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POTENTIAL EUTECTIC FAILURE MECHANISM
FOR STAINLESS STEEL CANS CONTAINING PLUTONIUM METAL

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ABSTRACT

Plutonium and iron are known to form a eutectic at a relatively low temperature, i.e., $\approx$ 400-410°C. A study has been conducted to assess the likelihood that the Pu/Fe eutectic reaction acts as a failure mechanism for stainless steel cans containing plutonium metal. The study consisted of a review of the metallurgical data obtained from diffusion couples and irradiated Pu-bearing metallic fuels, and a thermal analysis of Model 9975 packaging containing Pu metal in a stainless-steel can under a postulated fire scenario in a storage facility, i.e., 800°C for 4 hours.

The results of the study show that even in a 800°C fire with a duration of up to 4 hours, the Model 9975 packaging would provide adequate thermal protection, and the 3013 can temperature would stay significantly below the Pu/Fe eutectic temperature of $\approx$ 400-410°C. Indeed, even if the 3013 can reaches 400°C, the kinetics of the reaction is such that the walls of the 3013 can may survive several days at that temperature. Above 400°C, the progression depends strongly on the peak temperature and duration, as well as the thermal performance of the protective packaging. For facilities that store Pu metals in 3013 cans, whether bare, in Model 9975, and/or in other packagings, a review of the documented safety analysis should be performed, with special attention paid to the fire event. Compensatory measures should be taken, if deemed necessary.

INTRODUCTION

In the United States, excess plutonium-bearing materials are being consolidated for long-term storage for a period of up to 50 years. The form of the materials includes metals and oxides that are stabilized and packaged in welded, stainless-steel (SS) cans in accordance with the Department of Energy (DOE) standard DOE-STD-3013-2004.[1] For domestic transport, the 3013 can is placed inside a Model 9975 packaging, which is a 35-gallon drum with stainless-steel primary and secondary containment vessels, lead shielding, and Celotex material for thermal insulation and shock absorption.[2] Thousands of the Model 9975 packagings have been certified by DOE for shipment of Type B radioactive and fissile materials in accordance with Part 71, Title 10 Code of Federal Regulations (CFR), or 10 CFR 71, *Packaging and Transportation of Radioactive Material*. Thousands of the Model 9975 packagings are currently used for interim storage of Pu-bearing materials in the 3013 cans at DOE sites.

For plutonium metals, there is a recognized risk of potential eutectic formation between plutonium and iron in the stainless steel walls of the 3013 cans. The Pu/Fe eutectic temperature is $\approx$ 400 to 410°C, depending on the minor alloying elements (e.g., Ga) in Pu. Metallurgical interactions have been considered in DOE-STD-3013-2004, page 42, "*The potential for forming low-melting eutectics has been evaluated recently based on the available phase diagram data, diffusion data, and effect of surface oxide [Williamson 1999]. This study concluded that the storage of Pu metal and Pu-Ga alloys in stainless steel*

containers will not lead to the formation of liquids, or result in direct release of plutonium by means of diffusion mechanisms, as a result of storage at temperatures up to 250°C."

Certification of the Model 9975 packaging for transportation must satisfy the regulatory requirements in 10 CFR 71.71 and 71.73 for normal conditions of transport (NCT) and hypothetical accident conditions (HAC), respectively. The HAC consists of a sequence of tests that includes drop, puncture, fire, and immersion, for which a damaged packaging (from drop and puncture) must be able to survive an all-engulfing fire of 800°C for 30 minutes. Because of the Celotex insulation, the 3013 can in the Model 9975 packaging did not exceed the design temperature limit of 148°C in a HAC fire.

The use of the Model 9975 packagings for long-term storage of plutonium metals presents a different set of concerns, because the thermal performance of the packaging depends on the documented safety analysis (DSA) of the facility, and the severity of the fire (i.e., temperature and duration) assumed may vary from facility to facility. It is, therefore, possible that in a prolonged, high-temperature fire, the 3013 can and its plutonium metal contents could approach, or exceed, the Pu/Fe eutectic temperature of ≈ 400 to 410°C. To help address this concern, the Packaging Certification Program (PCP) of the DOE's Environmental Management (EM), Office of Safety Management and Operations, conducted an assessment of the Model 9975 packagings containing Pu metals in the 3013 cans. The assessment consisted of a two-pronged approach: (1) review of metallurgical data (e.g., phase diagrams, diffusion couples, and other relevant experiments) to help determine the kinetics of the Pu/Fe eutectic reaction as a function of temperature; and (2) thermal analysis of a 9975 packaging to assess the Pu/SS interface temperature in the 3013 can under different fire scenarios. The results of this assessment are highlighted in the remaining sections of this paper.

REVIEW OF METALLURGICAL DATA

The two main sources of the metallurgical data reviewed are the studies pertaining to the development of the standard DOE-STD-3013-2004 by the Los Alamos National Laboratory (LANL) in the late 1990s,[3,4] and research at Argonne National Laboratory (ANL) on the Pu-bearing metal fuels under the Integral Fast Reactor (IFR) program. Under the IFR program, over 2,600 U-Pu-Zr metal fuel pins were irradiated in subassemblies in the Experimental Breeder Reactor (EBR-II) and the Fast Flux Test Facility (FFTF) in the 1980s and 1990s.[5-9] The Pu content in these fuel pins ranged from 0 to 26 wt.%, and the Zr content ranged from 6 to 14 wt.%. The cladding materials were either austenitic stainless steels (316 or D9, which is a Ti-stabilized variation of 316) or tempered martensitic steels (HT9 or HT9M). The fuel/cladding interfacial temperatures during irradiation were typically from ≈ 400°C near the fuel bottom (where coolant entered the reactor core) up to ≈ 600°C near the fuel top. The time at power was ≈ 500 days to attain the normal burnup of ≈ 10-13 fissile at.%. When the reactor was not at power (e.g., between runs), the fuel pins would be held at the bulk sodium temperature of ≈ 370°C for EBR-II or ≈ 360°C for FFTF. The cumulative hold time at the bulk sodium temperature varied, but it was not unusual to be on the order of several hundred days. While fuel/cladding metallurgical interaction was always observed in discharged fuel pins, unintentional cladding rupture in the reactor due to the interaction was extremely rare. (The IFR fuel pin cladding was relatively thin, ≈ 380-560 μm wall, compared to the combined thickness of walls of ≈ 5,600 μm of the inner and outer 3013 cans.) Therefore, if the 3013 can temperature were to reach between 400 and 600°C during a fire, the IFR irradiation database may be applicable.

Also as a part of the IFR program, segments of irradiated fuel pins were heated isothermally in a furnace device called the Fuel Behavior Test Apparatus (FBTA),[10, 11] which was housed in a hot cell laboratory. The test temperature ranged from 625 to 800°C, and the test duration ranged from 5 minutes to 36 hours. The objectives of the FBTA tests were to determine (1) the threshold temperature for liquid-phase formation in irradiated fuel pins with prototypical fuel/cladding interfaces, and (2) the mechanism and rate of cladding penetration as functions of excursion temperature and the design and operating variables

of the pins. Over 130 such tests were performed. In a companion furnace device called the Whole Pin Furnace (WPF) system,[12, 13] integral irradiated fuel pins were subjected to elevated-temperature excursions simulating reactor loss-of-flow accidents. The objective was to investigate the combined effect of cladding thinning and internal plenum pressure on pin cladding integrity. The WPF test temperature ranged from 650 to 820°C, and the duration ranged from 3 minutes to 36 hours. Cladding rupture was attained in five of the seven tests in a manner as expected (i.e., by burst caused by the pin's internal fission-gas pressure after significant wall thinning due to metallurgical interaction). The rates of metallurgical interaction obtained from the WPF tests were consistent with those from the FBTA tests conducted without the internal gas pressure. The database from the FBTA and WPF tests may be useful in assessing the potential eutectic failure mechanism for stainless steel 3013 cans containing Pu metal, if the postulated can temperature is significantly above 600°C during a fire.

Diffusion-couple experiments were also performed at ANL to investigate the fundamental aspects of diffusion behavior involving fuel, cladding, and fission products.[14, 15] Some of the tests produced onset of melting. As these tests were geared for reactor applications, no unalloyed Pu was tested. Likewise, the test temperatures were generally high, i.e., > 600°C, to obtain meaningful interaction depths within a reasonable time (days).

For the purpose of distinguishing the kinetics of the Pu/Fe eutectic reaction and its implications on the 3013 cans, the discussion below is divided into three temperature regimes: (1) below 400°C, (2) between 400 and 600°C, and (3) above 600°C. The first temperature regime (< 400°C) envelops the normal storage condition of the 3013 cans; the second and the third temperature regimes correspond to the normal reactor operations and accident conditions of the IFR database, respectively, which also cover a significant range of high temperatures in the fire scenarios for the 3013 cans at a storage facility.

3013 Can Temperature below 400°C

In 1997, a technical assessment of the Pu/Fe compatibility[3, 4] was performed to establish the thermal limits for the Nuclear Materials Storage Facility (NMSF) at LANL. While it is understood that the Pu alloy is compatible with steel at temperatures below the 410°C melting point of the 90% Pu-10% Fe eutectic, the concern was on slow reaction at temperatures up to ≈ 140-150°C over an extended storage period (i.e., 50 years). In the assessment, Haschke provided an Arrhenius equation for estimating the rate of interaction between Pu and Fe,

$$R = \exp(A - B/T) \tag{1}$$

where   R = rate of interaction (μm/h); A = 15.1; B = 11,630; and T = temperature (K).

The uncertainty bands for constants A and B are ≈ ±10%, depending on the assumed activation energy (20 to 25 kcal/mol) in the B term. Haschke calculated the anticipated extent of interaction between Pu and Fe after 50 years at 140°C to be in the range of 0.5-10 μm, which poses no threat to the 3013 cans stored at the NMSF. Since the Pu diffusion in the steel is much slower than the Fe diffusion in Pu, much of the predicted reaction thickness is on the Pu side.

Using Eq. (1), one can estimate the depth of the reaction zone in a hypothetical fire involving a 3013 can at a Pu/SS interface temperature of 400°C. Assuming the fire lasts for 10 days, a very conservative assumption, the calculated depth of interaction would be ≈ 30-70 μm. This depth, even if entirely on the can side, should not challenge the integrity of the 3013 can, which has a wall thickness of ≈ 5,600 μm. (Note: The 3013 can is an assembly that consists of an outer can, an inner can, and a convenience can, all stainless steel. An approximate combined thickness is used in this assessment.)

Perhaps an even better indicator to judge the Pu compatibility in a 3013 can during a < 400°C fire is the IFR metal fuels irradiation from EBR-II and FFTF. The few fuel-pin ruptures were either intentional (to study fission product release after a cladding breach) or superficial end-plug or spacer-wire weld-related failures, or they were due to extreme high burnup and/or cladding temperature. Under normal operation with peak cladding temperature ≤ 600°C and burnup up to ≤ 13 at. % (≈ 500-day residence time in reactor), there was not a single confirmed pin failure due to fuel/cladding metallurgical interaction. Considering that the fuel pins were at high temperature for hundreds of days, this positive IFR cladding integrity bodes well for a Pu-metal-containing 3013 can surviving a 400°C fire with a much shorter duration.

3013 Can Temperatures of 400-600°C

In applying the IFR fuel pin irradiation database to assess a hypothetical storage facility fire in the 400-600°C temperature regime, one should recognize the following differences:

- the Pu content in the IFR fuel is diluted by U and Zr;

- the residual zirconia mold wash (used in injection casting of the fuel slugs) on the IFR fuel surface may act as a barrier to fuel/cladding interaction;

- the lanthanide fission products generated in the IFR fuel are known to exacerbate the fuel/cladding interaction; and

- the contact between the IFR fuel and cladding is generally tight because of fuel swelling during the irradiation.

The first two factors tend to lessen metallurgical interaction, thus making the IFR database less conservative with respect to the 3013 can fire scenario, whereas the last two factors act in the opposite direction. To assess the net results from these countervailing factors would require a more elaborate evaluation, which should be done if the IFR database is deemed essential for the resolution. For the present discussion, however, it is assumed that the pairs of factors effectively offset each other, and that the IFR database may be used as is for an assessment of the 3013 can compatibility.

During irradiation, solid-state interdiffusion of the U-Pu-Zr fuel and cladding constituents occurs across the fuel/cladding interface after fuel/cladding contact is made due to fuel swelling, typically after ≈ 100-200 days of operation. The reacted cladding band, which contains lanthanide fission products and fuel constituents, is regarded as a normal wastage for the cladding. Concurrent with this process is the migration of cladding constituents, mainly Fe, and in the case of austenitic steel, Ni, into the surface region of the fuel. As can be expected, the extent of this interdiffusion depends strongly on cladding temperature and irradiation time. Although Pu forms low-melting eutectics with both Fe and Ni (410°C for Pu/Fe and 475°C for Pu/Ni),[16] the interface did not melt in discharged IFR fuel pins with cladding temperatures up to ≈ 600°C.

Pahl[17] provided an equation to estimate the extent of cladding wastage from the fuel/cladding interfacial diffusion during the steady-state reactor irradiation:

$$D = 25.4\{[A \cdot \exp(-Q/RT)] \cdot (t - 158)\}^{1/2} \qquad (2)$$

where D = depth of interaction (μm);
$A = 1.718 \times 10^{11}$;
$Q = 49{,}461$ cal·mol^{-1};
$R = 1.987$ cal·K^{-1}·mol^{-1};
T = temperature (K); and

t = time (days).

Note that the time term in Eq. (2) is subtracted by 158 days, the average incubation time assumed to attain fuel-cladding contact. Figure 1 shows the calculated cladding wastage from the Pahl correlation (curve), along with several measured data after ≈ 500 days of irradiation (diamonds). The cladding wastage in the IFR pins is <150 μm after 500 days at 600°C peak cladding temperature.
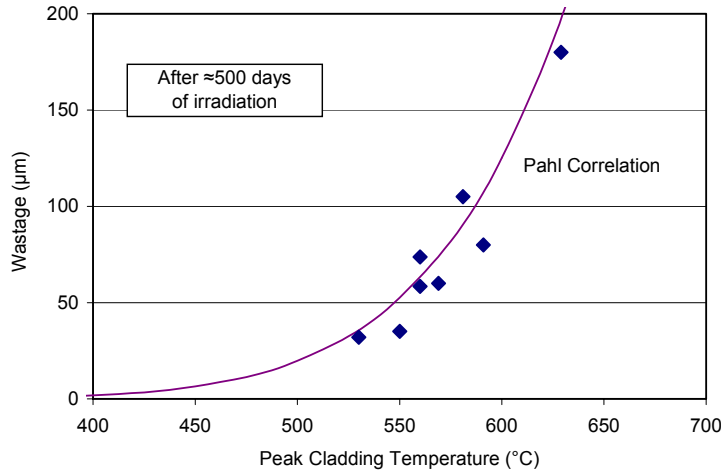

Figure 1. IFR cladding wastage from steady-state irradiation

Using Eq. 2, one can estimate the depth of the reaction zone in the 3013 can during a hypothetical fire of 10 days at a Pu/SS interface temperature of 600°C. The calculated depth of reaction in the can wall is ≈ 21 μm, which poses no threat to the integrity of the 3013 cans.

The ≈ 21-μm depth calculated by Eq. (2) at 600°C may appear somewhat inconsistent with the 30-70 μm depth calculated by Eq. (1) at 400°C, both for a 10-day-long fire. However, Eq. (2) calculates the interaction zone thickness only on the steel side, whereas Eq. (1) calculates the combined thickness of the interaction zone, which is mostly on the plutonium side. The apparent discrepancy may also be explained by how the underlying sets of data were generated. In the case of diffusion couples, i.e., Eq. (1), the faces of the materials were freshly cut, finely polished, and tightly clamped for the duration of the heating tests. For the IFR fuel pins, an as-fabricated interface existed between the fuel and cladding, a configuration that is probably more representative of the loading configuration of Pu metal in the 3013 cans.

3013 Can Temperatures above 600°C

If the 3013 can becomes severely overheated in a prolonged fire, the elevated-temperature test data obtained with the FBTA[10, 11] and WPF[12, 13] in a hot-cell laboratory may be useful. Both types of tests used irradiated fuel/cladding materials with pre-existing interdiffusion layers formed during the reactor irradiation.

The affected layers on the fuel and cladding may reach the solidus temperature during the onset of heating in the FBTA or WPF without the need of significant additional interdiffusion. (Heating in both FBTA and WPF was fast – typically reaching the target temperature in about a minute.) If liquid phase forms, the phase may consume part of the original solid-state interdiffusion layer in the cladding. If the heating event is prolonged, the reaction may then progress further into the previously unaffected cladding. If the temperature is not sufficient to cause melting, additional diffusion penetration may occur.

Over 130 FBTA tests were conducted, of which 92 used Pu-bearing fuels. The test temperature ranged from 625 to 800°C, and the test duration ranged from 5 minutes to 36 hours. After each test, the sample, a short segment of fuel pin, was transversely sectioned and polished. The cross section was examined on a metallograph to determine the extent of melting and cladding penetration. No interfacial melting was noted in any test with temperature ≤ 650°C, even with extended test durations (up to 36 hours). Above 675°C, melting was observed in some samples with longer test durations. Figure 2 shows the results from tests with and without melting.

U-26Pu-10Zr/316 SS
740°C, 7 hr in FBTA
Diffusional interaction, no melting

U-26Pu-10Zr/316 SS
850°C, 1 hr in FBTA
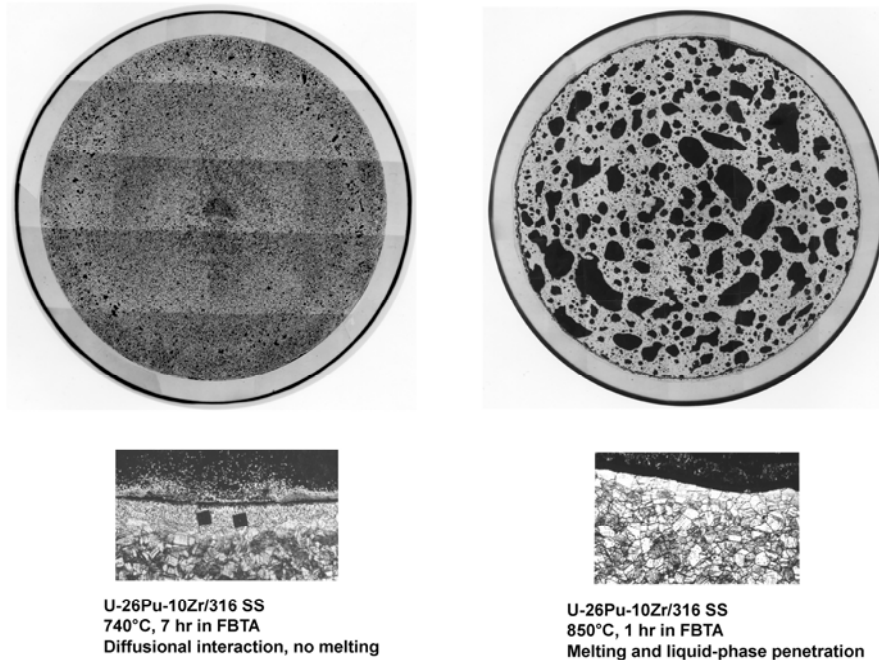Melting and liquid-phase penetration

Figure 2. Cross-sectional view of two samples after the FBTA tests. Samples were from the same fuel pin. No fuel or fuel/cladding interface melting in the sample shown on the left (740°C, 7 h). The lower photos show etched cladding and the nature of the diffusion cladding penetration. (The black diamonds in the cladding diffusion layer on the left are the indentation marks from microhardness measurements.) Notice that for the sample on the right (850°C, 1 h), while liquefaction affected the entire fuel cross section, the cladding is still largely intact. The thickness of cladding for this pin is 381 μm (0.015 in.).

The rates of cladding penetration from all the FBTA tests with a one-hour duration are shown in Fig. 3. (Penetration rate is defined as the measured maximum penetration divided by the 1.0-h test duration; it represents an effective rate and includes the accelerated penetration at the onset of heating.) Data scatter in the plot is due mainly to the wide variability of material, irradiation conditions, and fuel burnup. An Arrhenius correlation is shown in the figure that bounds the data band. This empirical correlation, given by Eq. (3) below, may be suitable for estimating the rate of wall thinning in a 3013 can during an elevated-temperature fire:

$$R = \exp (A - B/T) \qquad\qquad (3)$$

where R = rate of penetration (μm/s);
   $A = 6.75$; $B = 9{,}850$; and T = temperature (K).

Based on Eq. (3), the calculated wall thinning rate is ≈ 0.088 μm/s for a fire that produces a Pu/SS 3013 can temperature of 800°C. The depth of wall penetration would be ≈ 320 μm after one hour, and approximately 60% of the 3013 can wall (≈ 5,600 μm, inner and outer walls combined) would have been reacted after 10 hours at 800°C.
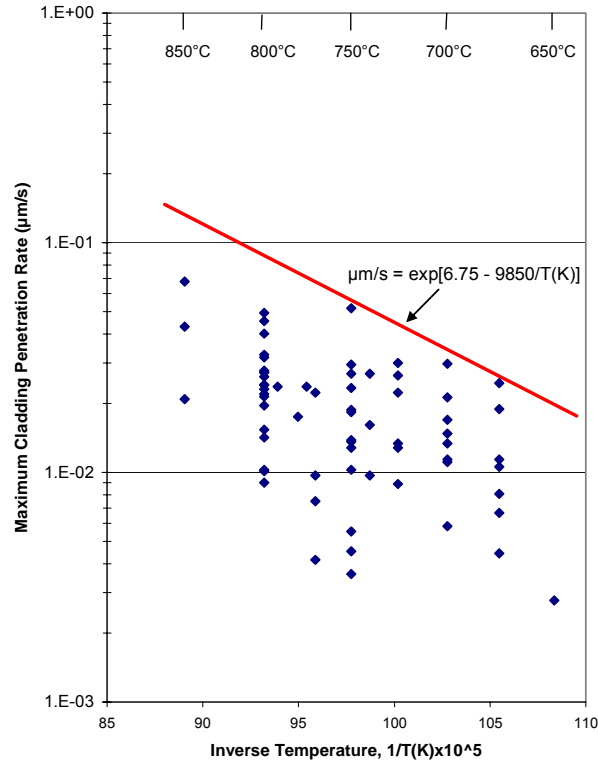

Figure 3. Effective cladding penetration rates from the FBTA tests for specimens tested for 1.0 hour

The cladding penetration data from the WPF tests agreed well with those from the FBTA tests. In the WPF tests where cladding breach occurred, the failure mode is consistent with one that takes into account the synergistic effects of both wall thinning and internal fission-gas pressure in the fuel pins. Figure 4 shows a cross-sectional view of an IFR fuel pin (U-19 wt.% Pu-10 wt.% Zr/HT9) that failed near the top end of the fuel after 112 minutes at 820°C.[11] Cladding breaching occurred near 12 o'clock with a very substantial wall thinning due to fuel/cladding metallurgical interaction, aided by fission-gas pressure loading. The gas pressure inside a 3013 can may become an issue during a long-duration fire at high temperature. In that case the WPF data may be used to aid the assessment.

Equations (1) to (3) may be used for estimating the rates and depths of reactions between Pu and Fe in 3013 cans during a facility fire. These kinetics equations are based on the data generated from diffusion-couple experiments, as well as irradiation and furnace experiments with IFR fuels. In 1988, ANL also performed a diffusion-couple experiment between U-22 wt.% Pu-23 wt.% Zr and HT9 at 650°C for 200 hours.[15] The measured thickness of the interaction band was ≈ 700 μm, of which ≈ 500 μm was on the fuel side. Whereas the ≈ 200 μm reaction on the cladding side is greater than the trend depicted in Fig. 1 for ≈ 500 days at 650°C, this wastage is an order of magnitude smaller than that extrapolated from Eq. (1), i.e., ≈ 2,400-3,500 μm at 650°C for 200 h. Given the large variations in the calculated interactions, one should be cautious when extrapolating the above equations outside the ranges of parameters in the experimental database.
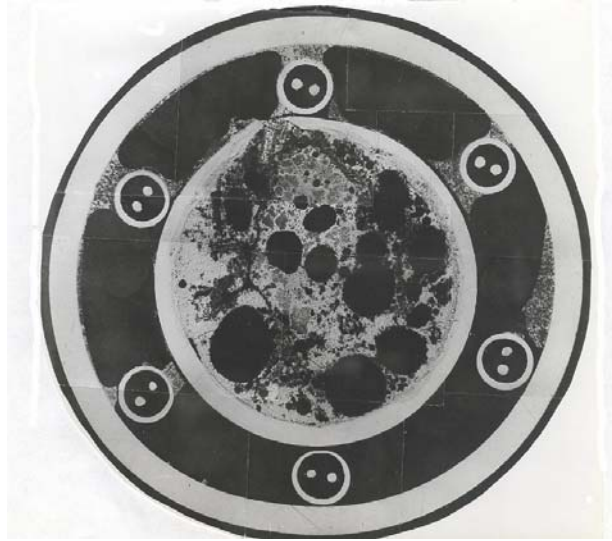
Figure 4.   Cross-sectional view of a IFR fuel pin (U-19 wt.% Pu-10 wt.% Zr/HT9) that failed near the top end of the fuel after 112 minutes at 820°C. The fuel pin is shown in the center of the picture surrounded by six thermocouples in the gap between the fuel pin and a furnace heat receptor. Cladding breaching occurred near 12 o'clock with a very substantial wall thinning due to fuel/cladding metallurgical interaction, aided by fission-gas pressure loading. The fuel has completely liquefied, or "foamed," with various coalesced fission gas bubbles (or voids), a few with diameters as large as half the radius of the fuel.

THERMAL ANALYSIS

The purpose of the thermal analysis of the Model 9975 packaging, shown schematically in Figure 5, is to assess the Pu/SS interface temperature in the 3013 cans under different fire scenarios. A convenient

(a)   (b)
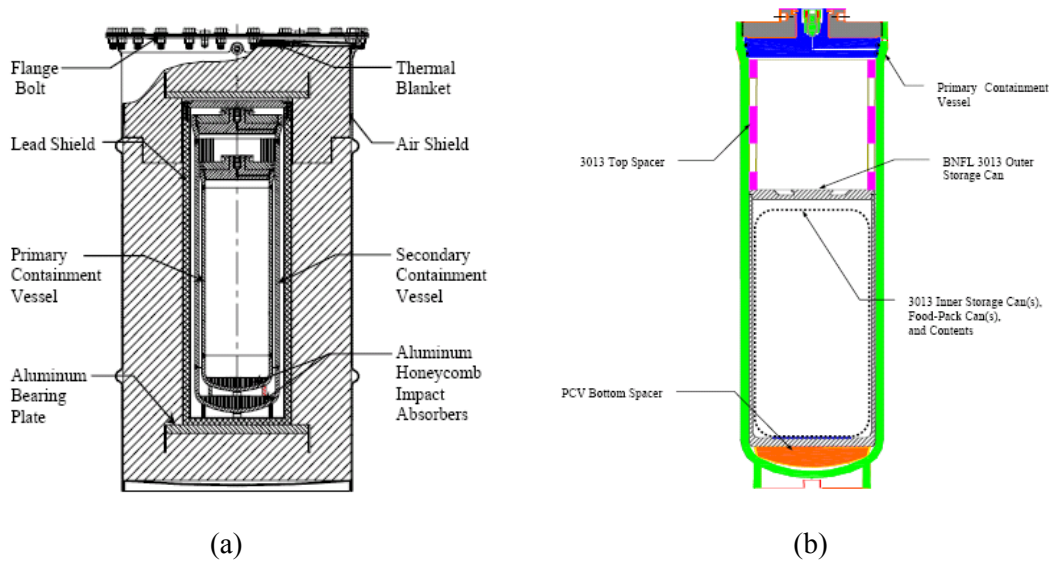
Figure 5.   Schematic of the Model 9975 transportation packaging: (a) cross-sectional view and (b) primary containment vessel containing a 3013 can assembly. The hatched area in (a) between the lead shield and the drum surface is the Celotex thermal insulation.

reference fire scenario is that of the 10 CFR 71 HAC fire at 800°C for 30 minutes, for which the existing thermal analysis[2] has shown that the peak Pu/SS interface temperature would be 106°C for an SRS 3013 configuration in a Model 9975 packaging. This calculated peak interface temperature is only slightly higher than the peak temperature (≈ 90°C) recorded near the O-ring of the primary containment vessel of Model 9975 packaging, which occurred 4 hours after the HAC fire test (30 minutes at 800°C) was terminated. The thermal analysis performed for the reference fire scenario of the 3013 can here differs from the previous HAC analysis in that the Model 9975 packaging modeled does not include the damage incurred from the free drop, crush, and puncture. However, it does include the bounding-content heat load (19 W), without solar insolation, in the calculations of the Pu/SS interface temperatures corresponding to selected fire scenarios, all at 800°C for up to 4 hours.

Modeling Consideration

A quasi-static approach has been adopted in the thermal analysis of the Model 9975 packaging that takes into account the shrinkage and charring of the Celotex (see Fig. 5a) during a fire. It consisted of a series of calculations, each for a 30-minute duration, with the thickness of the Celotex and the charred layer adjusted for succeeding calculations based on the results of the preceding calculation. Specifically, the results of a given case are reviewed, then the portion of Celotex above 260°C (500°F) is removed, and the portion above 149°C (300°F) is assigned the thermal properties of a charred layer before the next calculation is repeated. The temperature criteria are based on a study of thermal degradation of Celotex,[18] as well as the previous thermal analysis of a HAC test of a Model 9975 packaging conducted in the Radiant Heat Facility at Sandia National Laboratories.[19] The HAC thermal test was conducted at 816°C for 30 minutes, followed by a 15-hour cool-down while the Model 9975 packaging remained in the test facility. Temperatures were recorded for 16 hours from the start of heating, and the peak temperature for the primary containment vessel occurred 9 hours after the start of heating. By the end of 16 hours, the outer components were near the pre-test temperatures.

Post-test examination of the Model 9975 packaging found that the Celotex was uniformly charred over its outer surface (Fig. 6a), and its outside diameter was reduced by ≈ 2 cm. While the bulk of the Celotex ring segments maintained their configuration, portions near the top had broken off, and a web of fissures and cracks was evident on the surface. The thickness of the charred layer in the Celotex, shown in Fig. 6b

(a)   (b)

Figure 6.   Outside surface of the Celotex ring segments after the HAC thermal test of a Model 9975 packaging, (a), and cross-sectional view of the Celotex showing the charred outer layer, (b).

along the rim, is ≈ 4 cm, giving a total thickness of ≈ 5.2 cm of shrinkage and charred Celotex during the HAC thermal test. Since the original thickness of the Celotex ring segment is 12.8 cm (5 in.), the shrinkage and the charred layer are ≈ 15 and 30%, respectively, of the original thickness of the Celotex

for the duration of the test. If one assumes a constant rate of degradation of the Celotex at 800°C, ≈ 80% of the Celotex may be "consumed" in 60 minutes, and 100% in 90 minutes.

Figure 7 shows snapshots of the calculated temperature distributions in the various components of the Model 9975 packaging during an 800°C fire after 30, 60, 120, 180, and 240 minutes. Only halves of the packagings are shown, assuming shrinkage and charring of the Celotex were symmetrical about the center axis. The 3013 can shown along the center axis contains two stacked Pu buttons with a heat load of 19 W, and the calculated Pu/can interface temperature increases slowly with time, from 162°C after 30 minutes to 187°C after 240 minutes at 800°C. While the results may be encouraging, these calculated Pu/can interface temperatures are subject to considerable uncertainties in the values assumed for the shrinkage and the thermal physical properties and the thickness of the charred layer, which may not be conservative. In addition, the thermal model has not accounted for heat transfer through the gaps between the Celotex ring segments, or the cracks and fissures through the Celotex.

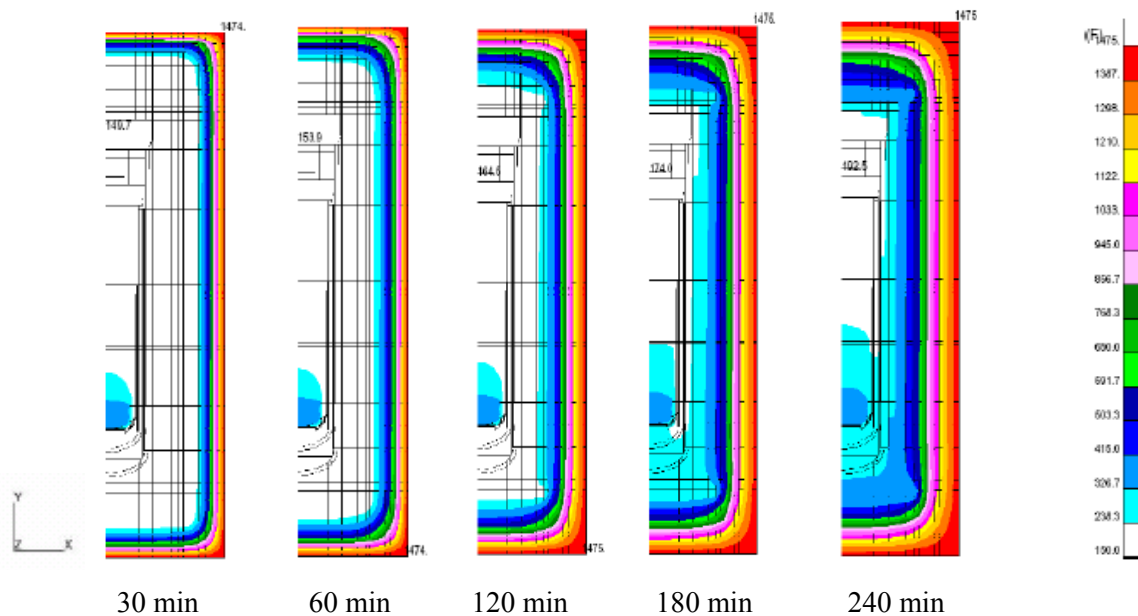| 30 min | 60 min | 120 min | 180 min | 240 min |

Figure 7.   Calculated temperature distributions in the Model 9975 packaging during a 4-h, 800°C (1472°F) fire. (Temperature scale in degrees Fahrenheit.)

Limiting Fire Analysis

At some point during an elevated-temperature, long-duration fire, the Celotex will no longer provide thermal insulation for the 3013 can in the primary and secondary containment vessels. There is no point to continue thermal analysis of the Model 9975 packaging after the Celotex is completely burnt, and a limiting case would be one that exposes a 3013 can in nested primary and secondary containment vessels to an 800°C fire. Since the primary containment vessel (PCV) and the secondary containment vessel (SCV) are made of 304L stainless steel with a nominal thickness of 6,553 and 7,112 μm (0.258 and 0.280 in.), respectively, and since the gap between the PCV and SCV is relatively small, i.e., 6,147 μm (0.24 in.), the temperature of the 3013 can is expected to reach the fire temperature in a short time (≤ 10 minutes). A further simplification of the limiting fire analysis can, therefore, assume a bare 3013 can directly exposed to a fire. This case has been analyzed by Gupta and McKeel,[20] and their approach and results are summarized below.

Gupta and McKeel assumed a heat source of 19 W in the 3013 can and an ambient temperature of 38°C; they also assumed a steady-state temperature of 50°C as the initial temperature for the contents and filling

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gas inside the 3013 can. The boundary fire conditions are a set of 12 fire curves with the peak fire temperature varying from 400 to 850°C for 1, 1.5, and 2 hours. To determine the limiting temperature and pressure of the 3013 can, Gupta and McKeel did a probabilistic structural analysis by taking into account variations in material strength, creep properties, failure criteria, and physical dimensions of the 3013 can. Based on the material strain limits that decrease with increasing temperature, the allowable pressure (taken as 70% of the failure pressure according to the Code of the American Society of Mechanical Engineers) for the 3013 can was calculated as a function of temperature in a fixed-duration fire of 1.5 h. The allowable pressure varies between 1,880 and 350 psig for a 3013 can exposed in a 1.5-h fire at 400 and 850°C, respectively.

For the pressure loading inside the 3013 can during a fire, Gupta and McKeel considered contributions from the generation of hydrogen (from radiolysis) and helium (from alpha decay), steam from desorption of moisture, and heating. They calculated the pressure inside the 3013 can as a function of temperature, assuming that the content is plutonium oxide stabilized according to the procedures in DOE-STD-3013-2004. The calculated internal pressure varies between 386 and 806 psig at 400 and 850°C, respectively. Figure 8 shows the calculated internal pressure and the allowable pressure for the 3013 can in a 1.5-h duration fire, with a fire temperature ranging between 400 and 850°C. The two curves intersect at 767°C at an allowable pressure of 720 psig. For a 3013 can containing Pu metal, the internal pressure will be lower than that shown in Fig. 8 for plutonium oxide because of the lower moisture level in the Pu metal. The corresponding increase in the internal pressure with temperature in the 3013 can containing Pu metal, therefore, would be smaller, and the intersection with the allowable pressure would occur at a temperature higher than 767°C.
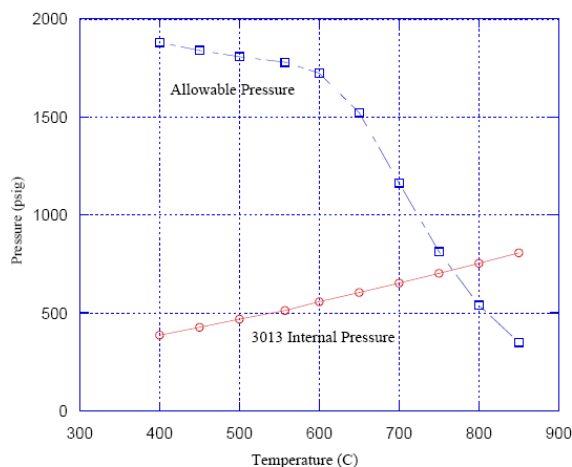

Figure 8.   Allowable pressure for the 3013 can in a 1.5-h fire at various temperatures calculated from creep strain limits, and internal pressure in the 3013 can containing plutonium oxide calculated as a function of temperature.

DISCUSSION

The review of metallurgical data showed that under normal storage conditions of the 3013 cans, either bare or in a Model 9975 transportation packaging, a eutectic reaction between the Pu metal and the 3013 can is unlikely to pose a threat to the integrity of the can. The eutectic reaction between Pu and Fe in the 3013 can may be slow even at temperatures as high as 600°C, as suggested by the IFR fuel/cladding compatibility studies and the EBR-II and FFTF reactor irradiation data. Above 650°C, the reaction rate becomes appreciable and increases significantly with temperature (Fig. 3). At 820°C, an IFR fuel pin (U-19 wt.% Pu-10 wt. % Zr/HT9) failed near the top end of the fuel after 112 minutes; the failure was caused by a very substantial cladding wall thinning due to fuel/cladding metallurgical reaction, aided by the

internal fission gas pressure that resulted in the final rupture of the cladding (Fig. 4). Based on Eq. (3) derived from the FBTA data of 1-h tests, approximately 60% of the 3013 can wall ($\approx$ 5,600 μm combined inner and outer walls) would be reacted after 10 h at 800°C.

The thermal analysis of the Model 9975 packaging showed that the calculated peak Pu/can interface temperature is low (187°C) during an 800°C fire of up to 4 h. While the results may be encouraging, the thermal models are subject to considerable uncertainties with respect to shrinkage and charring of the Celotex. However, as the Celotex is burnt and/or charred in a prolonged fire, the Pu/can interface temperature will rise and eventually reach the fire temperature after the insulation is completely lost. The limiting fire analysis of the 3013 can is then applicable, and the allowable pressure in the 3013 can would be $\approx$ 530 psig for another 1.5 h at 800°C, if creep deformation under the internal pressure were the only failure mechanism for the 3013 can. Inclusion of wall thinning due to Pu/can metallurgical reaction would reduce the allowable pressure, as suggested by the synergistic failure of the IFR fuel pin in the WPF heating simulation of the loss-of-flow accident in the reactor. Should the 1.5-h duration fire occur at a higher temperature (e.g., 850°C) or lower than 800°C but above 700°C, the allowable pressure for the 3013 can displayed in Fig. 8 may be used, in conjunction with Eq. (3), to address the expected synergistic effect of wall thinning from the Pu/can metallurgical interaction.

Eutectic reaction between Pu metal and Fe, therefore, is a potential failure mechanism for the stainless steel 3013 can containing Pu metal, especially for bare 3013 cans during an elevated-temperature, long-duration fire at a storage facility. For the 3013 cans stored in nested primary and secondary containment vessels inside a Model 9975 packaging, the likelihood of the Pu/Fe eutectic reaction is substantially reduced owing to the thermal protection provided by the Celotex insulation of the Model 9975 packaging. After the complete loss of insulation in the Model 9975 packaging in a prolonged fire, the release of radioactivity would occur only after successive breaching of the primary and secondary containment vessels.

SUMMARY AND RECOMMENDATION

The review and analysis showed that even in an 800°C fire with a duration of up to 4 hours, the Model 9975 packagings would be safe as the 3013 can temperature would stay significantly below the Pu/Fe eutectic temperature of $\approx$ 400 to 410°C. Indeed, even if the 3013 can reaches 400°C, the kinetics of the reaction is such that the walls of the 3013 can may survive several days at that temperature. Above 400°C, the progression depends strongly on the peak temperature and duration, as well as the thermal performance of the protective packaging. For facilities that store Pu metals in 3013 cans, whether bare, in the Model 9975, and/or in other packagings, a review of the documented safety analysis for the facility should be conducted, with attention paid to the fire event. Compensatory measures should be taken, if deemed necessary.

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