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**Characterization of Uranium Corrosion Products Involved in the March 13, 1998 Fuel
Manufacturing Facility Pyrophoric Event**

by

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ABSTRACT

Uranium metal corrosion products from ZPPR fuel plates involved in the March 13, 1998 pyrophoric event in the Fuel Manufacturing Facility at Argonne National Laboratory – West were characterized using thermo-gravimetric analysis, X-ray diffraction, and BET gas sorption techniques. Characterization was performed on corrosion products in several different conditions: immediately after separation from the source metal, after low-temperature passivation, after passivation and extended vault storage, and after burning in the pyrophoric event. The ignition temperatures and hydride fractions of the corrosion product were strongly dependent on corrosion extent. Corrosion products from plates with corrosion extents less than 0.7% did not ignite in TGA testing, while products from plates with corrosion extents greater than 1.2% consistently ignited. Corrosion extent is defined as mass of corrosion products divided by the total mass of uranium. The hydride fraction increased with corrosion extent. There was little change in corrosion product properties after low-temperature passivation or vault storage. The burned products were not reactive and contained no hydride; the principal constituents were UO_2 and U_3O_7 . The source of the event was a considerable quantity of reactive hydride present in the corrosion products. No specific ignition mechanism could be conclusively identified. The most likely initiator was a static discharge in the corrosion product from the 14th can as it was poured into the consolidation can. The available evidence does not support scenarios in which the powder in the consolidation can slowly self-heated to the ignition point, or in which the powder in the 14th can was improperly passivated.

I. INTRODUCTION

A. Background

The pyrophoric event which occurred on March 13, 1998 in the Fuel Manufacturing Facility (FMF) on the Argonne National Laboratory – West (ANL-W) site involved corrosion products collected from highly enriched uranium (HEU) metal fuel plates used in the Zero Power Physics Reactor (ZPPR), also located on the ANL-W site. The corrosion products, known to be a mixture of uranium oxide (UO_{2+x}) and pyrophoric uranium hydride (UH_3), formed during extended vault storage of the fuel plates over a period from 1982 to 1994. The unique storage configuration of the plates was the root cause of the severe corrosion—the uranium metal plates were clad in stainless steel jackets with porous metal endplugs. The porous nature of the endplugs allowed access of ambient gas to the uranium metal plates, and the presence of the cladding created a crevice environment which supported the formation of hydride. The corrosion was eventually halted through the use of an O_2 and H_2O getter. The history of the ZPPR fuel plate corrosion problem and an initial characterization of the corrosion products is detailed in reference [1].

The corroded plates were identified as a storage vulnerability by the U.S. Department of Energy (DOE) in a 1993 assessment [2]. In order to address the vulnerability and recycle the HEU present in the plates, a processing scheme for separation of useful uranium metal from the cladding and the corrosion products was developed and implemented. The procedure [3] entailed decladding the plates in an inert atmosphere glovebox and separating the loose corrosion products from the metal coupons (“coupon” refers to an individual uranium metal piece, “plate” refers to a clad assembly of two or more coupons). After separation, the metal coupons were collected and induction cast into a single large ingot. The uranium metal was eventually shipped to BWX Technologies as feedstock for research reactor fuel.

The separated corrosion products underwent a passivation procedure intended to prevent pyrophoric events during subsequent handling and vault storage. In a pass-through Ar glovebox containing approximately 3% O_2 , the products were ground into a fine powder using a mortar

and pestle, spread into a thin layer, and exposed to the O₂-containing gas for a minimum of two hours. The products were then placed into polyethylene bottles and transferred out of the glovebox to an enclosed air hood. Inside the hood the passive nature of the products was verified by vigorous agitation (stirring and pounding with a screwdriver) prior to their placement into a container (food-pack can) for vault storage. The corrosion products were stored with the intention that they would eventually be fully converted to oxide using a higher-temperature process. This procedure was used to process 376 kg of HEU over the course of about 1 year; 4.2 kg of corrosion products were separated, passivated, and placed into vault storage.

B. Event Description and Subsequent Investigation

The full details of the pyrophoric event were presented in the formal investigation report [4] and only a brief summary will be presented here. Because a separate, quart-size food-pack can was used for each casting batch (usually corresponding to 40 plates), the 4.2 kg of corrosion products collected during processing were distributed in 35 cans, each bearing less than 250 g. It was desired to consolidate the corrosion products into fewer containers to conserve storage space in the vault. The consolidation operation was begun on the morning of March 13, 1998. Six food-pack cans were transferred at a time into an enclosed air hood in the FMF south room. The six cans were opened and their contents poured into a larger steel consolidation can, and then the next six cans were transferred into the enclosure. The contents of 13 food-pack cans were emptied into the consolidation can in this manner without incident. At this point the consolidation can was approximately 75% full. As the contents of the 14th can were being poured into the consolidation can, the technician performing the operation noticed that the material from the food-pack can began sparking. Flames quickly formed above the material in the consolidation can and in the 14th food-pack can.

The operator initially attempted to extinguish the fire using Met-L-X compound, a metal fire extinguishant which is primarily a mixture of sodium chloride and magnesium aluminum silicate. The Met-L-X was effective in extinguishing the material in the smaller food-pack can, but the fire in the consolidation can could not be extinguished. A gas stream emanating from the burning powder in the consolidation can ejected the Met-L-X applied. At this point the fire

department was called and the building evacuated. Fire department personnel re-entered the building one hour later and reported that the fire was no longer burning (it had self-extinguished), and that no apparent damage to the enclosure or hood had occurred. Later inspection of the area revealed that corrosion product material had been expelled from the consolidation container, which had discolored due to the heat of the burning powder. Figure 1 is a photograph of the consolidation can in the Lexan enclosure following the fire. The consolidation can had been placed into a steel catch-pan; material ejected from the consolidation can is visible in the catch-pan. The 14th can containing vault-stored corrosion product is in the bottom right corner

Figure 1. Consolidation can in FMF hood after the pyrophoric event.

An investigative team was formed to determine the cause of the fire. The team examined the event from both technical and conduct-of-operations perspectives. Their conclusions were presented in ref. [4]. The direct cause of the fire was identified as a failure to passivate the corrosion products in at least one of the food-pack cans, and the root cause was identified as a lack of understanding of the nature of the corrosion products. The team could not conclusively identify the mechanism by which burning was initiated. Two possible scenarios were presented. The first was a thermal excursion scenario whereby the tall geometry of the consolidation can led to ignition by preventing adequate heat removal from slowly oxidizing powder in the can. In the second scenario, the 14th food-pack can was assumed to be the ignition source, implying that the material in this can was different than that in the previous 13 cans. The potential differences identified were: (1) the material in the 14th can was fundamentally different; (2) the material in the 14th can was improperly passivated; and (3) the material in the 14th can had changed (become more reactive) during storage. Additional experiments were recommended to better understand the ignition mechanism.

A number of administrative and procedural deficiencies were also found in the investigation, and these were listed as contributing causes of the event. The principal technical deficiencies identified were that the technical understanding of the pyrophoric behavior of the corrosion products was inadequate, and that the two qualitative experiments performed to assess the effectiveness of the low-temperature passivation technique (described in ref. [5]) were fundamentally flawed. The team recommended that further work be done to better understand the nature of the corrosion products, and that sampling and analysis be performed to evaluate the vulnerability of the 21 containers of corrosion product remaining in the vault.

This report presents the results of an extensive characterization of the ZPPR HEU corrosion products performed in response to the above recommendations. The overall goal of the study was to determine the chemical reactivity of the corrosion products in various conditions. Reactivity was directly measured using a thermo-gravimetric analyzer (TGA). Further characterization was also performed using X-ray diffraction (XRD) and gas sorption analysis. XRD was used to measure the fractions of hydride and oxide phases present in the products, and gas sorption analysis was used to measure the specific surface area of the products.

The characterization was performed on samples of corrosion products in the following conditions: (1) immediately following de-cladding of the plates; (2) after low-temperature passivation according to the original procedure; (3) after passivation and long-term vault storage; and (4) after burning in the fire. The variation of properties with corrosion extent was also assessed for the first three conditions.

II. MATERIALS AND PROCEDURES

A. Materials Analyzed

As mentioned in the Introduction, the objective of this investigation was to measure the properties of the ZPPR corrosion products for different conditions. Measuring the properties of the corrosion products at each stage of the passivation and storage process increases the understanding of how the material evolved, and enables a better analysis of the fundamental causes of the pyrophoric event to be made. The variation in properties with corrosion extent was also determined for each condition. Previous work [6, 7] had observed an effect of corrosion extent on the reactivity of the corrosion products, with corrosion products from severely corroded plates showing greater reactivity than those from lightly corroded plates. This effect was not considered in the qualitative experiments performed to validate the initial passivation procedure [5] and may have been an important factor in the pyrophoric event. For all of the different conditions described below, the extent of corrosion was quantified as the mass of loose corrosion product divided by the total uranium mass of the plate or plates from which the corrosion products were collected. For batches of material with multiple plates, this figure represents an average extent.

1. Unpassivated Corrosion Products

The first condition for which the properties of the corrosion products were measured was immediately after de-cladding of the plates and separation of the corrosion products from the metal coupons. An extensive study of the corrosion products in this condition was performed prior to the pyrophoric event as part of a research program funded by the US

DOE National Spent Nuclear Fuel Program (NSNFP). In this study, the corrosion products from six plates with varying corrosion extents were analyzed using TGA, BET, and XRD. Complete procedures and results are presented in ref. [7]; the results relevant to the present investigation will be presented and discussed in this report.

Additional unpassivated corrosion products were sampled and analyzed as part of a series of tests to determine the effect of the original passivation procedure on the characteristics of the corrosion products. Ten plates which showed moderate corrosion were selected from the vault inventory. These plates were divided into two sets of five corresponding to less and more severe visible extents of corrosion. The plates were de-clad in the small HEU glovebox in a pass-through Ar atmosphere, and the corrosion products collected from each set of plates were combined into two separate "batches."

The motivation for combining the corrosion products was to best simulate the original passivation procedure, in which the corrosion products from (typically) 40 plates were combined into a single batch. Two batches of products were tested to insure that the possible influence of corrosion extent on the effectiveness of passivation was considered. Weighing of the plates and the separated corrosion products revealed that the corrosion extents for the two batches were 1.16% and 1.41%. A two-gram sample of the corrosion products in the unpassivated condition was taken from each batch immediately after decladding of the plates. These samples were placed into polyethylene bottles and transferred to the FMF Characterization glovebox for TGA analysis..

2. Passivated Corrosion Products

After initial sampling, the two batches of corrosion products were passivated according to the original, low-temperature procedure [3]. The O₂ content in the HEU glovebox was increased to 3.5 vol.% by admitting a small flow of air. The two batches were separately ground to a fine powder using a mortar and pestle and then left to sit in the O₂-containing environment for two hours. A second set of samples for TGA analysis was then taken from the passivated corrosion products. The samples were placed into polyethylene bottles and

transferred to the FMF Characterization glovebox. Measurement of the corrosion product characteristics immediately before and after passivation was intended to provide a clear indication of the effect of the passivation step and minimize the possible influences of other variables.

3. Corrosion Products After Passivation and Extended Vault Storage

Of the 35 cans of corrosion products generated during the ZPPR fuel processing campaign, only 14 were involved in the event on March 13, 1998. Twenty-one cans of nearly identical material remained in the vault. Characterization of these corrosion products was the initial objective of this investigation. The amount of corrosion product in each can varied from 19 to 211 grams. Since the corrosion product in each can was typically collected from 40 plates (some of the cans contained product from only 20 plates), there was a similarly broad variation in average corrosion extent of the batches of plates from which the products were collected. Corrosion products in this condition are subsequently referred to as "vault-stored."

TGA tests to measure the reactivity of the vault-stored products were performed on samples from every can. XRD and BET analyses were performed on samples from selected cans. The cans were transferred from the vault to the FMF Characterization glovebox (purified Ar atmosphere) for sampling and storage. The cans were opened in the glovebox and two-gram samples of the corrosion products were taken. Sub-samples for TGA, XRD, and BET analyses were taken from the two-gram samples. The remainder of the corrosion products were placed into polyethylene bottles and stored in the glovebox until they could be fully converted to oxide at high temperature. Details of the tests performed are presented below in Section 2.3.

4. Corrosion Products After Burning in the Pyrophoric Event

One of the first actions after the pyrophoric event was to collect the corrosion products which had burned and transfer them to the small HEU glovebox in FMF. The glovebox initially had a pass-through Ar atmosphere. After transfer into the glovebox, the burned corrosion products were spread out on stainless steel pans. Air was gradually admitted into the

glovebox, and the products were intermittently ground and agitated while the O₂ level increased. The material was exposed to an air atmosphere for one hour and intermittently agitated during this period. The material was then placed into a steel can and stored under vacuum in the glovebox transfer port pending further disposition. At a later time, the corrosion products were returned to the glovebox for sampling. Three separate two-gram samples of the material were taken for TGA and XRD analysis to verify that the material was truly inert. The samples were placed into polyethylene bottles and transferred to the FMF Characterization glovebox. After sampling, the corrosion products were returned to the transfer port pending the results of the testing.

B. Analysis Procedures

1. Gas Sorption Analysis

BET gas sorption analysis was performed on corrosion products in the vault-stored condition to compare their specific surface areas with those obtained for unpassivated powders in the earlier study [7]. The specific surface area is also a required parameter for analysis of the oxidation kinetics measured in a TGA test. The measurements were made on the same samples that were subsequently used for TGA testing—gas sorption analysis does not alter the sample, and the two-gram TGA samples were an appropriate size for BET testing. Analysis was performed using a Quantachrome Quantasorb analyzer and standard BET techniques with Kr gas as the adsorbate, He gas as the carrier, and N₂ gas for calibration. Adsorption was carried out at liquid N₂ temperature; three consecutive measurements were made on each sample. The test matrix and results are shown in Table I. Analysis was generally performed without any outgassing of the sample, as exposure of hydride to outgassing conditions may result in decomposition. Two samples that were known to contain very little hydride were outgassed overnight at 250°C with a He purge; these tests are also shown in Table I.

2. Oxidation Testing

Oxidation testing using the TGA analyzer was performed to assess the chemical reactivity characteristics of the corrosion product powders. Testing was performed using a modified Shimadzu TGA-51H analyzer in the FMF Characterization glovebox. Details of the testing apparatus and analysis techniques are presented in refs. [5] and [7]. A summary of the reactivity tests is shown in Table II; individual test results are listed in the Appendix. The standard test used was the burning curve test. In this test a 200 mg sample is heated at 15°C/min in a flowing Ar-20%O₂ atmosphere while the sample weight and furnace control thermocouple temperature are monitored. Ignition of the sample is clearly indicated by a sharp, simultaneous increase in both values; the ignition temperature is defined as the furnace temperature at this point. The sample is then allowed to oxidize to completion, which is indicated by the sample weight becoming stable. For samples which are known to contain hydride, the total weight change during burning is used to calculate the fraction of hydride in the sample via the stoichiometry of the hydride-oxygen reaction.

Oxidation tests were also performed in an isothermal mode. In an isothermal test, the sample is heated to the test temperature in a pure Ar atmosphere. When the test temperature is reached and stabilized, an Ar-30%O₂ reacting gas is admitted into the sample chamber by opening a solenoid valve in its supply line. Mixing of the reacting gas with a pure Ar purge gas reduces the oxygen concentration in the sample chamber to 20%. The weight of the sample is recorded for the duration of the test. Oxidation tests performed in this investigation were typically 300 or 600 minutes long.

Isothermal testing was performed on samples of vault-stored corrosion product for two purposes—to enable a comparison of low-temperature reaction rates with those previously measured for unpassivated products, and as a simulation of the passivation process. In the latter case, it was originally hypothesized that reaction of the hydride-bearing corrosion products with O₂ would reduce their reactivity by the formation of a passive oxide film on the surface of the hydride. This was the principle on which the original passivation scheme was based. To better test the hypothesis, corrosion product samples were first isothermally reacted with O₂ below the

ignition temperature, then cooled to room temperature and tested in a burning curve mode. An increase in ignition temperature after isothermal oxidation testing would indicate a passivation effect. The effect of low-temperature passivation according to the original procedure was assessed by testing of corrosion products before and immediately after passivation, as described in section 2.1.2.

3. X-Ray Diffraction

XRD was used for identification of metal, oxide and hydride phases present in the corrosion product samples. The XRD test matrix and results are shown in Table III. For samples that contained hydride, standardless analysis was performed using Sietronics phase analysis software to quantify the fractions of hydride and oxide for comparison with the results of the TGA tests. Samples for XRD analysis were taken from the same corrosion product samples that were used for TGA testing. The samples were transferred to the ANL-W Analytical Laboratory (AL) for analysis. All XRD samples were crushed to a fine powder in a high-purity Ar glovebox and loaded into a sealed environmental chamber. The loaded chamber was transferred out of the glovebox to the diffractometer. Diffraction was performed on a Scintag X1 powder diffractometer using Cu K-alpha radiation.

III. RESULTS

A. Specific Surface Areas

The results of the BET specific surface area analyses are shown in Table I. The data for unpassivated corrosion products are taken from ref. [7]. In the present investigation, BET analysis was performed only on samples of vault-stored corrosion products. The specific surface areas of the vault-stored products were essentially identical to those of the unpassivated products. The specific surface areas from all non-outgassed samples fell within the range of 0.5 to 1.0 m²/g, with the majority of the values approximately 0.7 to 0.8 m²/g. There was also no apparent effect of corrosion extent on specific surface area.

TABLE I. BET Results Summary

Material	Corrosion Extent* (%)	Specific Surface Area (m ² /g)
Unpassivated Product		
Plate 2249	0.64	0.50-0.52
Plate 3411	1.08	0.74-0.76
Plate 2962	1.53	0.95-1.04
Plate 3930	1.67	0.76-0.77
Plate 3401	1.83	0.73-0.78
Plate 2652	1.98	0.75-0.80
Vault-Stored Product		
SB97-1	0.33	0.93
SB97-1 (outgas)	0.33	2.67-2.97
BWHEU-F-IC008	0.85	0.76-0.79
BWHEU-F-IC008 (outgas)	0.85	2.15-2.23
RAM97-9/10	1.07	0.71-0.76
RAM97-23/24	1.80	0.83-0.84
BWHEU-F-IC009	1.83	0.89-0.99

*: Defined as mass of corrosion product divided by total uranium mass.

The two samples that were outgassed showed significantly higher specific surface areas after outgassing. For material from can SB97-1, the specific area increased from 0.9 to 2.8 m²/g; for material from can BWHEU-F-IC008, the specific area increased from 0.75 to 2.2 m²/g.

B. Burning Curve Reactivity

Table II summarizes the results of burning curve tests performed on unpassivated, passivated, and vault-stored material. The entries in Table II are sorted by material condition and sub-sorted by corrosion extent. Each entry corresponds to the results from 2 or 3 individual tests. The important properties measured in these tests are the ignition temperature and hydride fraction. The complete individual test data are shown in Appendix Tables A-I and A-II. The data from individual unpassivated plates are from ref. [7].

TABLE II. Summary of Corrosion Product Reactivity Characteristics

Material	Total U Wt. (g)	Corrosion Product Wt. (g)	Corrosion Extent (%)	UH ₃ Content ¹ (%)	Ignition T. (°C)
Unpassivated Product					
Plate 2249	222	1.42	0.64	N/A ²	N/A*
Plate 3411	222	2.40	1.08	17-19	144-166
Batch 1	1104	12.86	1.16	N/A	N/A
Batch 2	1108	15.62	1.41	13-15	145-166
Plate 3401	220	4.04	1.83	47-61	142
Plate 2652	220	4.35	1.98	29-39	134-137
Passivated Product					
Batch 1	1104	12.86	1.16	N/A	N/A
Batch 2	1108	15.62	1.41	18	159-161
Vault-Stored Product					
SB97-1	5747	19.07	0.33	N/A	N/A
RAM97-32/33	11469	43.86	0.38	N/A	N/A
RAM97-30/31	11492	50.62	0.44	N/A	N/A
RAM97-28/29	11489	54.42	0.47	N/A	N/A
RAM97-21/22	11737	89.06	0.76	4-5	190-215
RAM97-25	5893	48.95	0.83	N/A	N/A
BWHEU-F-IC008	5948	50.50	0.85	N/A	N/A
RAM 1-2	7947	72.81	0.92	N/A	N/A
RAM 3-4	8996	83.42	0.93	N/A	N/A
RAM97-17/18	11801	114.91	0.97	10-11	171-183
RAM97-22/23	11739	120.60	1.03	N/A	N/A
RAM97-9/10	11746	125.87	1.07	14-17	159-166
RAM97-5/6	11737	129.68	1.10	17-18	154-164
RAM97-7/8	11746	140.71	1.20	11	176-181
RAM97-33/34	11735	141.51	1.21	12-13	166-174
RAM97-13/14	11789	151.64	1.29	18-21	153-155
RAM97-11/12	11761	153.26	1.30	15-18	153-155
RAM97-19/20	11790	177.93	1.51	15-16	161-167
RAM97-23/24	11736	210.83	1.80	22-25	153-157
BWHEU-F-IC009	11694	214.50	1.83	27-29	160-166

1: Calculated from weight gain after complete oxidation.

2: N/A—Material did not ignite in burning curve tests.

Figure 2. Typical burning curve plot for TGA test in which ignition occurred (FMFVLT 15, vault-stored corrosion product).

Figure 2 shows a typical burning curve plot for a test in which ignition occurred. The sharp increases in sample weight and furnace control thermocouple reading at ignition are clearly visible. The sample weight increases in a linear manner during burning, and the furnace temperature oscillates as the temperature controller attempts to maintain the preset furnace ramp rate. The sample weight plateaus after burning is complete; the increase in weight to this initial plateau was used to compute the hydride fraction. Most burning curve tests were terminated when the first plateau was reached. If the test was not terminated at the initial plateau, a second increase in sample weight was observed, at a temperature of approximately 400°C. This higher-temperature weight gain consistently occurred for all materials and is believed to correspond to oxidation of UO_{2+x} originally present in the sample to U_3O_8 . As described below, XRD analyses of samples after testing to high temperatures showed only U_3O_8 oxides, while samples terminated immediately after burning still showed UO_{2+x} .

Figure 3. Typical burning curve plot for a TGA test in which ignition did not occur (FMFVLT 06, vault-stored corrosion product).

Table II does not show data for tests in which ignition did not occur, as these tests did not have an ignition temperature or a hydride fraction that can be measured by TGA. Figure 3 shows a typical burning curve plot for a test which did not show ignition. There is an initial weight loss believed to correspond to water vapor desorption. At approximately 200°C the weight increases, but ignition does not occur. The change in weight is not dramatic (compare to Fig. 2), and there is no deviation of the furnace temperature from the preset rate. The rate of weight increase slows at 300°C and then re-accelerates at approximately 400°C. This weight gain occurs at the same temperature as the second weight gain in tests which did ignite and is also believed to correspond to oxidation of UO_{2+x} to U_3O_8 .

The results presented in Table II indicate a strong dependence of ignition temperature and hydride fraction on corrosion extent for all conditions. The general trend observed is lack of reactivity for low corrosion extents and increasing reactivity with increasing extent. For conditions in which ignition occurred, increasing corrosion extent correlates with increasing hydride fraction and decreasing ignition temperature. Figures 4 and 5 are plots of hydride

fraction and ignition temperature as a function of corrosion extent for all conditions showing the trends. There is considerable scatter, but ignition consistently occurred for corrosion extents above 1.2% and consistently did not occur for corrosion extents below 0.7%. For samples which ignited, the hydride fraction appears to be linearly dependent on corrosion extent. Ignition temperature is less strongly dependent on corrosion extent. Ignition temperature decreases with increasing corrosion extent to 1.2%, but is relatively independent of corrosion extent above 1.2%.

As shown in Figs. 4 and 5, there are few differences in reactive properties between the three different corrosion product conditions. The data from the three conditions fall within the same scatterband for both ignition temperature and hydride fraction. The lack of change in properties due to passivation is clearly demonstrated by comparing corrosion products from the same batch before and after passivation (Table II). The only change is that there is less scatter in the data for the passivated products compared to the unpassivated products. The reduction in scatter is believed to stem from the homogenization of the corrosion products during the grinding step of passivation.

The results of the burning curve tests on the burned corrosion products collected after the pyrophoric event are shown in Fig. 6. None of the samples tested ignited, but significant weight gains at approximately 400°C were observed, followed by weight loss at higher temperature. The weight gain is again attributed to oxidation of UO_{2+x} . XRD identified this lower oxide in the burned material (see below). The source of the high-temperature weight loss is unknown, but the volatilization of some component of the MET-L-X extinguishant that was mixed in with the corrosion product is suspect.

Figure 4. Plot of ignition temperature versus corrosion extent for ZPPR corrosion products. Data points with an ignition temperature of zero did not ignite.

Figure 5. Plot of TGA hydride fraction versus corrosion extent for ZPPR corrosion products. Data points with a hydride fraction of zero did not ignite in TGA tests.

Figure 6. Burning curve plots for TGA tests on burned ZPPR corrosion products. None of the samples ignited.

Figure 7. Plot of isothermal oxidation rates versus reciprocal temperature for ZPPR corrosion products.

C. Isothermal Oxidation Kinetics

Figure 7 is a standard Arrhenius plot of oxidation rates versus reciprocal temperature for isothermal tests on both unpassivated and vault-stored corrosion products; conditions and data for the isothermal tests are presented in Appendix Table A-III. Isothermal tests were performed on corrosion products from two cans with different corrosion extents. The oxidation rates shown are best linear fits to weight gain versus time data for each test, as described in ref. [7]. The shapes of the weight gain versus time curves for tests on the vault-stored products were similar to those for tests on unpassivated products, i.e. the rate of weight gain slowly decreased throughout each test. There was little difference in the oxidation rates measured for the two material conditions. The data for the two cans of vault-stored corrosion products lie within the scatterband for the unpassivated products.

The effects of pre-oxidation on subsequent burning curve reactivity were assessed by performing burning curve tests on the partially oxidized samples from the isothermal tests. The results of these tests are also presented in Table A-III. Significant pre-oxidation resulted in an increase in ignition temperature. For material from can BWHEU-F-IC009, the ignition temperature increased from approximately 160°C to 208°C following oxidation at 150°C. A similar increase was observed for material from can RAM97-9/10. The magnitude of the ignition temperature increase depended on the extent of pre-oxidation. Little increase was observed when the weight gain incurred in the isothermal test was low.

D. X-Ray Diffraction

Table III summarizes the results of the XRD analyses. The phases identified in each sample are listed. For samples which contained oxide and hydride, the result of the quantitative analysis of the XRD pattern is shown, with the corresponding TGA result for comparison. For samples containing phases other than oxide and hydride, the major and minor peaks of the pattern are identified. Hydride peaks were observed for all unpassivated and vault-stored samples, even for those which did not ignite in TGA testing. The quantitative analysis results showed a dependence of UH_3 content on corrosion extent similar to that observed in TGA tests.

The samples which did not ignite in TGA testing showed low hydride fractions in the XRD analysis.

No hydride was observed in the post-test XRD pattern of a TGA sample from can BWHEU-F-IC009. After ignition and burning to the initial plateau at 250°C, the sample showed peaks from both UO_{2+x} and U_3O_8 . TGA oxidation of a sample from can BWHEU-F-IC009 to 620°C resulted in the conversion of lower oxides originally present in the sample to U_3O_8 . The hydride originally present in this sample was also reacted. XRD patterns of corrosion products which had burned in the pyrophoric event also showed no signs of hydride. The major peaks for both samples were UO_{2+x} , with minor peaks from U_3O_8 and NaCl. NaCl is the primary constituent of the MET-L-X extinguishant used to combat the fire.

TABLE III. XRD Results Summary

Material	Corrosion Extent (%)	Phases Identified	Wt.% UH_3 (XRD)	Wt.% UH_3 (TGA)
Unpassivated Product				
Plate 2249	0.64	UO_{2+x} , UH_3	3	No Ignition
Plate 2652	1.98	UO_{2+x} , UH_3	47	29-39
Vault-Stored Product				
SB97-1	0.33	UO_{2+x} , UH_3	4	No Ignition
RAM97-21/22	0.76	UO_{2+x} , UH_3	9	4-5
BWHEU-F-IC008	0.85	UO_{2+x} , UH_3	4	No Ignition
RAM97-1/2	0.92	UO_{2+x} , UH_3	4	No Ignition
RAM97-9/10	1.07	UO_{2+x} , UH_3	18	14-17
RAM97-23/24	1.80	UO_{2+x} , UH_3	26	22-25
BWHEU-F-IC009	1.83	UO_{2+x} , UH_3	42	27-29
Vault-Stored Product After Burning Curve Testing				
BWHEU-F-IC008	0.85	U_3O_8	N/A	N/A
Oxidized to 620°C				
BWHEU-F-IC009	1.83	UO_{2+x} , major	N/A	N/A
Oxidized to 250°C		U_3O_8 , minor		
Burned Product				
Sample 2	N/A	UO_{2+x} , major	N/A	No Ignition
		NaCl, U_3O_8 , minor		
Sample 3	N/A	UO_{2+x} , major	N/A	No Ignition
		NaCl, U_3O_8 , minor		

*: UO_{2+x} denotes oxide which may be UO_2 , U_3O_7 , or a mixture of both.

IV. DISCUSSION

A. Effect of Corrosion Extent on Properties

1. Specific Surface Area

There was no effect of corrosion extent on the specific surface areas measured for unpassivated and vault-stored corrosion products. For the non-outgassed condition, the specific surface areas were generally between 0.7 and 1.0 m²/g, regardless of corrosion extent. Only one outlier from this range is present, at 0.5 m²/g for a corrosion extent of 0.64%. The lack of a corrosion extent effect on specific area was discussed in ref. [7]. The explanation given was that the hydride and oxide constituents of the corrosion products have similar specific surface areas, so that a varying fraction of hydride with corrosion extent does not affect the net specific area measured. A second possible explanation is that the presence of adsorbed water vapor may mask changes in the true specific area.

Outgassing of the vault-stored product samples resulted in a significant increase in specific surface area. Both of the samples contained little hydride and lost weight during initial heating in burning curve tests. The weight loss is believed to correspond to desorption of water vapor from the corrosion product powder surfaces. Adsorption of water onto powders lowers the measured specific surface area because the water molecules mask available adsorption sites from the adsorbate in BET testing [8]. Hence the higher specific surface areas of the outgassed samples are believed to better represent the true surface area of the oxide corrosion products.

It is unclear what implications these observations have on the accuracy of the results for the hydride-bearing corrosion product powders. Low-temperature weight losses were also observed during burning curve testing of some hydride-bearing corrosion products, indicating water vapor adsorption onto the products. However, the similarity of specific areas for hydride-bearing materials which did not show initial weight loss and those which did

suggests that the effect of water vapor adsorption for hydride-bearing corrosion products may be small.

2. Chemical Reactivity

The ignition temperature and hydride fraction of the corrosion products were found to be strongly dependent on corrosion extent. These effects are shown clearly in Table II and Figs. 4 and 5. The dependence is a result of variations in the extent of localized corrosion for different plates. As documented in ref. [1], the hydride component of the corrosion products (a black powder) tends to be associated with areas of severe localized corrosion, while light gray oxide flakes are associated with general corrosion. Plates with more localized corrosion (more hydride) tend to have a greater overall amount of corrosion product and hence greater corrosion extent. Plates which have only a small amount of corrosion product generally do not have any areas of localized corrosion and hence little hydride. As discussed below, the ignition temperature is dependent on the hydride fraction, with higher hydride fractions resulting in lower ignition temperatures.

Variable behavior was observed in the region between 0.7% and 1.2% corrosion extent. Some samples did not ignite, while others ignited and followed the trends shown by samples with higher extents. Such behavior is not unexpected, as plates with similar overall corrosion extent are expected to have differing levels of localized corrosion and therefore hydride fractions. This variability is expected to manifest itself near the threshold for consistent ignition—some corrosion products will have sufficient hydride for ignition and some will not.

The ignition temperature of a sample is dependent on its hydride fraction; the variation of ignition temperature with hydride fraction is shown in Fig. 8. The ignition temperature relatively quickly decreases with increasing hydride fraction until 15% is reached and decreases much more slowly (if at all) for hydride fractions greater than 15%. There is considerable scatter in the data.

Ignition is defined by a balance between heat generation and loss; the strong dependence of oxidation rates on temperature results in rapid self-heating when the rate of heat generation exceeds the rate of heat loss. Samples with higher hydride fractions have a greater heat generating capacity relative to the total mass of the sample, and so are expected to ignite at lower temperatures than samples with low fractions. Samples with very low hydride fractions may not ignite at any temperature, since the small amount of heat generated by oxidation of the hydride can be absorbed by a large quantity of intimately surrounding oxide. A possible explanation for the relative independence of ignition temperature from hydride fraction above 15% hydride is that sufficient hydride may be present so that the ignition temperature is determined by the intrinsic oxidation kinetics of the hydride, with the inert nature of the oxide exerting less influence. Hence less dependence on the fraction of oxide would be observed.

The results of the XRD analyses of the corrosion products support the TGA findings. Reasonable agreement was found between hydride fractions computed using the weight gain in TGA tests and those computed using the XRD standardless quantitative analysis software, but some differences did exist. The values from XRD analysis were typically higher than from TGA analysis, and XRD detected the presence of hydride for all unpassivated and vault-stored corrosion products, even for those samples which did not ignite in TGA tests.

The discrepancy between the hydride fractions measured using TGA and XRD may be related to water vapor adsorbed on the corrosion products. When corrosion product samples are heated, they initially lose weight. This weight loss is attributed to water vapor desorption, since no other volatile components have been identified in the corrosion products. The weight loss is significant for samples with low corrosion extents, as seen in Fig. 3. Most vault-stored samples which ignited also showed initial weight loss, until the weight gain due to oxidation became overriding. The loss is apparent in the initial portion of the weight curve in Fig. 2. The observed weight reading during a burning curve test is a net value incorporating weight gain due to oxidation and weight loss due to water vapor desorption. Hence the actual weight gains observed in ignition underestimate to some degree the true weight gain due to oxidation. This may account for the higher hydride fractions observed in XRD analysis, which are unaffected by water vapor adsorbed on the corrosion products. These results imply that the

XRD method is more appropriate for hydride fraction measurement, but the standardless quantitative analysis technique relies on assumptions (e.g. all oxide is UO_2) that reduce its accuracy. It is therefore useful to use both techniques.

No effect of corrosion extent was observed for isothermal oxidation data below the ignition temperature. The data from corrosion products with four different corrosion extents (two plates and two vault-stored cans) fall into essentially the same scatterband on Fig. 7. Because the data presented in Fig. 7 has been normalized by hydride surface area, the effect of differing hydride fractions is accounted for. There are therefore no intrinsic variations in low-temperature oxidation rates with corrosion extent.

The dependence of corrosion product properties on corrosion extent is in agreement with observations made during the examination of four ZPPR plates in 1985 [6]. The amount of uranium metal lost to corrosion product for the four plates was 1.53 g, 2.45 g, 5.13 g, and 14.85 g. Since a single plate weighs approximately 220 g, the corresponding corrosion extents are 0.7, 1.1, 2.3, and 6.8%. The equivalent corrosion extents on the basis used in the current investigation would be somewhat lower, as the corrosion product weights above account for all corrosion product (the plates were washed in nitric acid), rather than only loose corrosion products. Only oxide was present in the corrosion products from the two plates with lower corrosion extents, while considerable hydride was observed for the plates with the higher corrosion extents. The products from the plate with the most severe corrosion ignited during de-cladding in air. These observations match the current results. The values of the two lower corrosion extents (0.7 and 1.1%) fall within the range for which ignition is not consistently observed, while the two higher extents (2.3 and 6.8%) fall into the range of consistent ignition.

The qualitative experiments performed prior to start-up of HEU recovery operations in June 1996 [5] were clearly flawed in consideration of the dependence of corrosion product properties on corrosion extent. In the first experiment, 80 g of loose corrosion product was collected from four badly corroded plates. The corresponding corrosion extent is 9%, a value higher than any material tested in the present investigation. These corrosion products readily ignited when mechanically agitated at room temperature, consistent with the high extent.

In the second experiment, 80 g of loose corrosion product was obtained from 36 plates, with a corresponding corrosion extent of 1%. These corrosion products were passivated using the low-temperature technique and subsequently did not ignite at room temperature even under severe mechanical agitation. The false conclusion reached—based on the assumption that all corrosion products behaved similarly—was that the lack of ignition was due to passivation. It is now apparent that there was likely insufficient hydride in the corrosion products used in the second experiment to cause ignition under any conditions.

B. Changes in Properties Due to Passivation and Storage

Given the dependence of corrosion product properties on corrosion extent described above, any evaluation of changes in properties for different conditions must consider the effects of corrosion extent. This is accomplished by comparing data from different conditions on plots of properties versus corrosion extent. A significant difference will show as an outlying data point or curve on the property versus extent plot. The similarity of properties for unpassivated, passivated, and vault-stored corrosion products is shown in Figs. 4 and 5. Points from all three conditions lie within the same broad scatterbands on both plots. In addition, the lack of an effect of the low-temperature passivation process on the ignition temperature or hydride fraction was clearly demonstrated by the results obtained from the two batches of corrosion product which were tested before and immediately after passivation.

In retrospect, knowing the low-temperature oxidation rates for the corrosion products, the lack of changes due to passivation and storage are not surprising. The rate of oxidation is very slow near room temperature, so slow that it is difficult to measure using the TGA apparatus. The extrapolated rate at 25°C using data from ref. [7] is 6×10^{-10} mg/cm²/sec. At this rate, a 1% extent of reaction would require 80 hours, assuming a specific surface area of 1 m²/g and 20% hydride. Exposure of the corrosion products to oxygen for two hours in the passivation step will therefore react an insignificant quantity of hydride. Grinding during the passivation step has the potential to accelerate oxidation by crushing hydride particles and exposing fresh surfaces, however, this effect is apparently not significant, since no change is observed.

The longer-term duration of vault storage would be expected to result in a greater extent of reaction and passivation, but the experimental data does not indicate that the vault-stored material has significantly lowered hydride fractions. The lack of reaction is probably due to limited oxygen supply to the corrosion product, since the storage cans are sealed. In addition, the decreasing rate of oxidation with time observed in TGA tests could cause the long-term oxidation rates to be much slower than those measured over short durations in the TGA.

The results of the burning curve tests on vault-stored corrosion products pre-oxidized in isothermal tests demonstrates that partial reaction of hydride does raise the ignition temperature. However, a large fraction of the hydride must be reacted, and the change in ignition temperature is relatively small. In the extreme case (tests FMFVLT 73 and 74), reaction of 66% of the hydride present in the sample increased the ignition temperature by only approximately 45°C, from the baseline value of 163°C (Table 2) to 208°C. Reaction of lower fractions (~20%) increased the ignition temperature less than approximately 20°C. The effect of low-temperature passivation would be similar to that observed for tests FMFVLT 75 and 76, where reaction of 1.5% of the hydride did not increase the ignition temperature.

The increase in ignition temperature resulting from significant pre-oxidation is accounted for by the reduction in hydride fraction. Reaction of hydride in an isothermal oxidation test lowers the sample's hydride fraction for the subsequent burning curve test. As shown in Fig. 8, the ignition temperature decreases with increasing hydride fraction, especially for fractions less than 15%. The data for pre-oxidized material is highlighted with solid markers. The hydride fractions for these samples were computed using only the weight gains which occurred in the burning curve tests. Because a considerable fraction of the hydride initially present had reacted in the isothermal tests, the weight gains observed in the burning curve tests were typically much lower than for non-reacted samples. The data for the pre-oxidized samples generally fall within the scatterband of the other data, although some points lie at the upper bound. This suggests that the increase in ignition temperature is primarily due to the lowered hydride fraction, rather than some other effect.

Figure 8: Plot of ignition temperature as a function of hydride fraction for ZPPR corrosion products.

The lack of an effect of the low-temperature passivation step and results obtained in the isothermal tests indicate that true passivation—a significant reduction in reactivity due to formation of a thin, passive layer of oxide on the surface of a hydride particle—does not occur for ZPPR corrosion products. Formation of such passivating films has been indicated to lower the reactivity of hydride powders formed by reaction with hydrogen gas [9, 10]. True passivation may not occur for the ZPPR corrosion products because the hydride present is likely already coated with an oxide film, due to its formation in an oxidation process (as opposed to reaction with pure H_2 gas) and the intimate presence of oxide and water vapor. It is interesting to note that the ignition temperatures of ZPPR corrosion products are very similar to that reported for “passivated” hydride by Longhurst, 140°C [9]. Hydride associated with other uranium metal corrosion products, i.e. on metallic spent nuclear fuels, would also not be expected to show true passivation. The only means to guarantee safe handling and storage of these corrosion products is full conversion of the hydride at high temperature.

C. Sources and Mechanisms for the Pyrophoric Event

The fundamental issues that this study addresses are the cause of the pyrophoric event and the specific mechanism of ignition. The root cause of the event is clear. The corrosion product consolidated on March 13, 1998 was uranium oxide mixed with a substantial quantity of reactive uranium hydride. The reactivity of the corrosion products was essentially the same as immediately after de-cladding; the material was not at all passivated relative to its initial condition. However, the specific mechanism by which ignition of the corrosion product occurred is not so easily identified. As presented in Section 1, two possible mechanisms were proposed by the original investigative team—the thermal excursion scenario and the can 14 scenario [4].

In the thermal excursion scenario, oxidation slowly increased the temperature of the consolidated product to the ignition point because the tall cylindrical can would prevent effective heat loss from the powder. Simple analysis using oxidation data obtained for the unpassivated and vault-stored corrosion products shows this scenario to be extremely unlikely. As mentioned in section 4.2 above, the rate of oxidation for the corrosion products at 25°C is 6×10^{-10} mg/cm²/sec. After emptying 13 cans, there were 1.77 kg of corrosion product in the consolidation can. The specific surface area of the powder may conservatively be assumed to be 1.0 m²/g and the hydride fraction 20%. The total reacting surface area is therefore 350 m², and the net reaction rate is 2×10^{-3} mg/sec. The heat released in the reaction of UH₃ with O₂ is 1,490 kJ/mol UH₃. Conversion of the reaction rate to mol/sec and multiplication by the heat of reaction yields a heat generation rate of 1×10^{-2} J/sec. Assuming adiabatic heating of the corrosion product and using the specific heat for UO₂ (0.26 J/g/K), the rate of temperature increase is 2×10^{-5} K/sec. At this rate of increase, 13 hours are required for the powder to heat one degree. Since the operation was performed in less than 4 hours, the corrosion product could not have self-heated to the ignition point (at least 130°C). Hence, the thermal excursion scenario is not plausible.

In the investigation report, the can 14 scenario was divided into sub-scenarios relating why the can may have behaved differently and thus became the source of the ignition. These

sub-scenarios were: (1) the material in the 14th can was fundamentally different; (2) the material in the 14th can was improperly passivated; and (3) the material in the 14th can had changed (become more reactive) during storage. Because the results of this study indicate that there was no effect of the passivation step, the material in can 14 could not have been inadequately passivated relative to the other cans. The results also indicate that re-activation during storage did not occur, as the behavior of material after long-term vault storage was essentially the same as in the unpassivated state and after the low-temperature passivation step. Can 14 was different, however, in that it contained the largest quantity of corrosion product of all the material which had been poured into the consolidation can. Therefore its corrosion extent was the highest, and it likely had the largest hydride fraction and the lowest ignition temperature, hence it had the greatest pyrophoric potential. Sub-scenario 1 is therefore the most correct.

Combining the information obtained in this study with operator observations of the event itself (that the fire appeared to initiate in the can 14 material), the most likely scenario is ignition of the corrosion product in the 14th can as it was being poured into the consolidation can. The ignition may have been due to either static discharge or mechanical agitation. Static discharge appears most likely, such discharges are known to occur during rolling and tumbling of insulating powders. Little mechanical agitation occurs during simple pouring of powder, especially relative to the grinding and pounding performed prior to vault storage. The material in the 14th can was particularly susceptible to ignition from discharge since it had a relatively high hydride fraction and low ignition temperature. There is no good explanation for why such an event did not occur sooner, i.e. during checking of the powder prior to vault storage. Given the characteristics of the corrosion product powders, the potential for an event was always present during handling in air.

D. Characteristics of Burned Products

The TGA and XRD analyses of the corrosion products involved in the fire verified that burning during the event fully reacted the hydride originally present. No hydride peaks were observed in the XRD patterns, and no ignition was observed in the TGA tests. However, UO_{2+x} originally in the corrosion products was not converted to U_3O_8 , suggesting that the material was

either oxygen-starved during burning or that the maximum temperature did not exceed 400°C (the temperature needed to initiate rapid oxidation of UO_2). Since the steel consolidation can showed discoloration due to the heat of the fire, it is more likely that insufficient oxygen was available to form U_3O_8 . One implication of this finding is that UO_2 oxidation did not contribute to the severity of the fire, as had been postulated immediately after the event.

E. Lessons Learned

The occurrence of the fire and the results of this study have highlighted the inadequacy of the passivation procedure and the experiments which supported it. A new procedure has been developed and validated for full conversion of hydride present in ZPPR corrosion products to oxide. The products are now oxidized at 600°C for two hours in a atmosphere containing 3% O_2 . The temperature is sufficiently high to not only react hydride but also oxidize the lower uranium oxide to U_3O_8 , resulting in a very stable product. The low oxygen concentration limits self-heating while the hydride is oxidizing [7]. The inert nature of the converted products is routinely verified using TGA analysis. All of the remaining separated ZPPR corrosion products have been stabilized using the new procedure.

V. CONCLUSIONS

Hydride-bearing uranium metal corrosion products from ZPPR fuel plates involved in the March 13, 1998 pyrophoric event at ANL-W were characterized using TGA, XRD, and BET techniques. Characterization was performed on corrosion products in several different conditions: immediately after separation from the source metal, after low-temperature passivation, after passivation and extended vault storage, and after burning in the pyrophoric event. The following conclusions were reached:

1. The ignition temperature and hydride fraction of corrosion products were strongly dependent on corrosion extent. Corrosion products from plates with corrosion extents less than 0.7% did not ignite in TGA tests, while products from plates with corrosion

extents greater than 1.2% consistently ignited. The fraction of hydride in the corrosion product increased with corrosion extent.

2. There was little change in corrosion product properties after passivation or long-term vault storage. The passivation step did not alter either the ignition temperature or the hydride fraction of the corrosion products.
3. The burned products were not reactive and contained no hydride. The principal constituent was UO_{2+x} ; a minor amount of NaCl was also present.
4. Partial oxidation of the corrosion products decreases reactivity by increasing the ignition temperature, but a large reaction extent is required to achieve only a small increase in ignition temperature. Therefore, complete oxidation of the hydride is required to guarantee safe handling and storage.
5. The source of the fire was a considerable quantity of reactive hydride present in the corrosion products. No specific ignition mechanism could be conclusively identified; one possible initiator is static discharge in the corrosion product from the 14th food-pack can as it was being poured into the consolidation can. The available evidence does not support a scenario in which the powder in the consolidation can slowly self-heated to the ignition point.

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APPENDIX

TABLE A-I. TGA test matrix and results for burning curve tests on unpassivated and passivated corrosion products.

Test ID	Can ID	Corrosion Extent (%)	Sample Weight (mg)	Ignition (Y/N)	Ignition Temp. (°C)	Wt. Gain (mg)	Hydride Fraction (wt.%)
FMFINV 07	Batch 1, Unpassivated	1.16	174.0	N	N/A	N/A	N/A
FMFINV 09	Batch 1, Unpassivated	1.16	186.0	N	N/A	N/A	N/A
FMFINV 10	Batch 1, Unpassivated	1.16	187.5	N	N/A	N/A	N/A
FMFINV 08	Batch 1, Passivated	1.16	166.0	N	N/A	N/A	N/A
FMFINV 11	Batch 1, Passivated	1.16	168.0	N	N/A	N/A	N/A
FMFINV 01	Batch 2, Unpassivated	1.41	171.0	Y	166	4.1	14
FMFINV 02	Batch 2, Unpassivated	1.41	162.9	Y	145	3.5	13
FMFINV 03	Batch 2, Unpassivated	1.41	174.2	Y	160	4.2	15
FMFINV 04	Batch 2, Passivated	1.41	163.2	Y	159	4.9	18
FMFINV 05	Batch 2, Passivated	1.41	160.1	Y	161	4.8	18
FMFINV 06	Batch 2, Passivated	1.41	151.5	Y	160	4.6	18

TABLE A-II. TGA test matrix and results for burning curve tests on vault-stored corrosion products.

Test ID	Can ID	Corrosion Extent (%)	Sample Weight (mg)	Ignition (Y/N)	Ignition Temperature (°C)	Wt. Gain (mg)	Hydride Fraction (wt.%)
FMFVLT 20	SB 97-1	0.33	170.5	N	N/A	N/A	N/A
FMFVLT 21	SB 97-1	0.33	136.4	N	N/A	N/A	N/A
FMFVLT 24	RAM 97 - 32/33	0.38	124.4	N	N/A	N/A	N/A
FMFVLT 25	RAM 97 - 32/33	0.38	163.8	N	N/A	N/A	N/A
FMFVLT 18	RAM 30-31/97	0.44	179.4	N	N/A	N/A	N/A
FMFVLT 19	RAM 30-31/97	0.44	117.2	N	N/A	N/A	N/A
FMFVLT 22	RAM 97 - 28/29	0.47	195.5	N	N/A	N/A	N/A
FMFVLT 23	RAM 97 - 28/29	0.47	125.0	N	N/A	N/A	N/A
FMFVLT 36	RAM 97 - 21/22	0.76	161.2	Y	215	1.2	4
FMFVLT 37	RAM 97 - 21/22	0.76	129.7	Y	190	1.1	5
FMFVLT 16	RAM 97-25	0.83	189.8	N	N/A	N/A	N/A
FMFVLT 17	RAM 97-25	0.83	197.9	N	N/A	N/A	N/A
FMFVLT 04	BWHEU-F-IC008	0.85	189.0	N	N/A	N/A	N/A
FMFVLT 05	BWHEU-F-IC008	0.85	119.1	N	N/A	N/A	N/A
FMFVLT 06	BWHEU-F-IC008	0.85	167.1	N	N/A	N/A	N/A
FMFVLT 07	RAM 1&2	0.92	143.9	N	N/A	N/A	N/A
FMFVLT 08	RAM 1&2	0.92	118.4	N	N/A	N/A	N/A
FMFVLT 09	RAM 3&4	0.93	161.1	N	N/A	N/A	N/A
FMFVLT 10	RAM 3&4	0.93	131.8	N	N/A	N/A	N/A
FMFVLT 34	RAM 97 - 17/18	0.97	132.5	Y	171	2.4	11
FMFVLT 35	RAM 97 - 17/18	0.97	142.8	Y	183	2.4	10
FMFVLT 40	RAM97 - 22/23	1.03	184.6	N	N/A	N/A	N/A
FMFVLT 41	RAM97 - 22/23	1.03	186.8	N	N/A	N/A	N/A
FMFVLT 32	RAM 97 - 9/10	1.07	168.1	Y	166	4.0	14
FMFVLT 33	RAM 97 - 9/10	1.07	129.2	Y	159	3.6	17
FMFVLT 47	RAM 97 - 5/6	1.10	153.9	Y	164	4.4	17
FMFVLT 48	RAM 97 - 5/6	1.10	183.2	Y	154	5.4	18
FMFVLT 30	RAM 97 - 7/8	1.20	166.2	Y	176	3.1	11
FMFVLT 31	RAM 97 - 7/8	1.20	147.2	Y	181	2.8	11
FMFVLT 44	RAM 97 - 33/34	1.21	183.2	Y	152	3.9	13
FMFVLT 45	RAM 97 - 33/34	1.21	119.0	Y	174	2.4	12
FMFVLT 46	RAM 97 - 33/34	1.21	180.9	Y	166	3.9	13
FMFVLT 42	RAM 97 - 13/14	1.29	173.8	Y	153	5.4	18
FMFVLT 43	RAM 97 - 13/14	1.29	130.8	Y	155	4.6	21
FMFVLT 28	RAM 97 - 11/12	1.30	208.9	Y	153	6.2	18
FMFVLT 29	RAM 97 - 11/12	1.30	130.6	Y	155	3.4	15

TABLE A-II: TGA test matrix and results for burning curve tests on vault-stored corrosion products (continued).

Test ID	Can ID	Corrosion Extent (%)	Sample Weight (mg)	Ignition (Y/N)	Ignition Temperature (°C)	Wt. Gain (mg)	Hydride Fraction (wt.%)
FMFVLT 26	RAM 97 - 19/20	1.51	223.9	Y	161	5.9	16
FMFVLT 27	RAM 97 - 19/20	1.51	131.0	Y	167	3.4	15
FMFVLT 13	RAM 97 - 23/24	1.80	129.3	Y	156	5.4	25
FMFVLT 14	RAM 97 - 23/24	1.80	148.3	Y	153	5.8	23
FMFVLT 15	RAM 97 - 23/24	1.80	130.6	Y	157	4.9	22
FMFVLT 50	RAM 97 - 23/24	1.80	240.6	Y	152	9.2	23
FMFVLT 01	BWHEU-F-IC009	1.83	190.5	Y	160	8.8	27
FMFVLT 02	BWHEU-F-IC009	1.83	174.4	Y	161	8.6	29
FMFVLT 03	BWHEU-F-IC009	1.83	160.1	Y	166	7.7	29

TABLE A-III. TGA test matrix and results for isothermal oxidation of vault-stored corrosion products.

Test ID	Can ID	Sample Weight (mg)	Hydride Surface (cm ²)	Test Type	Test Temp. (°C)	Test Time (min)	Ignition (Y/N)	Kinetics	Ignition Temp. (°C)	Oxid. Rate Best Lin. Fit (mg/cm ² /sec)	Wt. Gain (mg)	Hydride Fraction (%)
FMFVLT62	BWHEU-F-IC009	160.4	412	Isothermal	125	240	No	Decreasing Rate	N/A	2.5E-07	1.73	27
FMFVLT63	BWHEU-F-IC009	160.4	412	Burning Curve	15 °C/min	N/A	Yes	N/A	181	N/A	7.4	27
FMFVLT64	BWHEU-F-IC009	166.1	476	Isothermal	125	240	No	Linear	N/A	2.6E-07	2.05	30
FMFVLT65	BWHEU-F-IC009	166.1	476	Burning Curve	15 °C/min	N/A	Yes	N/A	159	N/A	8.5	30
FMFVLT66	BWHEU-F-IC009	140.5	322	Isothermal	125	480	No	Decreasing Rate	N/A	1.9E-07	2.18	24
FMFVLT67	BWHEU-F-IC009	140.5	322	Burning Curve	15 °C/min	N/A	Yes	N/A	188	N/A	5.8	24
FMFVLT71	BWHEU-F-IC009	125.5	330	Isothermal	100	600	No	Decreasing Rate	N/A	4.0E-08	0.83	28
FMFVLT72	BWHEU-F-IC009	125.5	330	Burning Curve	15 °C/min	N/A	Yes	N/A	180	N/A	5.9	28
FMFVLT73	BWHEU-F-IC009	143.1	321	Isothermal	150	240	No	Decreasing Rate	N/A	6.3E-07	3.75	24
FMFVLT74	BWHEU-F-IC009	143.1	321	Burning Curve	15 °C/min	N/A	Yes	N/A	208	N/A	5.7	24
FMFVLT75	BWHEU-F-IC009	127.2	341	Isothermal	50	600	No	Erratic	N/A	N/A	0.09	29
FMFVLT76	BWHEU-F-IC009	127.2	341	Burning Curve	15 °C/min	N/A	Yes	N/A	151	N/A*	6.1	29
FMFVLT77	BWHEU-F-IC009	136.0	341	Isothermal	75	600	No	Decreasing Rate	N/A	8.8E-09	0.19	27
FMFVLT78	BWHEU-F-IC009	136.0	341	Burning Curve	15 °C/min	N/A	Yes	N/A	173	N/A	6.1	27
FMFVLT79	RAM97-9/10	190.4	192	Isothermal	100	600	No	Linear	N/A	7.4E-08	0.35	14
FMFVLT80	RAM97-9/10	190.4	192	Burning Curve	15 °C/min	N/A	Yes	N/A	183	N/A	4.4	14
FMFVLT81	RAM97-9/10	172.4	145	Isothermal	125	600	No	Linear	N/A	3.6E-07	0.64	11
FMFVLT82	RAM97-9/10	172.4	145	Burning Curve	15 °C/min	N/A	Yes	N/A	187	N/A	3.3	11
FMFVLT83	RAM97-9/10	175.6	163	Isothermal	50	600	No	Erratic	N/A	N/A*	-0.05	13
FMFVLT84	RAM97-9/10	175.6	163	Burning Curve	15 °C/min	N/A	Yes	N/A	169	N/A	3.7	13
FMFVLT85	RAM97-9/10	155.7	143	Isothermal	150	300	No	Decreasing Rate	N/A	1.1E-06	1.98	12
FMFVLT86	RAM97-9/10	155.7	143	Burning Curve	15 °C/min	N/A	Yes	N/A	214	N/A	3.2	12

*: Erratic rate too low for meaningful measurement.

Note: Hydride fraction shown is the total initial hydride fraction in the sample, computed from the sum of weight gains in the isothermal and burning curve tests.

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