inside the sealed inner 3013 container will depend on the volume of the inner container, the volume of the convenience container, and the volume of plutonium-bearing materials loaded into the container. Each of these volumes can be calculated, or accurately estimated, based on container dimensions and the characteristics of the plutonium-bearing materials. For example the volume occupied by a convenience container may be calculated by dividing the container weight by the density of the container material (generally a 300 series austenitic stainless steel) and the volume of the plutonium-bearing material can be calculated in the same fashion except that the particle density may not be accurately known for the impure oxide powders. However, the particle density can be satisfactorily estimated through weight measurements, knowledge of the particle packing factors and an established empirical relationship between bulk density and pycnometer density.

A wide variety of measurements have shown that, typically, the pressure in sealed plutonium-bearing material containers increases slightly with storage time. Originally, over-pressurization of properly packaged containers was considered to be a viable failure mechanism, however, laboratory testing and surveillance data have determined that to be very unlikely. For example, the measured pressure increase with stored containers undergoing surveillance has been less than 20 psi and the pressure increases in laboratory tests at bounding conditions are generally less than 100 psi.

Surveillance: A Statistical Approach to Validating Safe Storage

The goal of the surveillance program is to detect any incipient failures in the storage inventory before such failures affect the safety or integrity of the inventory.

Safety/integrity issues include container degradation, pressure buildup and changes in the plutonium-bearing materials or in the storage systems. The packaging and storage requirements were established to minimize, if not eliminate the potential for safety to be compromised. Therefore, if the packaging requirements program is totally successful, the surveillance program will not identify any issues and may appear inconsequential. However, unforeseen issues often emerge in unique or novel systems and surveillance is necessary to detect and mitigate any unanticipated emergent problem.

The amount or number of surveillances required to assure continuing safe performance in any program depends on several factors including: experience, understanding of the factors affecting performance and the risk involved with unsatisfactory performance. The total risk to the storage program is also the combination of risk factors, including: risk to the general public, risk to workers, economic risks and perception risks. When dealing with nuclear materials, especially plutonium, economic and perception risks often overwhelm any physical risks to plant personnel or the general public. Consequently, the success of the surveillance program for the 3013/9975 plutonium storage systems is dependent on enabling one of two very different statements. The program must be able to conclude that either:

1) "We have recently examined the inventory and found nothing", or
2) "We detected a potential issue and acted to mitigate the effects of that issue."

The statement that "We examined the inventory several years ago and found nothing" cannot satisfy the perception risk and can create economic risks simply by causing extensive interactions with intervener groups and regulatory agencies.

The 3013 container surveillance program is based on a statistical approach designed to validate safe storage through both destructive and non-destructive examination of containers from the storage inventory.

The non-destructive evaluations include weight measurements, radiography to determine the condition of the container inventory and the position of container lids and other pressure indicating devices and visual examinations. Because the corrosion program has identified the most likely sites for corrosion induced degradation in the 3013 containers, the radiographic studies can focus on these likely sites. The destructive examinations determine the condition of the container walls, the condition of the plutonium-bearing materials and the pressure and content of gasses inside the storage containers.

Discussion

The examples of science and engineering activities summarized above demonstrate, to a limited extent, the huge effort that is involved in assuring against failure during prolonged storage of plutonium-bearing materials. Failure prevention in such storage systems is paramount because of the environmental hazard of plutonium. The failure prevention process involves virtually all aspects of the handling, packaging and storage processes. For example, the storage containers and packaging processes are designed to meet the intent of the ASME Pressure Vessel Codes and numerous tests are conducted to ensure that containers conform to the appropriate acceptance criteria. Conformance to acceptance criteria is required for the materials selected and used, for the container fabrication processes and, as illustrated in the welding process section of this paper, in weld closures. Visual inspections, metallography and radiography are used on selected containers to assure that quality welds continue to be made. All containers are leak tested after welding. Although no significant degradation of the 3013 containers is anticipated, the continuing surveillance program is designed to detect any unanticipated degradation processes in their incipient stages. The use of multi-layer robust containment also assures that even if an unanticipated event compromises the inner containment vessel, plutonium-bearing materials will not be released to the environment.

Potential age-related degradation processes were considered and packaging processes controlled to mitigate, or at least minimize, the potential for degradation. Some potential degradation processes such as solid state interactions between the stored materials and the storage containers could be discounted through analysis and comparison with related experiences. Other processes, such as stress corrosion cracking could not be totally discounted and laboratory studies were established to help determine which portions of the stored inventory are most vulnerable. The observation of stress corrosion cracking in U-bend samples exposed to chloride containing plutonium oxide mixtures containing only 0.6 wt% moisture was unexpected at room temperature and within such a short period of time. Because of this observation, extensive new testing and analyses programs were instituted. The literature related to the corrosion and stress corrosion cracking processes is constantly being reviewed and analyzed and laboratory tests are initiated to assess the role of irradiation in accelerating the processes. The results of the corrosion studies are being published in the peer reviewed literature, as is other work in the failure prevention program.

The surveillance activities demonstrate that seven years of storage has not compromised the integrity of the containers examined. The program also demonstrates that pressure buildup inside the storage containers is not significant and there is no indication that the container pressure will reach the 100 psig maximum conservatively estimated by pre-exposure testing and analysis. The overall results of the surveillance program confirm the quality of the failure prevention program and provide assurance that container degradation is not occurring. However, the unanticipated observation of stress corrosion cracking in laboratory samples demonstrated the need for continuing surveillance and laboratory testing.

It is significant that this, currently very successful, failure prevention program has involved the cooperative efforts of hundreds of investigators from at least ten laboratories within the DOE complex. Discussion, team work, and expert assessment have been the cornerstones of the program. Hopefully, this paper and the compendium of related papers included in this issue and the Spring 2010 issue of the Journal of Nuclear Materials Management, will serve as an example of success through cooperation and demonstrate that failures in nuclear materials storage systems can be prevented through the application of engineering and science to design, fabrication, and operation problems.

Conclusions

The engineering and science determinations of the behavior of plutonium and plutonium oxide containers provide a technical basis to establish criteria for the packaging and storage of excess plutonium-bearing materials currently in the U. S. DOE inventory. Although this paper outlines only a small fraction of the supporting work, the data and analysis presented demonstrate the long term safety of materials packaged and stored according to the DOE 3013 Standard. This safety is assured by the prevention of container failures through: 1) the design, fabrication, and robust conservative nature of the 3013 container, 2) the strict plutonium packaging requirements, 3) ongoing laboratory activities that assess the behavior of container materials under simulated and actual storage conditions, and 4) the surveillance and monitoring of the 3013 storage containers.

The optimism expressed in this paper is certainly reflected by the willingness to declare the program to store plutonium-bearing materials a success before the program is completed. However, it is our judgment that the worth of saying "I told you" based on the results of a strong engineering and science program far exceeds that of an "I told you" after a failure has occurred. We hope that this paper and the associated papers also published in the Journal of Nuclear Materials Management will encourage other investigators to describe of how they used engineering and science in failure prevention processes to assure safe and environmentally friendly management of nuclear materials.

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[4] SRNL. 2008. Safety Analysis Report for Packaging – Model 9975, B(M)F-96, *Savannah River National Laboratory,* S-SARP-G-00003, Rev. 0.

List of Figures

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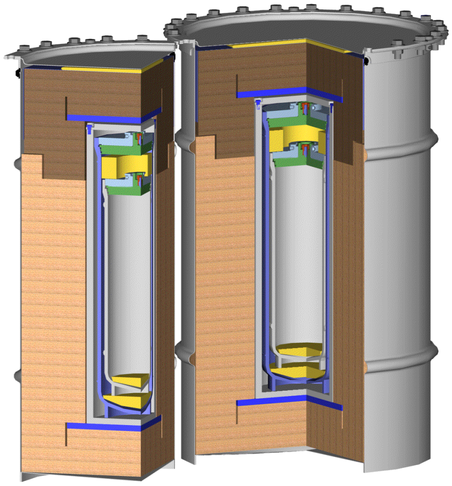

Figure 2. Schematic of 9975 Shipping Package

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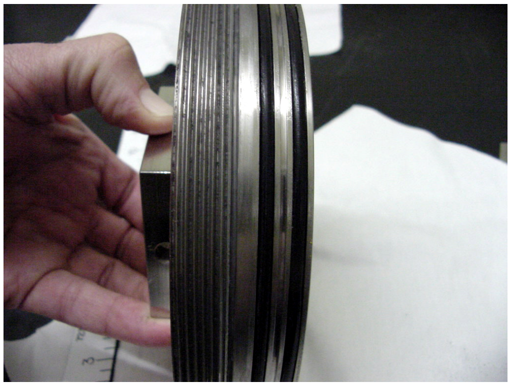

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Pu metal button

Stabilized Pu oxide

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Figure 6. GTA Weld Joint for 3013 Outer Container

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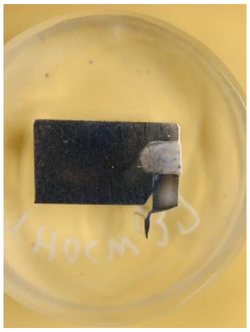

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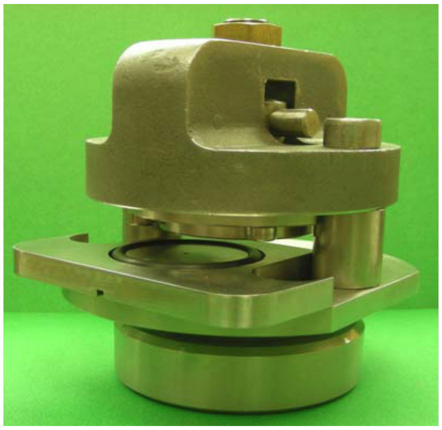

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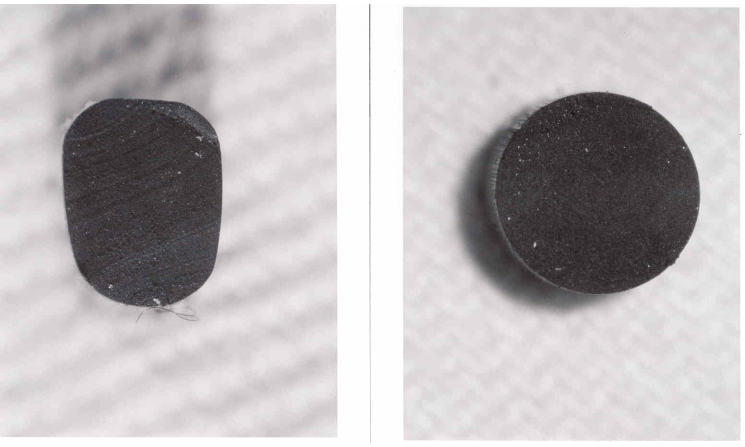

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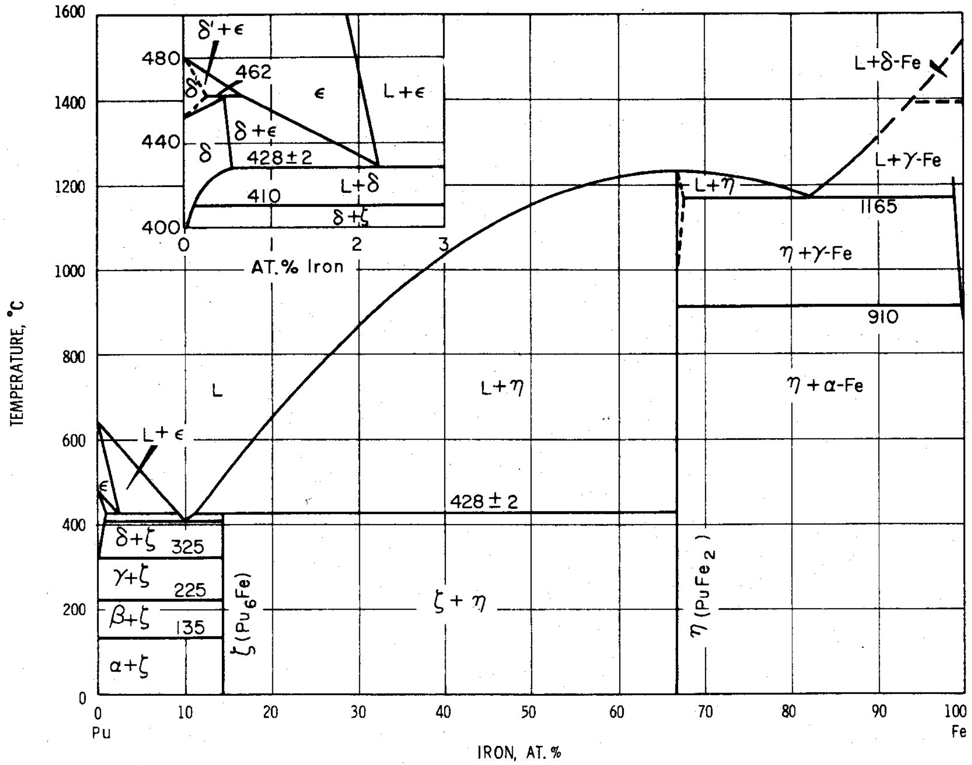

Fig. 7.11—Plutonium–Iron. From F. W. Schonfeld, in A. S. Coffinberry and W. N. Miner (Eds.), *The Metal Plutonium*, p. 243, The University of Chicago Press, Chicago, 1961.

Figure 11. The Plutonium-Iron Phase Diagram

Outside of 3013 Outer Can

Outside of 3013 Outer Can Closure

Figure 12. Stress Corrosion Cracks in 3013 Container Sections Exposed to Boiling $MgCl_2$ Solutions.

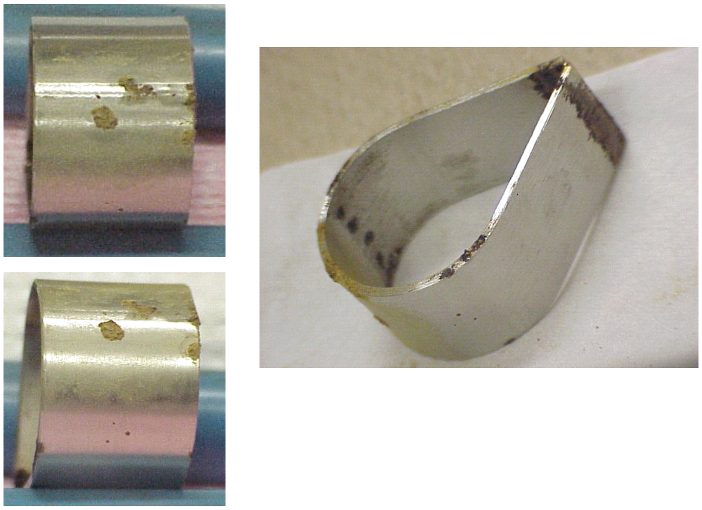

Figure 13. Stress Corrosion Cracks in Type 304L U-Bend Samples Exposed to Plutonium Oxide-Salt Mixtures.

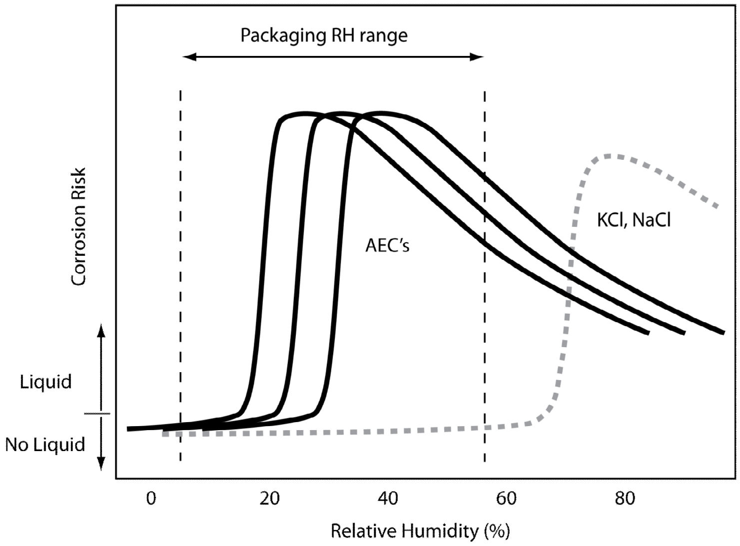

Figure 14. Conceptual plot of corrosion risk as a function of relative humidity within a container. Curves are shown for alkali chlorides (NaCl, KCl) [Dotted line] and for a representative collection of alkaline earth chlorides (labeled AEC's) [Solid lines]. Risk is shown as increasing rapidly beginning at the threshold for liquid formation (deliquescence). The range of relative humidity to which material was exposed during packaging is shown for comparison.