

Potential Eutectic Failure Mechanism for Stainless Steel 3013 Cans Containing Plutonium Metal Not Analyzed in the Safety Basis

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Summary

On November 22, 2005, the Manager of the Plutonium Finishing Plant (PFP) at Richland, WA issued an Occurrence Report (EM-RL-PHMC-PFP-2005-0032) after the PFP Plant Review Committee concurred with the determination of a Potential Inadequacy of the documented Safety Analysis (PISA) involving a potential eutectic failure mechanism for the stainless steel (SS) 3013 cans containing plutonium metal. The bounding Safety Basis accident analyzed and documented is the pressurized rupture of a 3013 can containing plutonium oxide in a 600°C fire. However, the Safety Basis accident did not consider the potential reaction of Pu metal and iron (Fe), the major component in the stainless steel 3013 can, at 410°C, the eutectic temperature of Pu and Fe, during a fire. Whether the 3013 can would fail by the Pu-Fe eutectic reaction depends on the severity of the fire, i.e., peak temperature and duration, and the thermal performance of the protective packaging, e.g., the 9975 packagings that contain the 3013 cans.

A significant number of the 3013 cans containing Pu metals are stored in the 9975 packagings, which are approved by DOE-EM for transportation according to 10 CFR 71, the Federal Regulations on Packaging and Transportation of Radioactive Materials. Subpart F of 10 CFR 71 describes package testing under *Normal Conditions of Transport (NCT)* and *Hypothetical Accident Conditions (HAC)* that consists of a sequence of tests of free drop, crush, puncture, thermal, and immersion. Approval of the 9975 packaging was based on testing under NCT and HAC, including a demonstration of acceptable thermal performance of a damaged packaging in an 800°C, 30-minute-long fire. Acceptable thermal performance of the 9975 packagings under a facility Safety Basis accident fire is not required by Federal Regulations and/or DOE Orders, because the 9975 packaging was designed and intended for transportation, not for long-term storage in a facility. The PISA identified for the PFP involving a potential eutectic failure mechanism for stainless steel 3013 cans containing Pu metal is thus a probable PISA for other sites, where the 9975 packagings, or other packagings such as the DOT 6M transportation packagings, are used for storage of 3013 cans containing Pu metals.

EM-60 has completed an assessment of the PISA for the 9975 packagings containing Pu metals in 3013 cans. The attached assessment report has been independently reviewed by the Los Alamos National Laboratory. EM-60 is confident that the 9975 packagings are safe during an 800°C, 30-minute-long duration fire, and that eutectic reaction between the Pu metal and the stainless steel 3013 cans will not occur because the calculated Pu/SS interface temperature is significantly below 400°C, which is also validated in a HAC thermal test. The EM-60 assessment has also concluded that based on experimental evidence in related studies and a previous furnace incident at Rocky Flats in 1985 (UOR Number 85-2-779 85-1), the eutectic reaction between Pu metal and Fe is a potential failure mechanism for the stainless steel 3013 cans containing Pu metal, particularly for the bare 3013 cans during an elevated-temperature, long-duration fire at a storage facility. The facilities that currently store 3013 cans (containing Pu metal) bare and in the 9975 and/or other packagings (e.g., DOT 6M) should review their documented Safety Basis with regard to fire protection and take any immediate compensatory measures, if deemed necessary.

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Introduction

On November 22, 2005, the Manager of the Plutonium Finishing Plant (PFP) in Richland, WA issued an Occurrence Report (EM-RL-PHMC-PFP-2005-0032) after the PFP Plant Review Committee concurred with the determination of a Potential Inadequacy of the documented Safety Analysis (PISA) involving a potential eutectic failure mechanism for the stainless steel (SS) 3013 cans containing plutonium (Pu) metal. The bounding Safety Basis accident analyzed and documented is the pressurized rupture of a 3013 can containing plutonium oxide in a 600°C fire. However, the Safety Basis accident did not consider the potential reaction of Pu metal and iron (Fe), the major component in the stainless steel 3013 can, at 410°C, the eutectic temperature of Pu and Fe,¹ during a fire. Whether the 3013 can would fail by the Pu-Fe eutectic reaction depends on the conditions of the fire, i.e., peak temperature and duration, and the thermal performance of the protective packaging, e.g., the 9975 packaging that contain the 3013 cans.

A significant number of the 3013 cans containing Pu metals are stored in the 9975 packagings,² which are approved by DOE-EM for transportation³ according to 10 CFR 71, the Federal Regulations on Packaging and Transportation of Radioactive Materials. Subpart F of 10 CFR 71 describes package tests under *Normal Conditions of Transport (NCT)* and *Hypothetical Accident Conditions (HAC)* that consist of a sequence of tests of free drop, crush, puncture, thermal, and immersion. Approval of the 9975 packaging was based on testing under NCT and HAC, including a demonstration of acceptable thermal performance of a damaged packaging in an 800°C, 30-minute-long fire. Acceptable thermal performance of the 9975 packagings under a facility Safety Basis accident fire is not required by Federal Regulations and/or DOE Orders, because the 9975 packaging was designed and intended for transportation, not for long-term storage in a facility. The PISA identified for the PFP involving a potential eutectic failure mechanism for stainless steel 3013 cans containing Pu metal is thus a probable PISA for other sites, where the 9975 packagings, or other packagings such as the DOT 6M transportation packagings, are used for storage of 3013 cans containing Pu metals.

EM-24 has completed a preliminary assessment of the PISA for the 9975 packagings containing Pu metals in 3013 cans in a two-pronged approach: (1) Review of metallurgical data, e.g., phase diagrams, diffusion couples, other relevant experiments, etc., 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. This report provides the results of the assessment and the associated recommendation.

1. Review of metallurgical data

The two main sources of the metallurgical data reviewed are those pertaining to the development of the DOE 3013 Standard⁴ by the Los Alamos National Laboratory (LANL) in the late 1990s,^{5, 6} and those accumulated at Argonne National Laboratory (ANL) from research on 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.⁷⁻¹¹ The Pu content in these 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 $\approx 400^\circ\text{C}$ near the fuel bottom (where coolant entered the reactor core) to up to $\approx 600^\circ\text{C}$ 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 $\approx 370^\circ\text{C}$ for EBR-II or

≈360°C for FFTF. The cumulative hold time at the bulk sodium temperature varied, but it is 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 reactor due to the interaction was extremely rare. (The IFR fuel pin cladding was relatively thin, i.e., ≈380-560 μm wall, compared to the combined ≈5,600 μm of the 3013 can's inner and outer walls.) Therefore, if the 3013 can temperature is 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)^{12,13} 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,^{14,15} 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 due to 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 FBTA and WPF tests database may be useful in assessing the potential eutectic failure mechanism for the stainless steel 3013 cans containing Pu metal, if the postulated can temperature is significantly above 600°C during a fire.

A number of diffusion-couples experiments were also performed at ANL to investigate the fundamental aspects of diffusion behavior involving fuel, cladding and fission products,^{16,17} 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, in order to obtain meaningful interaction depths within a reasonable time (days).

For 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^{5,6} 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,

$$R = \exp(A - B/T) \quad (1)$$

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 $\approx\pm 10\%$, 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 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 $\approx 30\text{-}70\ \mu\text{m}$. This depth, even if entirely on the can side, should not challenge the integrity of the 3013 can, which has a wall thickness of $\approx 4,000\ \mu\text{m}$. (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 $< 400^\circ\text{C}$ fire is the IFR metal fuels irradiation experience from EBR-II and FFTF. The few fuel-pin ruptures were either intentional (to study fission product release after a cladding breach), superficial end-plug or spacer-wire weld-related failures, or due to extreme high burnup and/or cladding temperature. Under normal operation with peak cladding temperature $\leq 600^\circ\text{C}$ 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 temperature for hundreds of days, this positive IFR cladding integrity database bodes well for a Pu-containing 3013 can to survive a 400°C fire, with a much shorter duration.

3013 can temperatures between 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, it is necessary to 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 PISA 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 $\approx 100\text{-}200$ 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),¹ no melting of the interface was observed in discharged IFR fuel pins with cladding temperatures up to ≈600°C.

Pahl¹⁸ provided an equation to estimate the extent of cladding wastage from the fuel/cladding interfacial diffusion during the steady-state reactor irradiation

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

where D = depth of interaction (μm);
 A = 1.718 x 10¹¹;
 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, along with several measured data after ≈500 days of irradiation. The cladding wastage in the IFR pins is < 150 μm after 500 days at 600°C peak cladding temperature.

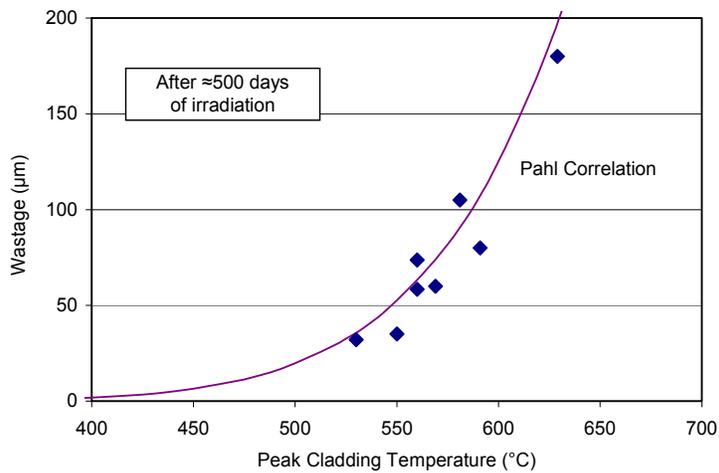


Fig. 1. IFR cladding wastage from steady-state irradiation.

Using Eq. 2, one can estimate the depth of 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 would be ≈21 μm, which poses no threat to the integrity of the 3013 cans.

The ≈21μm depth calculated by Eq. (2) at 600°C may appear inconsistent with the 30-70 μm depth calculated by Eq. (1) at 400°C, both for a 10-day-long fire. However, it should be noted that 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 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^{12, 13} and WPF^{14, 15} in a hot-cell laboratory may be useful. Both types of tests utilized irradiated fuel/cladding materials with pre-existed 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 test 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 utilized 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 $\leq 650^\circ\text{C}$, even with extended test durations (up to 36 hours). Above 675°C, melting was observed in some samples with more aggressive parameters. Figure 2 shows the comparison of results from two tests with and without melting.

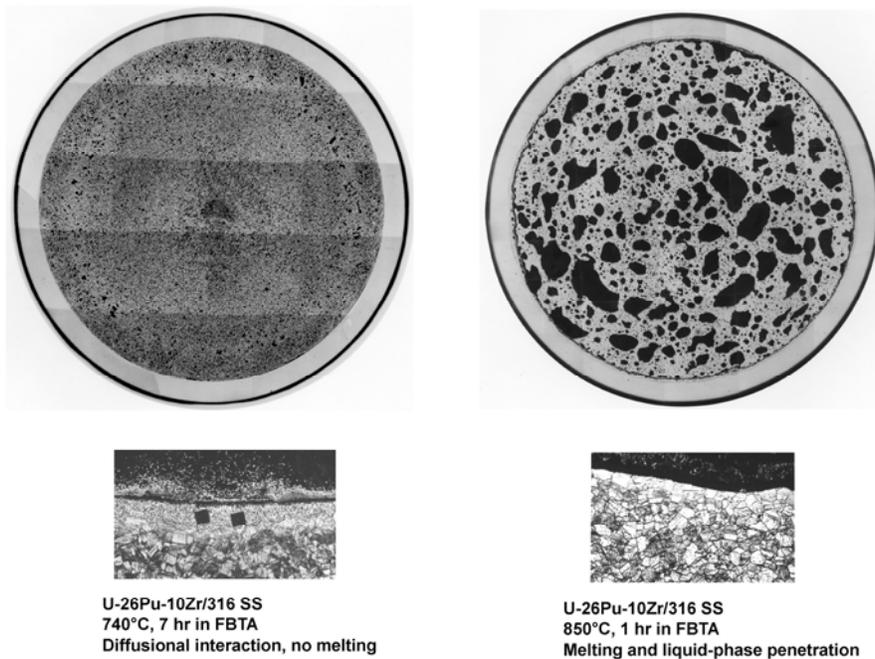


Fig. 2. Cross-sectional view of two samples after the FBTA tests. Samples were from the same fuel pin. Only diffusion interaction occurred in the sample shown on the left. The lower photos show etched cladding and the nature of the cladding penetration. (The black diamonds in the cladding diffusion layer on the left are the indentation marks from microhardness measurements.) Notice that for the sample on the right, 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 an 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:

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

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

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

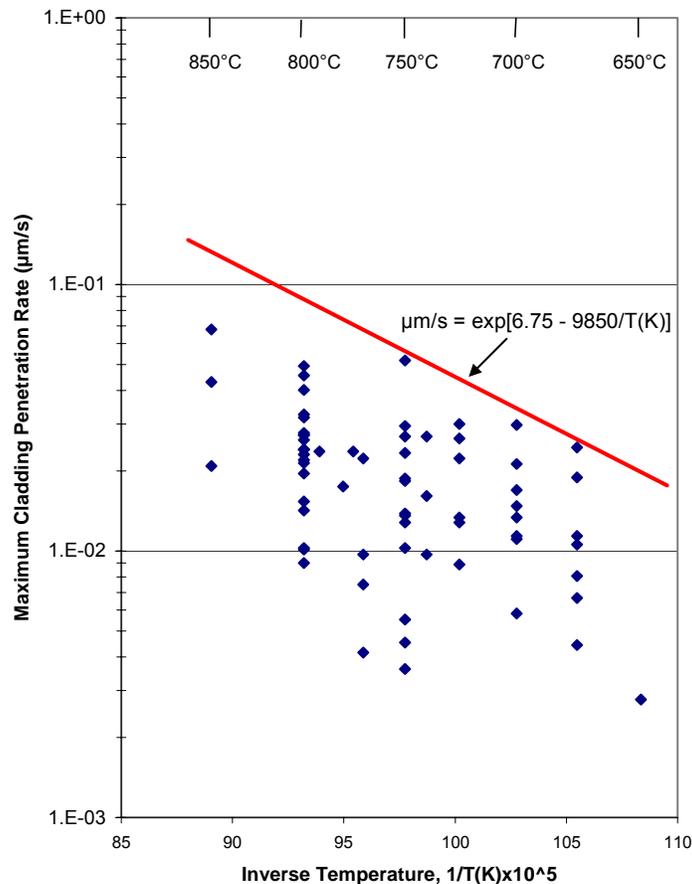


Fig. 3. Effective cladding penetration rates from the FBTA tests for specimens tested for 1.0 hour.

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 a IFR fuel pin (U-19wt.%Pu-10 wt.%Zr/HT9) that failed near the top end of the fuel after 112 minutes at 820°C.¹⁵ 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.

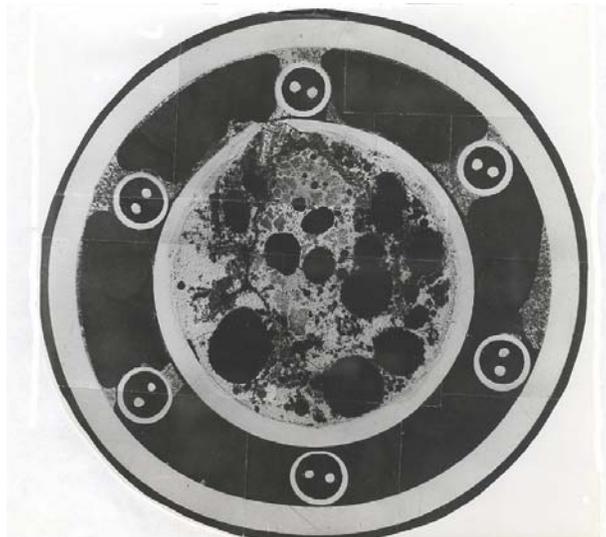


Fig. 4. Cross-sectional view of a IFR fuel pin (U-19wt.%Pu-10 wt.%Zr/HT9) that failed near the top end of the fuel after 112 minutes at 820°C. The fuel pin is shown in the center of the picture surrounded by 6 thermocouples in the gap between the fuel pin and a furnace heat receptor. Cladding breaching 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.

Eqs. (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 couples experiments, and irradiation and furnace experiments of IFR fuels. In 1988, ANL also performed a diffusion-couples experiment between U-22Pu-23Zr and HT9 at 650°C for 200 hours.¹⁷ The measured thickness of the interaction band was $\approx 700 \mu\text{m}$, of which $\approx 500 \mu\text{m}$ was on the fuel side. Whereas the $\approx 200 \mu\text{m}$ reaction on the cladding side is greater than the trend depicted in Fig. 1 for ≈ 500 days at 650°C, it is an order of magnitude smaller than those extrapolated from Eq. (1), i.e., $\approx 2,400\text{-}3,500 \mu\text{m}$ at 650°C for 200 h. Given the large variations in the calculated interactions, one should be cautious when extrapolating the equations outside the ranges of parameters in the experimental data base.

2. Thermal Analysis

The purpose of the thermal analysis of the 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 reference fire scenario is that of the 10 CFR 71 HAC fire at 800°C for 30 minutes, for which the existing thermal analysis² has shown that the peak Pu/SS interface temperature would be 106°C for the SRS 3013 configuration in a 9975 packaging. This calculated peak interface temperature is only slightly higher than

the peak temperature ($\approx 90^\circ\text{C}$) recorded near the O-ring of the primary containment vessel of a 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 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 a duration of up to 4 hours.

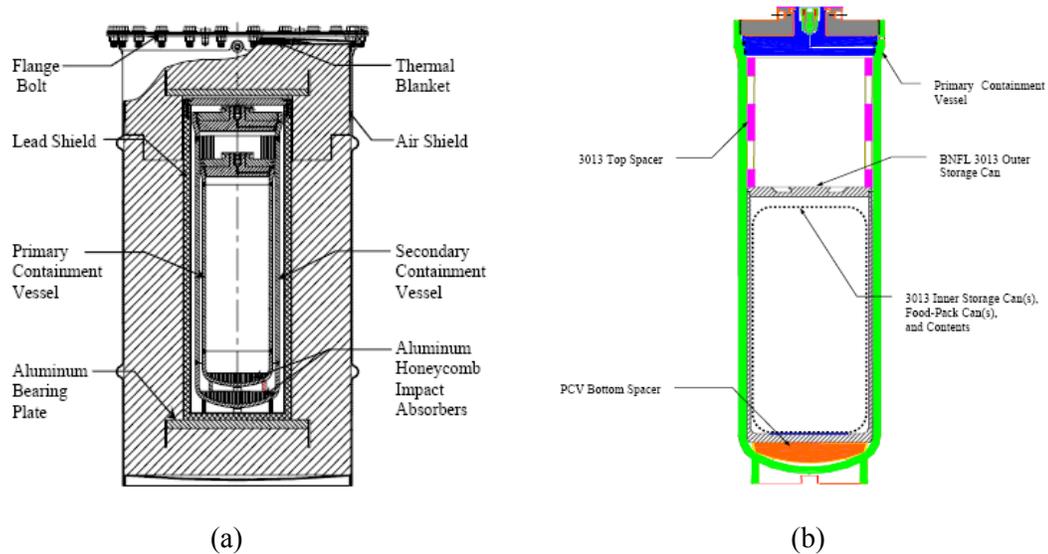


Fig. 5. Schematic of the 9975 packaging: (a) cross-sectional view, and (b) primary containment vessel containing a 3013 can assembly. The hatched area in (a) between the lead shield and the drum surface is the Celotex thermal insulation.

Modeling consideration

A quasi-static approach has been adopted in the thermal analysis of the 9975 packaging that takes into account of the shrinkage and charring of the Celotex 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 and 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 repeating the next calculation. The temperature criteria are based on a study of thermal degradation of Celotex,¹⁹ as well as the previous thermal analysis of a HAC test of a 9975 packaging conducted in the Radiant Heat Facility at the Sandia National Laboratory.²⁰ The HAC thermal test was conducted at 816°C for 30 minutes, followed by a 15-hour cooldown while the 9975 package 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.

Posttest examination of the 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 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 entire 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.



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

Figure 7 shows snapshots of the calculated temperature distributions in the various components of the 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, it should be noted that 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.

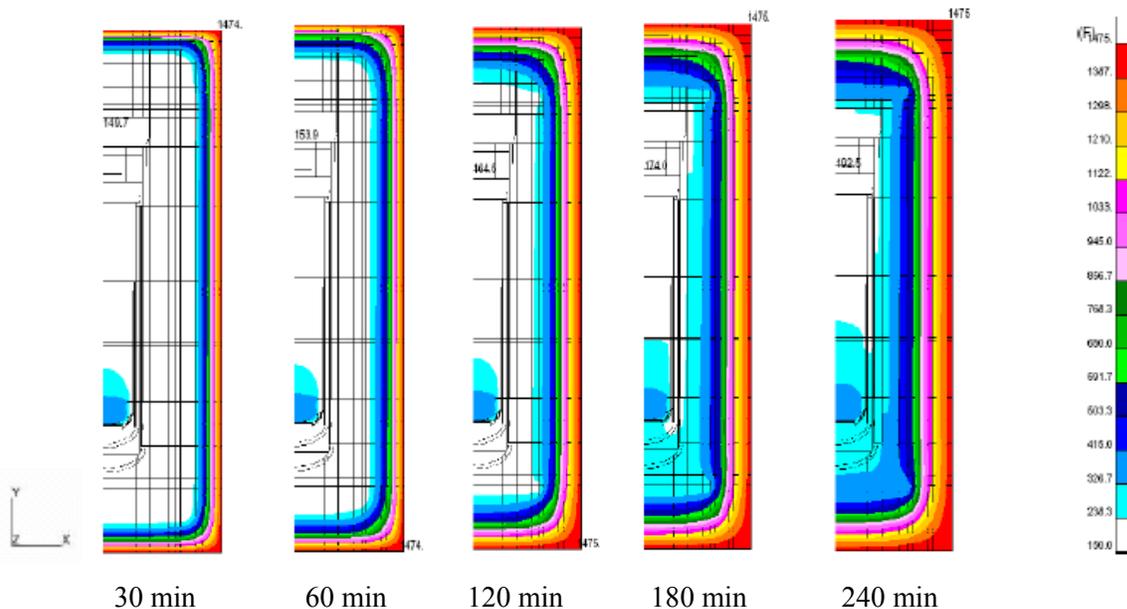


Fig. 7. Calculated temperature distributions in the 9975 packaging during a 4-h, 800°C (1475°F) fire. (Temperature scale in degrees Fahrenheit)

Limiting fire Analysis

At some point during an elevated-temperature, long-duration fire, it seems certain that 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 9975 packaging after the Celotex is completely burnt, and a limiting case would be one that exposes a 3013 can in a nested primary and secondary containment vessels to a 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, which has been analyzed by Gupta and McKeel²¹ 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 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 a duration of 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 ASME Code) 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 the DOE 3013 Standard.⁴ 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

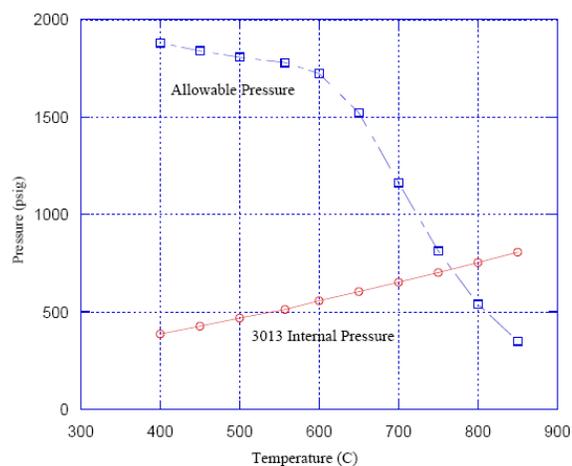


Fig. 8. Allowable pressure for the 3013 can in a 1.5-h fire at various temperatures calculated based on creep strain limits, and internal pressure in the 3013 can containing plutonium oxide calculated as a function of temperature.

in a 1.5-h duration fire, with a fire temperature ranging between 400 to 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.

3. Discussion

The review of metallurgical data showed that under normal storage conditions of the 3013 cans, either bare or in a 9975 transportation packaging, an 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-19wt.%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 ($\approx 5,600 \mu\text{m}$ combined inner and outer walls) would be reacted after 10 h at 800°C.

The thermal analysis of the 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 ≈ 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 a nested primary and secondary containment vessels inside a 9975 packaging, the likelihood of the Pu/Fe eutectic reaction is reduced substantially owing to the thermal protection provided by the Celotex insulation of the 9975 packaging. After the complete loss of insulation in the 9975 packaging in a prolonged fire, the release of radioactivity would occur only after successive breaching of the primary and secondary containment vessels. Given the stainless steel melt-through reported in the 1985 Rocky Flats furnace incident (UOR Number 85-2-779 85-1), the reaction rate could be fairly rapid as the molten plutonium-aluminum alloy apparently attacked and breached the stainless steel cup within 4 hours after the start of the furnace operation. [Dan Guzy, DOE/EH-3 provided a draft Discussion paper *Pu-Fe Eutectic Issue for Plutonium Containers*²² containing a reference to the 1985 Rocky Flats furnace incident. EM-24 will share information with EH-3 and others in order to reach a DOE consensus on any follow-up actions, if required, to address this generic issue.]

4. Summary and recommendation

EM-24 is confident that the 9975 packagings are safe during an 800°C, 30-minute-long fire, and that the eutectic reaction between Pu metal and the stainless steel 3013 cans will not occur because the calculated Pu/SS interface temperature is significantly below 400°C, which is also validated in a HAC thermal test. Whether the 3013 can would fail by the Pu-Fe eutectic reaction depends on the conditions of the fire, i.e., peak temperature and duration, and the thermal performance of the protective packaging. The facilities storing 3013 cans (containing Pu metal) in the 9975 and/or other packagings (e.g., DOT 6M) should review their documented Safety Basis with regard to fire and take any immediate compensatory measures, if deemed necessary.

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