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MEASURING BREAKAWAY OXIDATION BEHAVIOR

A. INTRODUCTION

Note: Public availability of this draft document is intended to inform stakeholders of the current status of the NRC staff's preliminary draft final rule package and associated documents for § 50.46c of Title 10 of the Code of Federal Regulations (10 CFR). These preliminary draft documents are in support of a February 4, 2016, Advisory Committee on Reactor Safeguards (ACRS) subcommittee meeting. This draft document has not been subject to all levels of NRC management review. Accordingly, the document may be subject to further revision before the staff provides the final draft rule language package to the Commission (currently scheduled to be provided to the Commission in February 2016).

Purpose

This regulatory guide (RG) describes a method that the U.S. Nuclear Regulatory Commission (NRC) considers acceptable to implement the requirements in Title 10 of the *Code of Federal Regulations* (10 CFR) 50.46c, "Emergency Core Cooling System Performance during Loss of Coolant Accidents (LOCA)" (Ref. 1), for an embrittlement mechanism, referred to as "breakaway oxidation," that may occur during prolonged exposure to elevated cladding temperature during a LOCA.

Applicable Rules and Regulations

- Regulations contained in 10 CFR 50.46c require the measurement and periodic confirmation of breakaway oxidation behavior for a zirconium-alloy cladding material based on an acceptable experimental technique.

Related Guidance

Written suggestions regarding this guide or development of new guides may be submitted through the NRC's public Web site under the Regulatory Guides document collection of the NRC Library at <http://www.nrc.gov/reading-rm/doc-collections/reg-guides/contactus.html>.

Electronic copies of this regulatory guide, previous versions of this guide, and other recently issued guides are available through the NRC's public Web site under the Regulatory Guides document collection of the NRC Library at <http://www.nrc.gov/reading-rm/doc-collections/>. The regulatory guide is also available through the NRC's Agencywide Documents Access and Management System (ADAMS) at <http://www.nrc.gov/reading-rm/adams.html>, under ADAMS Accession No. ML15238B044. The regulatory analysis may be found in ADAMS under Accession No. ML15323A122 and the staff responses to the public comments on DG-1261 may be found under ADAMS Accession No. ML15238B193.

- Regulatory Guide 1.223, “Determining Post-Quench Ductility” (Ref. 2), describes a method that the NRC staff considers acceptable for measuring the ductile-to-brittle transition for a zirconium-alloy cladding material.
- Regulatory Guide 1.224, “Establishing Analytical Limits for Zirconium-Alloy Cladding Material” (Ref. 3), describes acceptable methods to establish analytical limits on peak cladding temperature, integral time-at-temperature and limits related to breakaway oxidation behavior for zirconium-alloy cladding material.

Pre-Decisional

Purpose of Regulatory Guides

The NRC issues RGs to describe to the public methods that the staff considers acceptable for use in implementing specific parts of the agency's regulations, to explain techniques that the staff uses in evaluating specific problems or postulated accidents, and to provide guidance to applicants. Regulatory guides are not substitutes for regulations and compliance with them is not required. Methods and solutions that differ from those set forth in RGs will be deemed acceptable if they provide a basis for the findings required for the issuance or continuance of a permit or license by the Commission.

Paperwork Reduction Act

This regulatory guide contains and references information collections covered by 10 CFR Part 50 that are subject to the Paperwork Reduction Act of 1995 (44 U.S.C. 3501 et seq.). These information collections were approved by the Office of Management and Budget (OMB), control number 3150-0011.

Public Protection Notification

The NRC may not conduct or sponsor, and a person is not required to respond to, a request for information or an information collection requirement unless the requesting document displays a currently valid OMB control number.

B. DISCUSSION

Reason for Issuance

This regulatory guide was developed to support the performance-based rule in 10 CFR 50.46c. The rule requires that breakaway oxidation behavior is measured using an NRC-approved experimental technique. This guide provides an experimental technique that is acceptable for measuring the breakaway oxidation behavior for zirconium-alloy cladding materials.

Background

In 1996, the NRC initiated a fuel-cladding research program intended to investigate the behavior of high-exposure fuel cladding under accident conditions. This research program included an extensive LOCA research and testing program at Argonne National Laboratory (ANL) (See NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents" (Ref. 7)), as well as jointly funded programs at the Kurchatov Institute (See NUREG/IA-0211, "Experimental Study of Embrittlement of Zr 1%Nb VVER Cladding under LOCA-Relevant Conditions" (Ref. 4)), and the Halden Reactor Project (See IFE/KR/E 2008/004, "LOCA Testing of High Burnup PWR Fuel in the HBWR. Additional PIE on the Cladding of the Segment 650.5" (Ref. 5)), to develop the body of technical information needed to evaluate LOCA regulations for high-exposure fuel. The agency has summarized the research findings in Research Information Letter 0801, "Technical Basis for Revision of Embrittlement Criteria in 10 CFR 50.46" (Ref. 6).

The research program identified new cladding embrittlement mechanisms and expanded the NRC's knowledge of previously identified mechanisms. One of the embrittlement mechanisms investigated in NRC's LOCA research program is called "breakaway oxidation," which is described below.

Zirconium dioxide can exist in several crystallographic forms. The oxide phase that forms under normal operation is the monoclinic phase. Hydrogen can easily diffuse through this layer, allowing for hydrogen pickup into the zirconium metal throughout operation. The oxidation phase that forms under high temperature steam conditions expected during a LOCA is the tetragonal phase. This phase is dense, adherent and limits hydrogen pickup. However, conditions might occur during a small-break LOCA (such as extended time-at-temperature around 1,000 degrees Celsius (°C) (1,832 degrees Fahrenheit (°F)) that promote a transformation back to the monoclinic phase. The tetragonal-to-monoclinic transformation is an instability that initiates at local regions of the metal-oxide interface and grows rapidly throughout the oxide layer during the specific LOCA conditions described above. Because this transformation results in a rapid increase in oxidation rate, it is referred to as breakaway oxidation. Along with this increase in oxidation rate, there is significant hydrogen pickup. Hydrogen that enters in this manner during a postulated LOCA promotes rapid embrittlement of the cladding.

Figure 1 illustrates the damaging effects of breakaway oxidation. This sample of the Russian alloy E110 (an old version no longer representative of commercial cladding) was exposed to high-temperature steam oxidation for a hold time of 1,350 seconds at 1,000 °C (1,832 °F). Breakaway oxidation, delamination, and spallation are evident. Hydrogen pickup was approximately 4,200 weight parts per million (wppm), which is a level that results in embrittlement.

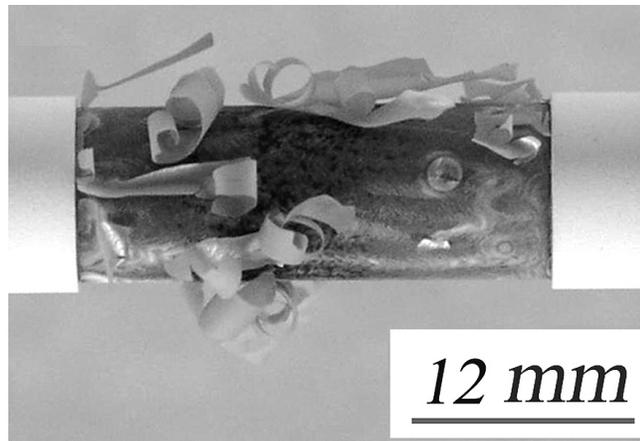


Figure 1. E110 cladding test specimen

Although all zirconium alloys will eventually experience breakaway oxide phase transformation when exposed to long durations of high-temperature steam oxidation, alloying composition and manufacturing process parameters (e.g., surface roughness) influence the timing of this phenomenon. Several domestic cladding alloys tested as part of the NRC's LOCA research program proved to be significantly less susceptible to early breakaway oxidation (NUREG/CR-6967).

Harmonization with International Standards

The International Atomic Energy Agency (IAEA) has established a series of safety guides and standards constituting a high level of safety for protecting people and the environment. IAEA safety guides present international good practices and increasingly reflect best practices to help users striving to achieve high levels of safety. Pertinent to this regulatory guide, IAEA Safety Guide NS-G-1.9, "Design of the Reactor Coolant System and Associated Systems in Nuclear Power Plants" (Ref. 8), issued September 2004 provides recommendations and guidance to regulatory bodies, nuclear power plant designers and licensees on the design of the reactor coolant systems and associated systems, including the emergency core cooling systems in order to maintain the integrity of the fuel cladding. This regulatory guide describes testing related to the development of analytical limits for emergency core cooling system performance evaluation and is consistent with the basic safety principles provided in IAEA Safety Guide NS-G-1.9.

Documents Discussed in Staff Regulatory Guidance

This regulatory guide endorses, in part, the use of one or more codes or standards developed by external organizations, and other third party guidance documents. These codes, standards and third party guidance documents may contain references to other codes, standards or third party guidance documents ("secondary references"). If a secondary reference has itself been incorporated by reference into NRC regulations as a requirement, then licensees and applicants must comply with that standard as set forth in the regulation. If the secondary reference has been endorsed in a regulatory guide as an acceptable approach for meeting an NRC requirement, then the standard constitutes a method acceptable to the NRC staff for meeting that regulatory requirement as described in the specific regulatory guide. If the secondary reference has neither been incorporated by reference into NRC regulations nor endorsed in a regulatory guide, then the secondary reference is neither a legally-binding requirement nor a "generic" NRC approved acceptable approach for meeting an NRC requirement. However, licensees and applicants may consider and use the information in the secondary reference, if appropriately justified, consistent with current regulatory practice, and consistent with applicable NRC requirements.

C. STAFF REGULATORY GUIDANCE

The purpose of the requirements in 10 CFR 50.46c is to ensure core coolability during and following a LOCA. If breakaway oxidation occurs, the embrittlement process is accelerated. Therefore, the analytical limits on time-at-temperature for post-quench ductility established in accordance with 10 CFR 50.46c paragraph (g)(1)(ii) may not preclude embrittlement and ensure core coolability. To address this, 10 CFR 50.46c paragraph (g)(1)(iii) requires measurement of breakaway oxidation behavior for a zirconium cladding alloy based on an approved experimental technique which is capable of determining the effect of composition changes or manufacturing changes on breakaway oxidation behavior.

This RG describes an acceptable experimental technique to measure and periodically confirm the breakaway oxidation behavior of a zirconium-alloy cladding material. This experimental technique is capable of determining the effect of composition changes or manufacturing changes on the breakaway oxidation behavior of a zirconium-alloy cladding material. This regulatory guide also provides guidance for establishing a frequency for confirmatory testing that is sufficient to provide reasonable assurance that the fuel manufacturing process will result in performance consistent with the analytical limits specified in accordance with paragraph (g)(1)(iii) of 10 CFR 50.46c.

C.1 Documentation of Requirements and Results

The method of documentation of a new fuel design is in a license amendment request or vendor topical report that is submitted to the NRC for review and approval. This amendment or report should include all technical information, justifications, the periodic confirmatory test program plan (PCTPP), etc., as described below.

C.2 Initial Measurement of Breakaway Oxidation Behavior of a Zirconium-Alloy Cladding Material

The experimental procedure provided in Appendix A to this regulatory guide defines an acceptable experimental technique to measure the breakaway oxidation behavior of a zirconium-alloy cladding material. This experimental technique is capable of determining the effect of composition changes or manufacturing changes on the breakaway oxidation behavior of a zirconium-alloy cladding material. Appendices B through E are provided to expand on critical aspects of the testing procedure in Appendix A. For previously approved zirconium-alloy cladding, the experimental results of breakaway oxidation testing should be submitted in order to establish the analytical limit for the initial 50.46c compliance demonstration. The NRC's LOCA research program characterized breakaway oxidation behavior for Zircaloy-2, Zircaloy-4, ZIRLO[®] and M5[®]. The NRC's LOCA research program was conducted in accordance with the experimental technique documented in Appendix A and therefore the data generated and documented in NUREG/CR-6867 could be used to characterize the breakaway oxidation behavior and establish the analytical limit for the initial 50.46c compliance demonstration for these alloys. For future zirconium-alloy cladding, the experimental results of breakaway oxidation testing should be submitted as part of the documentation supporting the staff's review and approval of the new fuel assembly design and/or new cladding material in order to document the analytical limit for future applications. The applicant should provide the results of experiments conducted as a function of temperature.

C.3 Periodic Confirmatory Test Programs

The regulations in 10 CFR 50.46c(g)(1)(iii) require that breakaway oxidation behavior is periodically confirmed.

To meet this requirement for zirconium-alloy cladding, a PCTPP should be defined and provided as part of the documentation supporting the staff's review and approval of the new fuel design. The PCTPP should address the potential for slight composition changes or manufacturing changes that could inadvertently alter the cladding's susceptibility to breakaway oxidation. The experimental procedure provided in Appendix A to this regulatory guide defines an acceptable experimental technique to periodically confirm the breakaway oxidation behavior of a zirconium-alloy cladding material. The PCTPP should include the definition of a periodic confirmatory test sample population or test frequency. The PCTPP should describe procedures and measures that will be followed when periodic test results show breakaway oxidation behavior is not consistent with the analytical limits specified in accordance with 10 CFR 50.46c (g)(1)(iii).

C.3.A Periodic Confirmatory Test Program Sample Population and Test Frequency

The regulation in 10 CFR 50.46c(g)(1)(iii) states that the frequency of confirmatory testing must be sufficient to provide reasonable assurance that fuel is being manufactured consistent with the specified analytical limits.

One approach to provide reasonable assurance that fuel is being manufactured consistent with the analytical limits would be to conduct periodic breakaway oxidation measurements on cladding samples from each zirconium-alloy ingot. Other sample populations may also be acceptable. If other sample populations or test frequencies are used, they must be identified and justified in the PCTPP submitted for the staff's review and approval.

The PCTPP should include a justification to reduce the frequency of periodic testing in accordance with a history of results showing no change in breakaway oxidation behavior. The bases and parameters for relaxing the frequency should be specified in the PCTPP.

Periodic testing can be conducted at a single temperature; the temperature associated with the established analytical time limit¹. Periodic testing can be performed for the period of time defined by the analytical limit; it is not necessary to continue testing for longer time periods and until breakaway oxidation is observed. An observation of a lustrous-black oxide or a measurement of less than 200 weight parts per million (wppm) hydrogen pickup (see Appendix B for further discussion on hydrogen pickup) after the test would be sufficient to demonstrate that breakaway oxidation had not occurred during the test. Only one test in each defined test sample population or test frequency is needed to demonstrate continued acceptable performance.

Periodic testing should be conducted on cladding material representative of the zirconium alloy cladding material at the end of cladding manufacturing, accounting for factors that may influence behavior between manufacturing and loading in the reactor (for example, surface scratches). As-manufactured cladding may be used if the initial measurement of breakaway oxidation behavior showed that surface scratches have insignificant effects (i.e., the results are within the allowable data scatter) on breakaway oxidation time.

C.3.B Periodic Confirmatory Test Program Records

There is no requirement to report results of periodic testing to the NRC; however results should be available for audit to verify that the referenced measurement for the onset of breakaway oxidation is valid for fuel loaded in the reactor.

¹ Guidance for establishing analytical limits for breakaway oxidation is provided in RG 1.224.

D. IMPLEMENTATION

The purpose of this section is to provide information on how applicants and licensees² may use this guide and information regarding the NRC's plans for using this regulatory guide. In addition, it describes how the NRC staff complies with 10 CFR 50.109, "Backfitting" and any applicable finality provisions in 10 CFR Part 52, "Licenses, Certifications, and Approvals for Nuclear Power Plants."

Use by Applicants and Licensees

Applicants and licensees may voluntarily³ use the guidance in this document to demonstrate compliance with the underlying NRC regulations. Methods or solutions that differ from those described in this regulatory guide may be deemed acceptable if they provide sufficient basis and information for the NRC staff to verify that the proposed alternative demonstrates compliance with the appropriate NRC regulations. Current licensees may continue to use guidance the NRC found acceptable for complying with the identified regulations as long as their current licensing basis remains unchanged.

Licensees may use the information in this regulatory guide for actions which do not require NRC review and approval such as changes to a facility design under 10 CFR 50.59, "Changes, Tests, and Experiments." Licensees may use the information in this regulatory guide or applicable parts to resolve regulatory or inspection issues.

Use by NRC Staff

The NRC staff does not intend or approve any imposition or backfitting of the guidance in this regulatory guide. The NRC staff does not expect any existing licensee to use or commit to using the guidance in this regulatory guide, unless the licensee makes a change to its licensing basis. The NRC staff does not expect or plan to request licensees to voluntarily adopt this regulatory guide to resolve a generic regulatory issue. The NRC staff does not expect or plan to initiate NRC regulatory action which would require the use of this regulatory guide. Examples of such unplanned NRC regulatory actions include issuance of an order requiring the use of the regulatory guide, requests for information under 10 CFR 50.54(f) as to whether a licensee intends to commit to use of this regulatory guide, generic communication, or promulgation of a rule requiring the use of this regulatory guide without further backfit consideration.

During regulatory discussions on plant specific operational issues, the staff may discuss with licensees various actions consistent with staff positions in this regulatory guide, as one acceptable means of meeting the underlying NRC regulatory requirement. Such discussions would not ordinarily be considered backfitting even if prior versions of this regulatory guide are part of the licensing basis of the facility. However, unless this regulatory guide is part of the licensing basis for a facility, the staff may not represent to the licensee that the licensee's failure to comply with the positions in this regulatory guide constitutes a violation.

If an existing licensee voluntarily seeks a license amendment or change and (1) the NRC staff's consideration of the request involves a regulatory issue directly relevant to this new or revised regulatory guide and (2) the specific subject matter of this regulatory guide is an essential consideration in the staff's

² In this section, "licensees" refers to licensees of nuclear power plants under 10 CFR Parts 50 and 52; and the term "applicants," refers to applicants for licenses and permits for (or relating to) nuclear power plants under 10 CFR Parts 50 and 52, and applicants for standard design approvals and standard design certifications under 10 CFR Part 52.

³ In this section, "voluntary" and "voluntarily" mean that the licensee is seeking the action of its own accord, without the force of a legally binding requirement or an NRC representation of further licensing or enforcement action.

determination of the acceptability of the licensee's request, then the staff may request that the licensee either follow the guidance in this regulatory guide or provide an equivalent alternative process that demonstrates compliance with the underlying NRC regulatory requirements. This is not considered backfitting as defined in 10 CFR 50.109(a)(1) or a violation of any of the issue finality provisions in 10 CFR Part 52.

Additionally, an existing applicant may be required to comply with new rules, orders, or guidance if 10 CFR 50.109(a)(3) applies.

If a licensee believes that the NRC is either using this regulatory guide or requesting or requiring the licensee to implement the methods or processes in this regulatory guide in a manner inconsistent with the discussion in this Implementation section, then the licensee may file a backfit appeal with the NRC in accordance with Management Directive 8.4, "Management of Facility-Specific Backfitting and Information Collection" (Ref. 9) and the guidance in NUREG-1409, "Backfitting Guidelines," (Ref. 10).

Pre-Decisional

GLOSSARY⁴

alpha layer	The zirconium phase that is characterized by a hexagonally close-packed crystal structure.
beta layer	The zirconium phase that is characterized by a cubic crystal structure.
breakaway oxidation	The fuel-cladding oxidation phenomenon in which the oxygen weight gain rate deviates from normal oxidation kinetics. This change occurs with a rapid increase of hydrogen pickup during prolonged exposure to a high-temperature steam environment, which promotes loss of cladding ductility.
loss-of-coolant accident	A postulated accident that would result in the loss of reactor coolant, at a rate in excess of the capability of the reactor coolant makeup system, from breaks in pipes in the reactor coolant pressure boundary up to and including a break equivalent in size to the double-ended rupture of the largest pipe in the reactor coolant system.
monoclinic oxide	A crystallographic form of zirconium dioxide, which is neither fully dense nor protective with respect to hydrogen pickup. This oxide phase develops during normal operation; however it has also been shown to develop under certain conditions that might occur during a small-break LOCA (such as extended time-at-temperature around 1,000 degrees C (1,832 degrees F)).
tetragonal oxide	A crystallographic form of zirconium dioxide that typically develops under LOCA conditions. This oxide phase is dense and adherent and is observed to be protective with respect to hydrogen pickup.

⁴

Definitions in this RG are specific to the RG and may not reflect all acceptable uses of the related terminology.

REFERENCES⁵

1. U.S. Nuclear Regulatory Commission (NRC), "Proposed Rule, "Performance-Based Emergency Core Cooling Systems Cladding Acceptance Criteria," Washington, DC, March 2014 (Agencywide Documents Access and Management System (ADAMS) Accession No. ML12283A174).
2. NRC, Regulatory Guide 1.223, "Determining Post Quench Ductility," Washington, DC, DATE.
3. NRC, Regulatory Guide 1.224, "Establishing Analytical Limits for Zirconium-Allóy Cladding Material," Washington, DC, DATE.
4. NRC, NUREG/IA-0211, "Experimental Study of Embrittlement of Zr-1%Nb VVER Cladding under LOCA-Relevant Conditions," Washington, DC, March 2005.
5. Institute for Energy Technology, IFE/KR/E-2008/004, "LOCA Testing of High Burnup PWR Fuel in the HBWR. Additional PIE on the Cladding of the Segment 650-5," Institute for Energy Technology, Kjeller, Norway, April 2008 (ADAMS Accession No. ML081750715).
6. NRC, Research Information Letter 0801, "Technical Basis for Revision of Embrittlement Criteria in 10 CFR 50.46," Washington, DC, May 30, 2008 (ADAMS Accession No. ML081350225).
7. NRC, NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," Washington, DC, July 2008.
8. IAEA Safety Guide NS-G-1.9, "Design of the Reactor Coolant System and Associated Systems in Nuclear Power Plants," issued September 2004.^{6,7}
9. NRC Management Directive 8.4, "Management of Facility-Specific Backfitting and Information Collection."
10. NRC, NUREG-1409, "Backfitting Guidelines," Washington, DC, July 1990.

⁵ All NRC documents that are publicly available may be accessed through the Electronic Reading Room on NRC's public Web site at <http://www.nrc.gov/reading-rm/doc-collections/> and through the NRC's Agencywide Documents Access and Management System (ADAMS) at <http://www.nrc.gov/reading-rm/adams.html>. The documents can also be viewed online or printed for a fee in the NRC's Public Document Room (PDR) at 11555 Rockville Pike, Rockville, MD. For problems with ADAMS, contact the PDR staff at 301-415-4737 or 800-397-4209; fax 301-415-3548; or e-mail to pdresource@nrc.gov.

⁶ Copies of International Atomic Energy Agency (IAEA) documents may be obtained through its Web site: <http://www.iaea.org/> or by writing the International Atomic Energy Agency P.O. Box 100 Wagramer Strasse 5, A-1400 Vienna, Austria. Telephone +431-2600-0, fax +431-2600-7, or e-mail at Official.Mail@IAEA.org

⁷ A copy of this document is available for review by the public at the NRC's Technical Library, by appointment, which is located at Two White Flint North, 11545 Rockville Pike, Rockville, Maryland 20852; telephone: 301-415-7000; e-mail: Library.Resource@nrc.gov.

APPENDIX A

PROCEDURE FOR CONDUCTING BREAKAWAY OXIDATION TESTS WITH ZIRCONIUM-ALLOY CLADDING MATERIAL

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A-1. Purpose and Scope of the Tests

Performance-based tests are needed to ensure that fuel-rod cladding retains ductility following long-time oxidation in steam at temperatures in the range of 800-1,050 degrees Celsius (degrees C) (1,472 to 1,922 degrees Fahrenheit (F)). Such long-time exposure to steam is especially relevant to postulated small-break loss-of-coolant accidents (LOCAs). All zirconium (Zr)-based cladding alloys will experience breakaway oxidation within this temperature range if steam exposure times are long enough. Concurrent with breakaway oxidation is an increase in hydrogen pickup, which can cause cladding embrittlement. This procedure describes isothermal tests, to be conducted with as-manufactured cladding samples, to determine the minimum breakaway oxidation time. The minimum breakaway oxidation time is defined as the minimum time required to pick up 200-weight parts per million (wppm) hydrogen through the cladding outer-surface oxide. The minimum time will vary with temperature.

A-2. Background

The oxide phase that forms under normal operation is the monoclinic phase. Hydrogen can easily diffuse through this layer, allowing for hydrogen pickup into the zirconium metal throughout operation. During a LOCA, the cladding outer surface will be exposed to steam at elevated temperatures. The oxidation phase that forms under high temperature steam conditions expected during a LOCA is the tetragonal phase, which is typically lustrous-black, dense, and protective with respect to hydrogen pickup. Additional discussion of this phenomenon is available in the following references:

- ORNL/NUREG-17, “Zirconium Metal-Water Oxidation Kinetics IV. Reaction Rate Studies” (Ref. A-1)
- Leistikow, S., and G. Schanz, “Oxidation Kinetics and Related Phenomena of Zircaloy-4 Fuel Cladding Exposed to High Temperature Steam and Hydrogen-Steam Mixtures under PWR Accident Conditions” (Ref. A-2)
- NUREG/CR-6967, “Cladding Embrittlement during Postulated Loss-of-Coolant Accidents,” (Ref. A-3)

For stoichiometric zirconium oxide (ZrO_2) formed under stress-free conditions, the tetragonal-to-monoclinic phase transformation temperature is high (about 1,150 degrees C (about 2,102 degrees F)). However, the tetragonal phase is stabilized at lower steam-oxidation temperatures by a combination of hypo-stoichiometry ($ZrO_{(2-x)}$), compressive stress, and perhaps grain size. Stress reversals (from compressive to tensile) and chemical impurities (e.g., fluorine) in the oxide layer and at the oxide-metal interface can induce early transformation from the tetragonal to the monoclinic phase. As this transformation results in an increase in the growth rate of the oxide-layer thickness and weight gain, it has been referred to in the literature as breakaway oxidation. Stress reversals generally develop at the oxide-metal interface after long-time (3,000–6,000 seconds (s)) exposure to steam at less than or equal to 1,050 degrees C (1,922 degrees F). The precursor to breakaway oxidation is the transition from a smooth oxide-metal interface to a scalloped interface. The amplitude of the scallops grows with increasing time until breakaway oxidation occurs. Based on surface appearance, metallographic imaging, and local hydrogen content, the instability initiates locally in the cladding outer-surface oxide and grows rather quickly in the circumferential and axial directions. For Zircaloy-4 (Zry-4) oxidized at 1,000 degrees C (1,832 degrees F), areas of gray spots or thin axial lines observed on the outer surface occur during the phase transformation. For ZIRLO[®] oxidized at the same temperature, these areas are yellow or tan.

Following the full transformation to monoclinic oxide, the metal–oxide interface is once again smooth and the outer-surface color is uniformly gray or yellow.

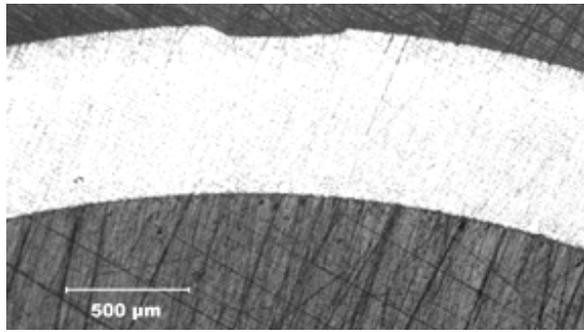
The presence of destabilizing trace impurities, especially fluorine, and possibly the absence of stabilizing impurities (e.g., calcium), can induce early breakaway oxidation at temperatures as high as the nominal phase transition temperature for stress-free ZrO₂. The Russian Zr-1 percent niobium (Nb) alloy E110 cladding is a classic example of a material that experiences early breakaway oxidation (less than 600 s), possibly because of the presence of fluorine impurities at the metal surface and within the metal substrate. For additional discussion, see NUREG/CR-6967 and NUREG/IA 0211, “Experimental Study of Embrittlement of Zr 1 percent Nb VVER Cladding under LOCA-Relevant Conditions” (Ref. A-4).

The increase in oxide-layer-thickness growth rate associated with breakaway oxidation does not directly cause cladding embrittlement within LOCA-relevant times. The low-oxygen beta or mixed alpha-beta layer remains ductile within LOCA-relevant times because of low oxygen concentration. However, hydrogen pickup associated with breakaway does cause ductility decrease and embrittlement. As shown in NUREG/CR-6967, cladding oxidized for 3,000–4,000 s at 970–1,000 degrees C (1,778–1,832 degrees F) loses ductility for hydrogen pickup values >400 wppm (see Appendix B of this RG). To ensure ductility as measured by ring-compression tests conducted at 135 degrees C (275 degrees F), the breakaway oxidation time in NUREG/CR-6967 is defined as the time corresponding to 200-wppm hydrogen pickup. The term “hydrogen pickup” refers to the measured hydrogen level for a sample normalized to the pre-oxidation mass of the sample from which the as-fabricated hydrogen content is subtracted. The term “hydrogen content” refers to the total hydrogen content in the post-oxidized sample normalized to the mass of the oxidized sample. At 200-wppm hydrogen pickup, there is little difference between the measured post-test hydrogen content of the sample and the hydrogen pickup. The hydrogen pickup rate following initiation of breakaway oxidation can be very fast, such that the time to increase from 200 wppm to >400 wppm can be as short as 100 s at oxidation temperatures in the range of 970–1,000 degrees C (1,778–1,832 degrees F). At lower oxidation temperatures, particularly less than 900 degrees C (less than 1,778 degrees F), the oxidation rate and hydrogen generation rate are considerably lower. As the hydrogen generation rate decreases, the rate of hydrogen pickup also decreases.

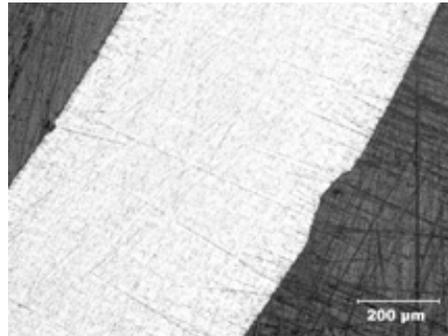
The transition from tetragonal to monoclinic oxide is an instability phenomenon dependent on many manufacturing variables, particularly those affecting cladding outer-surface conditions. For susceptible alloys such as E110 (NUREG/CR-6967), the presence of geometrical discontinuities from scratches, sample ends, and a thermocouple (TC) welded to the cladding will induce earlier breakaway oxidation. Also, for E110, high-surface roughness coupled with pretest cleaning in a hydrofluoric (HF)-containing acid induces very early breakaway oxidation in terms of both surface appearance and hydrogen pickup. For E110, the sequence of finishing operations is important. Etching with an HF-containing acid before polishing seems to have no significant effect on breakaway oxidation, while etching after polishing can have a very detrimental effect on breakaway oxidation time. Modern cladding alloys currently used in the United States are considerably more stable than E110. However, even these polished alloys with low surface roughness are sensitive to post-polishing cleaning methods. A good example of this is the breakaway oxidation times reported in the literature for Zry-4. For an older variant of Zry-4, the data generated by Leistikow and Schanz (Ref. A-2) give the minimum time to accumulate 200 wppm of hydrogen as 1,800 s, which occurs at an oxidation temperature of 1,000 degrees C (1,832 degrees F). In the article, “Influence of Hydrogen Simulating Burn-Up Effects on the Metallurgical and Thermal-Mechanical Behavior of M5[®] and Zircaloy-4 Alloys under LOCA Conditions” (Ref. A-5), Mardon, et al. report a hydrogen content of 200 wppm at about 5,400 s for modern, polished AREVA Zry-4 also oxidized at 1,000 degrees C (1,832 degrees F). NUREG/CR-6967 determined breakaway

oxidation times at about 1,000 degrees C (1,832 degrees F) (based on 200-wppm hydrogen pickup) of 3,800 s for an older variant of Zry-4 and 5,000 s for modern, polished AREVA Zry-4. In “Breakaway Phenomenon of Zr-based Alloys during a High-Temperature Oxidation,” Baek and Jeong (Ref. A-6) oxidized polished Zry-4 for 3,600 s at 1,000 degrees C (1,832 degrees F) and measured >600 wppm of hydrogen. For this case, the estimated time for 200-wppm hydrogen pickup is in the range of 3,000–3,300 s. The two studies with the lower breakaway oxidation times for Zry-4 have one critical step in common. In both studies, Zry-4 samples were cleaned in an HF-containing acid before steam oxidation: nitric-fluoric acid mixture and final cleaning in boiling water for the Leistikow and Schanz (Ref. A-2) tests; and 5 percent HF + 45 percent nitric acid (HNO₃) + 50 percent water (H₂O) with final ultrasonic cleaning in an ethanol and acetone solution for the Baek and Jeong (Ref. A-6) tests. In the Argonne National Laboratory (ANL) study described in NUREG/CR-6967, samples used to generate breakaway oxidation data were cleaned ultrasonically in ethanol followed by water. In the Mardon study (Ref. A-5), samples were degreased in acetone before testing.

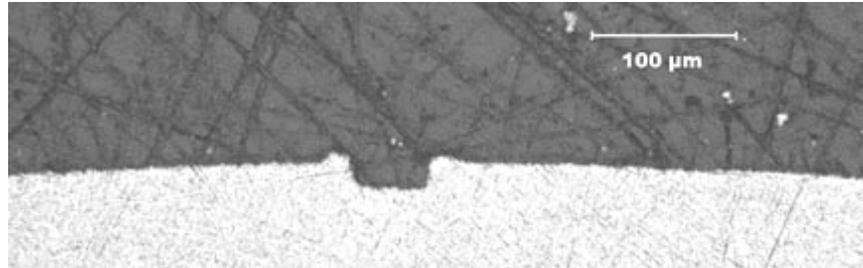
As breakaway oxidation may be sensitive to many variables related to surface finishing and cleaning, it is important to test samples that have undergone the full cleaning cycle, from the polishing phase through the operations at the fuel fabrication plant to the insertion of assemblies into the reactor. Cleaning with water, chemical detergents (e.g., Alconox), or organic solvents appears to have no significant effect on breakaway oxidation time. Cladding surface imperfections and scratches can act as initiation sites for breakaway oxidation because of the effects of the geometrical discontinuity on the stress state in the oxide and at the metal–oxide interface. Cladding surface scratches may occur when the fuel rods are inserted into the grid spacers or during fuel handling activities. A “design basis” or “bounding scratch” is a scratch that could occur under these expected activities. Examples of bounding, design-basis, and ANL-machined scratches are shown in Figure A-1. The scratches shown in Figure A-1(a) and (b) were induced by repeated insertion of fuel rod cladding into and out of grid spacers.



(a) Example of a bounding scratch ($\approx 50\text{-}\mu\text{m}$ (micrometer) deep into wall)



(b) Example of a design-basis scratch ($\approx 30\text{-}\mu\text{m}$ deep into wall)



(c) ANL-machined scratch used for breakaway oxidation studies ($\approx 20\text{-}\mu\text{m}$ deep into wall)

Figure A-1. Examples of scratches on the outer surface of cladding: (a) low-magnification image of a bounding scratch induced by excessive number of insertions in grid spacers, (b) medium-magnification image of an example design-basis scratch from insertion into grid spacers, and (c) high-magnification image of an ANL-machined scratch used in breakaway oxidation studies.

Breakaway oxidation test results reported in NUREG/CR-6967 are based on isothermal test conditions. The test times listed in NUREG/CR-6967 include the time (about 80 s) to ramp from 300 degrees C (572 degrees F) to the target temperature and the hold time at that temperature. The added ramp time is small relative to the hold times associated with breakaway oxidation. Additional studies by Yan et al., documented in “Breakaway Oxidation of ZIRLO Exposed to Transient Temperature Histories” (Ref. A-7), indicate that isothermal temperature tests generally give lower bound breakaway oxidation times as compared with breakaway times determined from tests with transient temperature histories. In one of the transient tests conducted by Yan et al., the temperature was held at the critical temperature

(980 degrees C; 1,796 degrees F) for 2,000 s, cycled five times between 930 degrees C (1,706 degrees F) and 1,030 degrees C (1,886 degrees F) for 400 s, and then held at 980 degrees C (1,796 degrees F) for 400 s. The hydrogen content and pickup were 230 plus or minus 80 wppm, which indicated that breakaway oxidation had occurred for this particular cladding alloy. Previous isothermal results for as-fabricated, pre-scratched, and pre-oxidized (less than 1 micrometer (μm) film) samples gave a minimum breakaway time of 3,100 plus or minus 300 s. For this particular transient, breakaway oxidation occurred at the lower bound of this range and was consistent with results for a pre-scratched sample oxidized under isothermal conditions.

The test times for the breakaway studies reported in NUREG/CR-6967 were generally less than or equal to 5,000 s. Some early tests, conducted at 7,200 s, resulted in excessive breakaway oxidation. Although there is no generic maximum time at elevated temperature for a LOCA, a maximum isothermal test time of 5,000 s appears reasonable based on other considerations, such as the Cathcart-Pawel equivalent cladding reacted (CP-ECR) limit in the balloon when ballooning and rupture are predicted to occur. To illustrate this point, the following example is provided. The minimum breakaway oxidation time for most cladding alloys is expected to occur in the temperature range of 950–1,000 degrees C (1,742–1,832 degrees F). For modern cladding alloys, the as-fabricated cladding wall thickness varies from 0.57 millimeter (mm) (0.022 inches) to 0.71 mm (0.027 in). For thin cladding that ruptures, even a relatively high CP-ECR value of 17 percent corresponds to less than 2,400 s at 1,000 degrees C (1,832 degrees F), less than 3,300 s at 975 degrees C (1,787 degrees F), and less than 4,600 s at 950 degrees C (1,742 degrees F). These times decrease significantly if wall thinning is included in the calculation. For thick cladding that ruptures, 17 percent CP-ECR corresponds to less than 3,300 s at 1,000 degrees C (1,832 degrees F), less than 5,100 s at 975 degrees C (1,787 degrees F), and less than 7,100 s at 950 degrees C (1,742 degrees F). With a modest 20 percent diametral ballooning or creep strain, these times for thicker cladding are reduced to less than 2,610 s at 1,000 degrees C (1,832 degrees F), less than 3,580 s at 975 degrees C (1,787 degrees F), and less than 5,000 s at 950 degrees C (1,742 degrees F). Thus, for most of these cases, breakaway oxidation times greater than 5,000 s would not be relevant because of the post-quench ductile-to-brittle transition (DBT) CP-ECR. The procedure for conducting tests for less than or equal to 5,000 s with emphasis on 950–1,000 degrees C (1,742–1,832 degrees F) oxidation temperatures is described in the following sections.

A-3. Sample Selection and Periodic Confirmatory Testing Frequency

A-3.1 Sample Selection

The samples selected for testing should be representative of the fueled cladding that is loaded into the reactor. In particular, samples should be exposed to the same post-polishing and outer-surface cleaning processes used before loading fuel assemblies into the reactor. Cleaning agents that have been found to be benign with respect to breakaway oxidation include water, chemical detergents (e.g., Alconox), and organic solvents (e.g., ethanol, acetone). However, the use of etching in an HF-containing acid mixture can initiate early breakaway oxidation in some alloys. These cleaning processes may be simulated in the laboratory.

Samples with a design-basis or bounding scratch should be tested once the minimum breakaway oxidation time and temperature are identified. The scratch depth and width for a design-basis or bounding scratch should be defined and supported based on manufacturing observations. Cladding tube scratching may be simulated in the laboratory.

If testing shows that post-polishing cleaning and scratches have an insignificant effect (i.e., results within data scatter) on the minimum breakaway oxidation time, then as-manufactured cladding may be used for periodic testing.

A-3.2 Periodic Confirmatory Testing Frequency

Breakaway oxidation is an instability phenomenon that is sensitive to surface roughness, surface and substrate impurities, and alloy constituents and impurities. Some processing factors that may be significant include: revised specifications that allow greater than 0.2- μ m surface roughness, a change of polishing material, introduction of post-polishing cleaning with an HF-containing acid mixture, and changing the cladding vendor. As it would take an extensive study to determine the breakaway-oxidation sensitivity for a particular cladding material to each of these variables, confirmatory tests should be conducted on a periodic basis. As stated in Section C of this Regulatory Guide, a test sample population or test frequency should be defined that can provide reasonable assurance that fuel is being manufactured consistent with the analytical limits specified in accordance with paragraph (g)(1)(iii) of 10 CFR 50.46c.

A-4. Sample Preparation and Characterization

A-4.1 Hydrogen Content Determination for As-Fabricated Samples

The hydrogen content of as-fabricated cladding is expected to be low (5–15 wppm) and to be available from the tubing vendor. It is used in the calculation to determine the hydrogen pickup during breakaway oxidation. If it is not available, it should be measured.

A-4.2 Minimum Sample Lengths for One- and Two-Sided Oxidation Tests

Most breakaway-oxidation testing has been performed with cladding sample lengths in the range of 25–50 mm (0.98-1.9 in.) for two-sided oxidation tests. These lengths were sufficient to minimize end effects. Therefore, the minimum sample length should be 25 mm (0.98 in.). Although there is no maximum limit prescribed, it should be no longer than the length of the uniform temperature region of the furnace. Uniform is defined as less than or equal to plus or minus 10 degrees C (less than or equal to plus or minus 18 degrees F) variation at the target temperature.

In preparing samples for one-sided oxidation tests, welded end caps are used to prevent steam from coming into contact with the cladding inner surface. To minimize larger end effects caused by the presence of welding heat-affected zones, the minimum sample length for one-sided oxidation tests should be 75 mm.

A-4.3 End-Cap Mass and Welding Procedure for One-Sided Oxidation Test Samples

Standard procedures are available for circumferential welding of end caps to cladding samples. Because the welds and end caps are not subjected to pressure, the end caps should be small and the masses should be minimized as they serve as sinks for hydrogen.

The room-temperature pressure inside the welded cladding sample should be low enough to give an internal pressure at the target oxidation temperature that is less than the external steam pressure. Also, it is recommended that the gas remaining inside the cladding sample be free of impurities (e.g., nitrogen).

A-4.4 Length, Outer-Diameter, and Wall-Thickness Measurements

Outer diameter and wall thickness vary somewhat along the length of fuel rod cladding. They should be measured and recorded for each sample. For cladding with a nominal diameter of 9.50 mm (0.37 in.), the actual diameter of the sample can vary from 9.46 to 9.50 mm (0.372-0.374 in.). The outer diameter should be determined to two decimal places (in mm) based on the average of the maximum and minimum diameters. For cladding with a nominal wall thickness of 0.57 mm (0.022in.), the actual wall thickness can vary from about 0.56 to 0.60 mm (0.022-0.023 in.). Wall thickness should be determined for each sample to two decimal places (in mm) based on four total measurements at locations about 90 degrees apart. The actual sample length should be measured and recorded to one decimal place accuracy (e.g., 25.1 mm). Also, the ends of the sample should be polished to remove burrs before sample-length measurement. While removing burrs, it is important to avoid scratching the cladding inner surface, especially with circumferential grooves, which would induce early hydrogen pickup. Also, the ends of the sample should be relatively flush (90 plus or minus 5 degrees relative to the longitudinal axis). Outer diameter, wall thickness, and length are used to normalize sample weight gain to exposed surface area.

A-4.5 Pretest Cleaning with Chemical Detergent or Organic Solvent and Rinsing

Appendix X1, "Guide to Specimen Preparation," to American Society for Testing and Materials (ASTM) G2/G2M-06, "Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680 Degrees F [360 Degrees C] or in Steam at 750 Degrees F [400 Degrees C]," describes sample cleaning procedures in Section X1.2 (Ref. A-8). These procedures should be followed for breakaway oxidation tests. Specifications and requirements in Sections X1.1 (on tubes with a second material on the inner diameter) and X1.3 (on etching) should not be used. Based on NUREG/CR-6967 and subsequent work by ANL, caution should be exercised when using an HF-containing acid mixture as part of the test cleaning process (see Appendix C of this RG). Light etching with acid containing HF can be used to facilitate pre-hydrating, as long as samples are polished before the oxidation tests.

A-4.6 Pretest Sample Weight Measurement (after Drying)

Pretest sample weight should be measured to the nearest 0.1 milligram (mg). Because drying after cleaning may take several hours, it is also permissible to measure pretest sample weight after cleaning with an organic solvent, such as ethanol, that vaporizes quickly. The pretest weight is used in the determination of sample weight gain. Although weight gain is not used as a metric for breakaway oxidation in these tests, it is used as a partial validation of the reported isothermal oxidation temperatures and a check on steam flow conditions.

A-5. Temperature Heat Up and Cool Down Rates and Heating Methods

A-5.1 Temperature Heat Up and Cool Down Rates

For long-time isothermal tests, heating and cooling rates are not expected to be critical parameters. However, long heating and cooling times should be avoided because they may induce breakaway oxidation at earlier isothermal-temperature times. The total ramp time from 650 degrees C (1,202 degrees F) to the target temperature (heating phase) and from the target temperature to 650 degrees C (1,202 degrees F) should be less than 10 percent of the isothermal test time. It is also not clear if temperature overshoot during the heating phase has any effect on isothermal breakaway oxidation time. However, temperature overshoot should be limited to less than or equal to 20 degrees C (less than or equal to 36 degrees F) for less than or equal to 20 s.

Rapid cooling by means of water quench is not required for breakaway oxidation tests. However, for very slow-cooling furnaces, quench may be used to reduce the cooling time.

A-5.2 Radiant Heating

Radiant heating in a quad-elliptic furnace has been used to generate breakaway-oxidation data (Refs. A-1, A-3, and A-6). This heating method, along with furnace power controlled by feedback from a thermocouple (TC) on or near the sample, allows for controlled heating rates and relatively fast cooling times (less than 100 s from 1,000 degrees C to 650 degrees C; from 1,832 to 1,202 degrees F). For 25-mm-long samples (0.98-in.) with a 9.50-mm (0.37-in.) outside diameter, axial temperature variations are negligible, but circumferential temperature variations are in the range of 10–15 degrees C (18–27 degrees F). These can be reduced by using radiant-heating furnaces with more than four lamps. However, the circumferential variation has a practical value because a range of temperatures (e.g., 1,000 plus or minus 10 degrees C (1,832 plus or minus 18 degrees F)) can be investigated with a single sample. With proper thermal benchmarking, radiant-heating furnaces are acceptable for conducting breakaway oxidation tests.

A-5.3 Resistance Heating

Most breakaway oxidation tests (e.g., Leistikow and Schanz, NUREG/IA-0211 and Mardon) have been conducted in resistance-heating furnaces. Compared with radiant-heating furnaces, these furnaces have a larger uniform temperature zone and have very slow heating and cooling rates. Faster heating and cooling rates are achieved by controlled movement of the sample into and out of the furnace. The movement of the sample into and out of the furnace should be defined and repeated for each test. Benchmark tests should be performed to determine the precise heating and cooling rates achieved using the defined movement procedures. This is necessary information for the determination of the time to reach the target isothermal temperature. Resistance-heating furnaces are acceptable for conducting breakaway oxidation tests.

A-5.4 Induction Heating

Induction heating has the advantage of rapid heating and cooling rates. It has been used in the CINOG program in France (Ref. A-8) to generate weight-gain kinetics data for Zry-4, M5[®],¹ and developmental alloys. Although the weight gain data appear reliable, it is not clear what impact this heating method would have on initiation of breakaway oxidation. It is also not clear whether the use of optical pyrometry to measure temperature requires etching of the cladding surface. Because of the uncertainties about induction heating, optical pyrometry, and required surface preparation, induction heating should not be used for breakaway oxidation studies.

A-5.5 Direct Electrical Heating

Direct electrical heating of cladding has been used in the past for LOCA-relevant studies. Because resistance and heating rate change with temperature and because of the unknown effects of such heating on breakaway oxidation, direct electrical heating of cladding should not be used for breakaway oxidation studies. However, indirect electrical heating may be an acceptable method for internal heating of another material inside the cladding to generate a heat flux simulating heating of the cladding by means of decay heat from the fuel.

¹ M5[®] is a registered trademark of AREVA NP.

A-6. Temperature Control and Monitoring

A-6.1 Thermocouples

For the temperatures relevant to this breakaway oxidation test procedure, the TCs used to record temperature and control furnace power should be either Type S (platinum (Pt)/10% rhodium-Pt) or Type R (Pt/Rh 87%/13%-Pt). The TCs should be calibrated using instrumentation and standards that are traceable to the National Institute of Standards and Technology (NIST), or another internationally-recognized standards organization and proof of traceability should be available for inspection. Typically, this service is provided by the TC vendor, who, for an extra fee, provides a certificate of calibration. The licensee should have available a certificate of calibration for every TC used to directly or indirectly to monitor sample temperature in the breakaway oxidation study. This certificate should include the results of the calibration at a minimum of two temperatures: 800 degrees C and 1,000 degrees C (1,472 and 1,832 degrees F). Copies of these certificates should also be included with the data report.

A-6.2 Thermal Benchmarks

Thermocouples should not be welded directly onto the outer surface of the cladding sample used to define the zirconium alloy's breakaway oxidation behavior. The geometric discontinuity at the TC-sample junction can induce early breakaway oxidation, which would be an artifact. Also, the presence of the TC during testing and its removal after testing will affect the accuracy of the post-test sample weight.

In most cases, the control TC will be welded onto the sample holder or as close to the sample as possible without contacting the sample. This requires thermal benchmarks to be performed to establish the relationship between the control TC that will be used during data-generating tests and the temperature of the sample outer surface. The thermal benchmarking should be performed at a minimum of two temperatures: 1,000 degrees C and 800 degrees C (1,472 and 1,832 degrees F). For the work reported in NUREG/CR-6967, two or three TCs (120 degrees apart) were welded directly onto the benchmark sample outer surface. These readings were compared with the readings of three TCs welded onto the sample holder at a location just above the sample. For radiant-heating and large-diameter (about 11 mm (0.43 in.)) cladding, three TCs were welded directly to the cladding outer surface to better define the average and one-standard-deviation cladding temperature. For smaller diameter cladding (9.50 mm (0.37 in.)), only two TCs welded directly to the cladding surface were needed. For the thermal benchmark tests, it is important that these be conducted under the same flowing steam conditions used in the data-generating tests.

For resistance-heating furnaces, the same thermal-benchmarking method described for radiant-heating furnaces can be used. However, other methods can be used to determine the relationship between the sample temperature and the holder temperature. These furnaces come with a built-in TC that controls the power to the furnace. Thermal benchmarking can be done with a suspended and moveable TC to map out the axial variation in temperature for a sample assembled into a test train. Recorded temperatures can be compared with the TC or TCs welded to the sample holder. Circumferential temperature variations are generally small for such furnaces. The large uniform hot zone of a resistance-heating furnace also permits the inclusion of cladding specimens that are instrumented with a thermocouple next to the test specimen. It may be possible to conduct each test with an instrumented, non-oxidized cladding specimen to establish specimen temperature; however details would need to be provided to make clear the location of the non-oxidized sample relative to the test sample for the entire

test duration. The results of the thermal benchmark tests should be documented and included in the data report.

A-6.3 Weight-Gain Benchmarks

After thermal benchmarking, samples should be tested without TCs welded onto the sample to determine the weight gain. These tests should be conducted at 800 degrees C and 1,000 degrees C (1,472 and 1,832 degrees F). The test times should be less than those that result in breakaway oxidation. The results of the weight-gain benchmark should be compared with the published or vendor-proprietary, material-specific databases. The results of the weight-gain benchmark tests should be documented and included in the data report.

A-7. Water Quality, Steam Flow Rate, and Steam Pressure

A-7.1 Water Quality

Purified water is recommended for generating steam. Laboratory-grade Type I and Type II water are both of sufficient purity for breakaway oxidation tests at greater than or equal to 650 degrees C (greater than or equal to 1,202 degrees F). These recommendations on water quality are intended to prevent initiating early breakaway oxidation caused by experimental artifacts.

A-7.2 Steam Flow Rate

The average steam flow rate used in breakaway oxidation studies should be determined (and reported) from the mass of condensed water collected during these long-time tests or by the mass of water that is input to the steam chamber divided by the test time and normalized to the net cross-sectional area of the steam chamber. The average steam flow rate should be in the range of 0.5 to 30 mg/square centimeter per second ($\text{cm}^2 \cdot \text{s}$). Justification for this range is provided in the following paragraphs.

Leistikow and Schanz and Uetsuka (“Oxidation of Zircaloy-4 under Limited Steam Supply at 1000 and 1300degrees C” (Ref. A-9)) studied the effects of low steam flow rates on the oxidation kinetics of Zry-4 at 1,000 degrees C (1,832 degrees F). Their results are summarized in Leistikow and Schanz, Figure 9 (Ref. A-2). In terms of flow rate normalized to the cross-sectional area of the test chamber, the oxidation kinetics began to decrease because of steam starvation for flow rates less than $0.05 \text{ mg}/(\text{cm}^2 \text{ s})$. For the Leistikow and Schanz work, the sample length was 30 mm (1.18 in.) and oxidation was two-sided. Aomi, et al. (M. Aomi, M. Nakatuka, et al., “Behavior of BWR Fuel Cladding Tubes under Simulated LOCA Conditions” (Ref. A-10)) studied the relationship between weight gain and steam flow rate for oxidation temperatures up to 1,200 degrees C (2,192 degrees F). They found that the weight gain for fixed test times and temperatures was independent of steam flow rates in the range of 0.8 to $7.8 \text{ mg}/(\text{cm}^2 \text{ s})$. Kawasaki, et al. (“Oxidation of Zircaloy-4 under High Temperature Steam Atmosphere and Its Effect on Ductility of Cladding” (Ref. A-11)) also performed high-temperature oxidation tests to determine the range of steam flow rates for which the weight gain for a given test time was independent of steam flow rate. They report this range as 3 to $28 \text{ mg}/(\text{cm}^2 \text{ s})$.

For breakaway oxidation studies conducted in steam at less than or equal to 1,050 degrees C (1,922 degrees F), the results of Leistikow and Schanz, Uetsuka, and Aomi, et al. are particularly relevant for the minimum steam flow rate. However, because individual sample lengths (greater than or equal to 25 mm (0.98 in.) for two-sided tests and greater than or equal to 75 mm (2.95 in.) for one-sided tests) include lengths longer than those used in the Leistikow and Schanz study and as many as five two-sided test samples may be stacked inside the test chamber, the minimum steam flow rate is set at

0.5 mg/(cm² s), which is 10 times the minimum given in Leistikow and Schanz and Uetsuka. For the results presented in NUREG/CR-6967, the normalized steam flow rate was 5.3 plus or minus 0.8 mg/(cm² s). This rate is well above the minimum rates determined from Leistikow and Schanz, Uetsuka, Aomi, et al., and Kawasaki, et al.

It is desirable to have a steam flow rate higher than 0.5 mg/(cm² s) to reduce temperature overshoot during the heating phase for bare cladding. Baek and Jeong cite a fast heating rate of 50 degrees C/s (90 degrees F/s) and a temperature overshoot for about 20 s at the end of the heating ramp with a steam flow rate of 10 mg/(cm² s). Although the maximum steam flow rate may not be as critical as the minimum steam flow rate, the use of steam flow rates greater than 30 mg/(cm² s) should be justified by data that indicate local temperature can be accurately recorded. It is possible that very high steam flow rates may cause TCs to record local temperatures lower than the average sample temperature because of the “fin-cooling” effect.

A-7.3 Steam Pressure

Breakaway oxidation tests should be conducted at a steam pressure at or slightly above atmospheric pressure. This is consistent with the pressures that were used in previous breakaway oxidation studies. Additional supporting information can be found in references for the work of Leistikow and Schanz, NUREG/CR-6967, Baek and Jeong and Uetsuka.

A-8. Test Procedure

The specific details of the test procedure depend on the heating furnace used. Described below are the steps used in the NRC’s LOCA research program, along with some generalizations that would apply to other heating and cooling methods than the radiant-heating furnace used in that study. Detailed steps for NUREG/CR-6967 testing are documented in Y. Yan, “Work Plan for the Breakaway Oxidation of ZIRLO™ Cladding at 800-1015degrees C” (Ref. A-12).

A-8.1 Test Train and Test chamber

The test train or sample holder and the test chamber form a unit that should be designed to contain the steam flow and to prevent impurities, especially nitrogen, from entering the chamber. By using steam that has a pressure slightly greater than the surrounding atmosphere, the test train and test chamber do not have to be leak-tight to a high level to serve the functions of providing a pathway for steam flow and protecting the sample from gas-phase impurities.

In choosing the material for the test train or sample holder, it is desirable to have a non-oxidizing or limited-oxidizing material such as stainless steels or nickel (Ni) alloys (e.g., Inconel 600). However, the sample must be protected from direct contact with materials such as iron (Fe) and Ni alloys because of the low-temperature eutectics for Zr and these elements. Hofmann and Markiewicz (“Chemical Interactions between As-Received and Pre-Oxidized Zircaloy 4 and Inconel 718 at High Temperatures” Ref. A-13) studied the reaction rates and eutectics of Zry-4 and Inconel 718. They also presented binary phase diagrams for Zr-Fe and Zr-Ni, which have eutectic temperatures as low as about 930 degrees C and 980 degrees C, respectively (1,706 and 1,796 degrees F, respectively). In NUREG/CR-6967, alumina inserts and zirconia washers were used between the Inconel holder and the sample to prevent such reactions from occurring. Testing laboratories may institute controls other than those used in NUREG/CR-6967 to prevent eutectic reactions between Zr-based alloys and the test train materials.

A-8.2 Purging Test chamber and Stabilizing Steam Flow

Before heating and initiating steam flow, the test chamber is filled with gas representative of the environment of the test facility (e.g., usually air). The test chamber should be purged with a high-purity inert gas (e.g., argon) before introducing steam flow or with low-temperature steam before the temperature ramp. Deviations that may have a significant effect on test results include heating the sample to the target temperature in an inert gas before introduction of steam flow. Impurities in the inert gas will result in an oxide or oxide-nitride film on the cladding that is not LOCA-relevant. If steam is used to purge the test chamber, then steam flow should be maintained for 500 s before initiating the temperature ramp.

Steam flow should be initiated at a test chamber temperature of about 30 degrees C (86 degrees F). After introduction of steam into the chamber, furnace heating should commence for a pretest initial sample hold temperature between 100 and 300 degrees C (212 and 572 degrees F). When selecting the initial sample hold temperature, any known phase transition temperatures should be avoided. Stabilization of steam flow and the initial sample hold temperature should occur within 500 s.

A-8.3 Ramping Temperature and Holding Temperature at Target Value

The target test temperature is predetermined. It should be based on the average sample temperature. Depending on the heating method used, axial and circumferential variations could be significant. For a single sample, the axial temperature variation should be less than or equal to 10 degrees C (18 degrees F) and the circumferential temperature variation should be less than or equal to 20 degrees C (36 degrees F). These variations are the differences between the maximum and minimum temperatures.

For resistance furnaces, the sample heating rate is controlled by the rate of movement of the sample into the furnace heating zone. For radiant-heating furnaces, the heating rate is controlled through feedback from a TC welded onto the holder to the furnace power. For the radiant heating furnace used in NUREG/CR-6967, the temperature ramp rate was programmed to be very fast (greater than 50 degrees C/s (90 degrees F/s) from 300 degrees C (572 degrees F) to within 50–100 degrees C (122–212 degrees F) of the target temperature and slow (2–3 degrees C/s (3.6–5.4 degrees F/s)) from that temperature to the target temperature. This programmed ramp was designed to eliminate temperature overshoot. Typical test times from 650 degrees C to 1,000 degrees C (1,202 to 1,832 degrees F) were less than 80 s. It is recommended that the heating rate from 650 degrees C (1,202 degrees F) to the target temperature be greater than or equal to 5 degrees C/s (greater than or equal to 9 degrees F/s) for breakaway oxidation tests. This heating rate may not be representative of small break LOCA heating rates. However, the purpose of establishing test procedures for breakaway oxidation testing is to provide a means of performing repeatable and consistent measurements for the onset of breakaway oxidation. The basis for this ramp rate is that testing at ANL showed early breakaway oxidation for one alloy (E110) when slow heating rates were used and early breakaway oxidation for another alloy (ZIRLO[®]) when fast heating rates (including temperature overshoot) were used.

A-8.4 End of Heating Phase and Cool Down

After the target test time has been reached, furnace power should be turned off while steam flow is maintained. The rate of temperature decrease will depend on the heating method used and the method of removing the sample from the furnace. For in situ cooling, the steam flow should be maintained until the sample temperature reaches 800 degrees C (1,472 degrees F). For the NUREG/CR-6967 work, this corresponded to a hold temperature of 700–720 degrees C (1,292–1,328 degrees F). Following this step,

there should be ample moisture in the test chamber to maintain a steam environment for cooling from 800 to 650 degrees C (1,472 to 1,202 degrees F).

Direct quench from the target value hold temperature can also be used, however it is noted that this rapid cooling method has been shown to have a detrimental effect on cladding post-quench ductility. Direct quench methods are acceptable because they will produce conservative results. For direct quench cooling from the target value hold temperature, it is not necessary to maintain a prescribed cool down rate or steam cooling to a particular temperature.

A-8.5 Determination of Test Time

The isothermal test time should be the time interval between reaching within 20 degrees C (36 degrees F) of the target temperature during the heating ramp to cooling within 20 degrees C of the target temperature during the cooling ramp. Depending on heating and cooling rates, this time will be about equal to the time at which the sample is at constant temperature. If recommended heating and cooling times are used, the test time can be determined as the time above 650 °C (1,202 degrees F) or the time between initiation of the heating ramp and the initiation of the cooling ramp.

A-9. Post-test Measurements and Characterization

A-9.1 Sample Drying Time

To determine an accurate post-test sample weight, it is important that the sample be free of moisture. For drying in stagnant air, the drying time should be ≥ 2 hours. This time can be reduced significantly by the use of forced-air drying. Sample weight will continue to decrease during the drying process until it reaches a minimum and holds at that minimum. Whatever drying method is used, the drying time should be verified by weight measurements.

A-9.2 Weight Measurement and Use of Weight Gain to Verify Oxidation Temperature

The post-test sample weight should be measured to the nearest 0.1 mg as specified in Section 7.1.3 of ASTM G2/G2M-06. The weight gain (in mg) is determined by subtracting the pretest weight from the post-test weight and normalizing this value to the steam-exposed surface area of the sample. Although this normalized weight gain is not used to determine breakaway oxidation time, it is used to validate temperature control and monitoring as well as the adequacy of steam flow and test procedures.

A-9.3 Visual Examination of Sample Outer Surface

The sample outer surface should be examined visually and photographed. If the outer surface is smooth and lustrous-black, then breakaway oxidation has not occurred and no further characterization is needed. If the outer surface is rough and dull-black, grey or yellow then the sample may be well beyond the breakaway oxidation time as defined by the 200-wppm hydrogen pickup criterion. If the sample shows any indication of discoloration (see Appendix C of this RG), the hydrogen content of the post-test sample should be measured and evaluated against the 200-wwpm hydrogen pickup criterion.

Because of stress reversal at the ends of the sample caused by the geometric discontinuity, it is possible that discoloration will appear only at the ends of the sample. Such a discontinuity is an experimental artifact. However, discoloration and breakaway only at the sample ends are useful data because they indicate that the cladding material is sensitive to stress discontinuities and is close to the

breakaway oxidation time. This artifact can be minimized or eliminated by machining a longitudinal scratch (25 plus or minus 5 μm deep and >25 plus or minus 5 μm wide) along the sample. Based on results presented in NUREG/CR-6967, such a scratch will induce breakaway oxidation away from the sample ends before the ends experience breakaway oxidation (see Appendix C of this RG).

A-9.4 Hydrogen Analysis for Samples with Outer-Surface Discoloration (Relative to Lustrous-black)

Samples with outer-surface discoloration away from the sample ends and samples with rough, dull-black outer-surface oxide should be further characterized by measuring the hydrogen content on a ring sectioned from the middle section of the sample, at least 5 mm (0.19 in.) from the segment ends. The hydrogen-analysis sample should be a ring that is sectioned to be 2–3 mm (0.078-0.118 in.) long and to include a region of discoloration. The selection of this ring is very important for scratch-free samples, as hydrogen concentration is likely to have local variations ranging from 20 to 600 wppm for a corresponding average ring hydrogen content of 200 wppm. For pre-scratched samples, the hydrogen concentration along the sample is relatively uniform. As such, the precise location of the hydrogen-analysis ring is not critical. For some cladding materials, breakaway spreads very rapidly at high-oxidation temperatures (e.g., 1,000 degrees C (1,832 degrees F)) along the length and around the circumference of the sample, such that the average hydrogen content increases from 200 wppm to 600–1000 wppm in less than 200 s (NUREG/CR-6967). However, for lower oxidation temperatures (e.g., 800 degrees C (1,472 degrees F)), the time lag between the observation of surface discoloration and significant hydrogen pickup may be much longer (Leistikow and Schanz).

For repeat tests at the same temperature and time, the hydrogen content for each test should be measured and compared with the 200-wppm hydrogen pickup to determine if breakaway has occurred.

There are several ways to measure hydrogen content in metals. Vacuum fusion is one method. The recommended method is documented in ASTM E1447-09, “Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity/Infrared Detection Method” (Ref. A-14). If a method other than ASTM E1447-09 is used, the method should be documented and available for inspection.

ASTM E1447-09 was used successfully to determine the hydrogen content in other metals, such as Zr alloys. For additional information, the detailed procedure used to generate the results in NUREG/CR-6967 is documented by T. Burtseva in “Procedure for Hydrogen Analysis of Refractory Metals” (Ref. A-15).

The necessary instrumentation (e.g., LECO RH-404 hydrogen determinator) and calibration standards (titanium calibration coupons with known hydrogen content) should be traceable to the National Institute of Standards and Technology (NIST), or another internationally-recognized standards organization and proof of traceability should be available for inspection. Titanium coupons with a hydrogen content close to 200 wppm (at the time of publication, a calibration sample with 218-wppm was available, for example), as this is the hydrogen content criterion for breakaway oxidation in this Regulatory Guide. As these machines are very sensitive, it is important to perform calibration at least once in any given day before data generation. For hydrogen-content output that does not match visual observations (e.g., high hydrogen for lustrous-black oxide or low hydrogen for gray or yellow regions of oxidized cladding), post-test calibration verification should be performed by testing a standard as an unknown (i.e., with the same calibration constant determined before testing).

A-9.5 Criterion (200-wppm Hydrogen Pickup) for Breakaway Oxidation Based on Retention of Ductility

The criterion to determine if breakaway oxidation has occurred is the measurement of 200 wppm, or greater, hydrogen pick up. The as-fabricated hydrogen content should be subtracted from the hydrogen content measured following a breakaway oxidation test to determine the hydrogen picked up during the test for comparison to the 200 wppm hydrogen pickup criterion. This criterion is an empirical limit based on observations from two-sided oxidation tests. The 200 wppm criterion is applicable to both one- and two-sided tests.

The basis for this criterion is as follows. As shown in Appendix B, cladding rings with hydrogen pickup values less than or equal to 440 wppm oxidized at 970–1,000 degrees C (1,778-1,832 degrees F) are ductile at 135 degrees C (275 degrees F) and brittle for hydrogen pickup values greater than or equal to 600 wppm. The ductile-to-brittle transition is likely to occur for a hydrogen pickup of about 500 wppm. Thus, ductility is retained with an appropriate amount of conservatism for average hydrogen pickup values and post-test hydrogen values less than or equal to 200 wppm. At 970–1,000 degrees C (1,778-1,832 degrees F) oxidation temperatures, significant hydrogen pick up and the transition from ductile to brittle behavior may occur within 100–200 s. The 200-wppm -hydrogen breakaway criterion is reasonable and justified at the higher oxidation temperatures at which the minimum breakaway oxidation time is most likely to occur.

A-9.6 Characterization for One-Sided and Two-Sided Oxidation Test Samples

Breakaway oxidation tests can be performed on open-ended cladding segments (two-sided oxidation tests) or segments with welded endcaps that prevent inner-diameter oxidation, (one-sided oxidation tests). There are important factors to consider when selecting either two- or one-sided oxidation tests. The following information is provided to improve data quality.

For one-sided oxidation tests, oxide is grown only on the sample outer surface. Thus, hydrogen pickup can only occur through the outer-surface oxide. However, possible hydrogen loss to the end caps, which act as a sink for hydrogen, needs to be considered. Hydrogen loss to the end caps may occur by means of solid-state diffusion or gas-phase transport within the sample interior. Of these two mechanisms, gas-phase transport may be the dominant mechanism for hydrogen transport. The inner surface is in the beta or mixed alpha-beta phase regime. Diffusion across the thin cladding wall, desorption from the cladding inner surface, and adsorption on the inner end-cap surfaces will result in a decrease in hydrogen content in the cladding metal. This effect will be more significant at the higher oxidation temperatures. It is recommended that hydrogen analysis be performed on a sample sectioned 1 inch from both weld joints to avoid measurement in regions that may have been affected by hydrogen loss to the end-caps. If significant hydrogen diffusion to the end caps is observed, then the mass of the end caps should be reduced and the end caps should be redesigned to provide minimal cross-sectional area for hydrogen diffusion.

For two-sided oxidation tests, surface characteristics of breakaway oxidation may be observed on the inner diameter earlier than expected. Metallographic examination could be used to verify that breakaway occurred at the outer-surface oxide before it occurred at the inner-surface oxide. If breakaway oxidation occurred at both inner and outer oxide layers, then the test time should be reduced until only outer-surface breakaway has occurred. Based on one test result reported in NUREG/CR-6967, a cladding sample oxidized for about 3,500 s at 1,000 degrees C (1,832 degrees F) experienced complete tetragonal-to-monoclinic transformation at the cladding inner surface and no such transformation at the cladding outer surface. However, the associated hydrogen pickup was only 100 wppm. Because of the curvature of

the inner surface, the oxide tends to be under higher compressive stress than on the outer surface. As such, cracks that form in the monoclinic oxide tend to be very tight, which limits the amount of steam absorbed into these cracks and the amount of hydrogen released and available for pickup. Because samples which experience breakaway oxidation on the inner diameter could produce early breakaway oxidation, which would not be expected in reactor, results from two-sided oxidation tests should be used with caution. Two-sided oxidation tests may be easier to conduct and the results based on these tests would be conservative, therefore two-sided oxidation tests are acceptable.

A-10. Test Temperatures

To determine the minimum breakaway oxidation times, oxidation temperatures should include the following high temperatures: 1,050 degrees C, 1,030 degrees C, 1,015 degrees C, 1,000 degrees C, 985 degrees C, 970 degrees C, 950 degrees C and 800 degrees C (1,922 degrees F, 1,886 degrees F, 1,859 degrees F, 1,832 degrees F, 1,805 degrees F, 1,778 degrees F, 1,742 degrees F and 1,472 degrees F)—resulting in eight separate tests. The maximum test time should be 5,000 s or the time to exceed the post-quench ductility (PQD) DBT CP-ECR at the test temperature, whichever is shorter.

The basis for the above test temperature includes studies from Leistikow and Schanz. Leistikow and Schanz studied the oxidation kinetics and breakaway oxidation for Zry-4 over a range of temperatures (600–1,600 degrees C (1,112–2,912 degrees F), with temperature increments of 50 degrees C (90 degrees F)) for very long times (less than or equal to 25 hours). The results are extremely useful in demonstrating that breakaway oxidation time is not a monotonic function of oxidation temperature. Reinterpreting their data in terms of the 200-wppm-hydrogen criterion for breakaway, Leistikow and Schanz found minimum breakaway times of about 1,800 s at 1,000 degrees C (1,832 degrees F) and about 3,600 s at 800 degrees C (1,472 degrees F). These minimum times occurred at temperatures close to the phase change temperatures for Zry-4 (about 980 degrees C (1,490 degrees F) for the $\alpha+\beta\rightarrow\beta$ transition and about 810 degrees C for the $\alpha\rightarrow\alpha+\beta$ transition). Intermediate temperatures (e.g., 1,025 degrees C, 985 degrees C, 825 degrees C, and 775 degrees C (1,877, 1,805, 1,517 and 1,427 degrees F)) were not investigated, and relatively few oxidation temperatures (1,000 degrees C, 900 degrees C, 800 degrees C, and 650 degrees C (1,832, 1,652, 1,472 and 1,202 degrees F)) were characterized in terms of increase in hydrogen content with test time. Also, although Zry-4 may be less sensitive to HF-containing acid cleaning than Nb-bearing alloys, it is not clear whether or not the cleaning process (HF-acid mixture) influenced the results.

Others have measured breakaway times for various Zr alloys. Based on the results presented in References A-2, A-3, A-6, as well as work documented by Y. Yan, et. al. in “Update on Breakaway Oxidation of Westinghouse ZIRLO™ Cladding” (Ref. A-16), “Breakaway Oxidation Tests for M5® Cladding” (Ref. A-17), and “Progress Report on Breakaway Oxidation of Bare and Prefilmed ZIRLO™” (Ref. A-18), it appears highly likely that the minimum breakaway oxidation time will occur at a temperature near the upper phase-transformation temperature at which oxidation and hydrogen-generation rates are high relative to the lower phase-transformation temperature. For Zircalloys, Zr-1Nb-1Sn, and Zr-1Nb alloys, the upper phase-transformation temperatures are in a rather narrow range (about 965–985 degrees C (1,769 to 1,805 degrees F)). The lower phase-transformation temperatures for these alloys span a larger range (about 650–810 degrees C (1,202 to 1,490 degrees F)).

If the outer surface is smooth and lustrous-black, indicating breakaway oxidation has not occurred for any of the test temperatures, then two additional tests should be conducted at 1,000 degrees C (1,832 degrees F) for 5,000 s or the time to exceed the PQD DBT CP-ECR to confirm repeatability. Finally, three additional tests should be conducted at 1,000 degrees C (1,832 degrees F) for 5,000 s, or the time to exceed the PQD DBT CP-ECR, on samples with a bounding or design-basis scratch. If the outer surface

is smooth and lustrous-black following the tests at these test conditions on scratched samples, it can be concluded that scratches have an insignificant impact on breakaway oxidation behavior. If the outer surface is smooth and lustrous-black following all tests at 1,050 degrees C, 1,030 degrees C, 1,015 degrees C, 1,000 degrees C, 985 degrees C, 970 degrees C, 950 degrees C and 800 degrees C (1,922 degrees F, 1,886 degrees F, 1,859 degrees F, 1,832 degrees F, 1,805 degrees F, 1,778 degrees F, 1,742 degrees F and 1,472 degrees F), including tests on scratched samples, there is no need to measure hydrogen pick up and no further testing is necessary to characterize the breakaway behavior.

If the outer surface is rough and dull-black following any test in the initial oxidation temperature set, then the sample may be well beyond the breakaway oxidation time as defined by the 200-wppm hydrogen pickup criterion, and the hydrogen content should be measured. If breakaway oxidation is observed to occur at less than 5,000 s or below the time required to reach the PQD DBT CP-ÉCR at the given test temperature, testing should continue for shorter times until no breakaway oxidation is observed (either according to the surface condition or the 200 wppm hydrogen pickup criterion). The minimum time and corresponding temperature should be reported. Two additional tests should be conducted at this minimum time and temperature because of anticipated data scatter for hydrogen pickup. Finally, three additional tests at the minimum breakaway time and temperature should be conducted on a sample with a bounding or design-basis scratch to determine the influence of a surface defect on the measured time to breakaway behavior. If the scratched sample experiences breakaway oxidation behavior at the same time, or within 500 seconds of the non-scratched sample, it can be concluded that scratches have an insignificant impact on breakaway oxidation behavior. If the scratched sample experiences breakaway oxidation behavior at a time more than 500 seconds shorter than the non-scratched sample at the same temperature, then this time should be reported as the minimum breakaway oxidation time and scratched samples should be used for periodic confirmatory breakaway oxidation testing.

Appendix E of this RG provides an overview and logic diagram to illustrate the testing matrix described above.

The NRC staff recommends that testing be initiated at 1,000 degrees C (1,832 degrees F) for a test time of 5,000 s. If breakaway is observed based on visual examination and the hydrogen pickup is greater than 200 wppm, then the test time at 1,000 degrees C (1,832 degrees F) should be reduced until the hydrogen pickup is less than 200 wppm or until no discoloration is observed on the cladding outer surface. Subsequent tests at higher (e.g., 1,015 degrees C or 1,859 degrees F) and lower (e.g., 985 degrees C or 1,805 degrees F) temperatures should be conducted at the minimum time (less than or equal to 5,000 s) for 1,000 degrees C (1,832 degrees F). If breakaway is observed at a lower test time for a temperature other than 1,000 degrees C (1,832 degrees F), then that minimum time should be used as the maximum test time for subsequent temperatures. This process is documented in NUREG/CR-6967.

APPENDIX A REFERENCES²

- A-1. U.S. Nuclear Regulatory Commission (NRC), ORNL/NUREG-17, "Zirconium Metal-Water Oxidation Kinetics IV. Reaction Rate Studies," Washington, DC, August 1977 (Agencywide Documents Access and Management System (ADAMS) Accession No. ML052230079).
- A-2. Leistikow, S., and G. Schanz, "Oxidation Kinetics and Related Phenomena of Zircaloy-4 Fuel Cladding Exposed to High Temperature Steam and Hydrogen-Steam Mixtures under PWR Accident Conditions," *Nuclear Engineering and Design*, 103: 65–84.³
- A-3. NRC, NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," Washington, DC, July 2008.
- A-4. NRC, NUREG/IA-0211, "Experimental Study of Embrittlement of Zr-1%Nb VVER Cladding under LOCA-Relevant Conditions," Washington, DC, March 2005.
- A-5. Mardon, J.P., J.C. Brachet, L. Portier, V. Maillot, T. Forgeron, A. Lesbros, et al., "Influence of Hydrogen Simulating Burn-Up Effects on the Metallurgical and Thermal-Mechanical Behavior of M5[®] and Zircaloy-4 Alloys under LOCA Conditions," ICONE13-50457, *13th International Conference on Nuclear Engineering*, Beijing, China, May 16-20, 2005.
- A-6. Baek, J.H., and Y.H. Jeong, "Breakaway Phenomenon of Zr-based Alloys during a High-Temperature Oxidation," *Journal of Nuclear Materials*, 372: 152–159.^{3,4}
- A-7. Yan, Y., T.A. Burtseva, and M.C. Billone, "Breakaway Oxidation of ZIRLO Exposed to Transient Temperature Histories," ANL letter report to the NRC, July 31, 2009 (ADAMS Accession No. ML092710523).
- A-8. American Society for Testing and Materials (ASTM) G2/G2M-06, "Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680 degrees F [360 degrees C] or in Steam at 750 degrees F [400 degrees C]," ASTM International, West Conshohocken, PA, 2006.^{3,5}
- A-9. Uetsuka, H., "Oxidation of Zircaloy-4 under Limited Steam Supply at 1000 and 1300 degrees C," Kernforschungszentrum Karlsruhe (KfK) 3848, Kernforschungszentrum Karlsruhe GmbH, Postfach 360, 76021 Karlsruhe, 1984.³

² All NRC documents that are publicly available may be accessed through the Electronic Reading Room on NRC's public Web site at <http://www.nrc.gov/reading-rm/doc-collections/> and through the NRC's Agencywide Documents Access and Management System (ADAMS) at <http://www.nrc.gov/reading-rm/adams.html>. The documents can also be viewed online or printed for a fee in the NRC's Public Document Room (PDR) at 11555 Rockville Pike, Rockville, MD. For problems with ADAMS, contact the PDR staff at 301-415-4737 or (800) 397-4209; fax (301) 415-3548; or e-mail pdr_resource@nrc.gov.

³ A copy of this document is available for review by the public at the NRC's Technical Library, by appointment, which is located at Two White Flint North, 11545 Rockville Pike, Rockville, Maryland 20852; telephone: 301-415-7000; e-mail: Library.Resource@nrc.gov.

⁴ Copies of this paper may be purchased through ScienceDirect Website: <http://www.sciencedirect.com>

⁵ Copies of American Society for Testing and Materials (ASTM) standards may be purchased from ASTM, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, Pennsylvania 19428-2959; telephone (610) 832-9585. Purchase information is available through the ASTM Web site at <http://www.astm.org>.

- A-10. Aomi, M., M. Nakatuka, et al., "Behavior of BWR Fuel Cladding Tubes under Simulated LOCA Conditions," ICONE-7435, 7th International Conference on Nuclear Engineering, 1999. This document is freely available online at <http://www.jsme.or.jp/monograph/pes/1999/ICONE7/PAPERS/TRACK09/FP7435.PDF>
- A-11. Kawasaki, S., T. Furuta, and M. Suzuki, "Oxidation of Zircaloy-4 under High Temperature Steam Atmosphere and Its Effect on Ductility of Cladding," *Journal of Nuclear Science and Technology*, 15(8): 589–596.^{3,6}
- A-12. Yan, Y., "Work Plan for the Breakaway Oxidation of ZIRLO™ Cladding at 800-1015 degrees C," Argonne National Laboratory (ANL) Intra-Laboratory Memo, IPS-490-00-02, June 1, 2007 (ADAMS Accession No. ML15229A184).
- A-13. Hofmann, P., and M. Markiewicz, "Chemical Interactions between As-Received and Pre-Oxidized Zircaloy-4 and Inconel-718 at High Temperatures," Kernforschungszentrum Karlsruhe (KfK) 4729, Kernforschungszentrum Karlsruhe GmbH, Postfach 360, 76021 Karlsruhe, June 1994. This document is freely available online at <http://bibliothek.fzk.de/zb/kfk-berichte/KFK4729.pdf>
- A-14. ASTM E1447-05, "Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity/Infrared Detection Method," ASTM International, West Conshohocken, PA, 2005.^{3,5}
- A-15. Burtseva, T., "Procedure for Hydrogen Analysis of Refractory Metals," ANL Intra-Laboratory Memo, IPS-467-00-00, Argonne National Laboratory, Argonne, IL, November 25, 2005 (ADAMS Accession No. ML15226A331).
- A-16. Yan, Y., T. Burtseva, and M. Billone, "Update on Breakaway Oxidation of Westinghouse ZIRLO Cladding," ANL letter report to the NRC, Jan. 8, 2009 (ADAMS Accession No. ML091330334).
- A-17. Yan, Y., T. A. Burtseva and M.C. Billone, "Breakaway Oxidation Tests for M5® Cladding," ANL letter report to the NRC, July 31 2009 (ADAMS Accession No. ML092710536).
- A-18. Yan, Y., T. Burtseva and M.C. Billone, "Progress Report on Breakaway Oxidation of Bare and Prefilmed ZIRLO," ANL letter report to the NRC, May 30, 2007 (ADAMS Accession No. ML080800314).

⁶ Copies of this paper may be purchased through Taylor & Francis Online. Website: <http://www.tandfonline.com>

APPENDIX B

RATIONALE FOR THE 200-WPPM HYDROGEN PICKUP CRITERION FOR BREAKAWAY OXIDATION

Table B-1 summarizes the increase in hydrogen pickup; with test times for three of the cladding materials tested by Argonne National Laboratory (see NUREG/CR-6967, “Cladding Embrittlement during Postulated Loss-of-Coolant Accidents” (Ref. B-1)). The hydrogen pickup rate was rapid for two of the cladding materials and more gradual for one of them. Given that breakaway oxidation is an instability phenomenon that can spread rapidly in the axial and circumferential directions, it is important to establish a hydrogen pickup or content limit for which cladding retains ductility. The criterion of 200-weight parts per million (wppm) hydrogen pickup was established before initiation of the NUREG/CR-6967 breakaway oxidation study. It was subsequently confirmed by conducting ring compression tests for samples sectioned from the breakaway oxidation samples. Table B-2 and Figure B-1 summarize the results of these ring-compression tests. Ductility is maintained for less than or equal to 435 wppm average hydrogen pickup. Thus, the 200-wppm hydrogen pickup criterion is conservative by a factor of at least two. However, it is not overly conservative for high oxidation temperatures because the time needed to increase from 200 wppm to >400 wppm hydrogen pickup could be as low as 100 seconds (s).

Table B-1. Summary of Hydrogen Pickup vs. Test Time for Several Cladding Materials Oxidized at 970–1,000 degrees C

Cladding Material	Test T, degrees C	Test Time, s	Hydrogen Content, wppm	Hydrogen Pickup, wppm	Comment
15×15 Low-Tin Zry-4 (Old)	985	3,600 3,800 3,900	186 40–60 1,260	170 20–40 1,320	Pre-scratched Lustrous-black outer surface Large Gray Areas on outer surface
15×15 Low-Tin Zry-4 (Modern)	985	5,000 5,400	286 411	280 410	Gray Line on outer surface Large Gray Area on outer surface
17×17 ZIRLO® (Modern)	985	3,400 3,400 3,600	174 50 267	175 20 270	Yellow Area along Pre-scratch Lustrous-black outer surface Yellow Circle on outer surface

Table B-2. Ductility at 135 degrees C vs. Hydrogen Pickup for Several Cladding Materials Oxidized at 970–1,000 degrees C

Cladding Material	Test T, degrees C	Hydrogen Content, wppm	Hydrogen Pickup, wppm	Offset Strain at 135 degrees C, %
15x15 Low-Tin Zry-4 (Old)	985	186	170	5.2
		1,260	1,320	0.9
15x15 Low-Tin Zry-4 (Modern)	985	286	280	6.0
		270	260	5.9
17x17 ZIRLO® (Modern)	985	174	175	5.1
	985	214	215	>2
	970	416	435	4.8
	1,000	555	600	0.8
	985	731	765	0.8
	985	987	1040	0.8

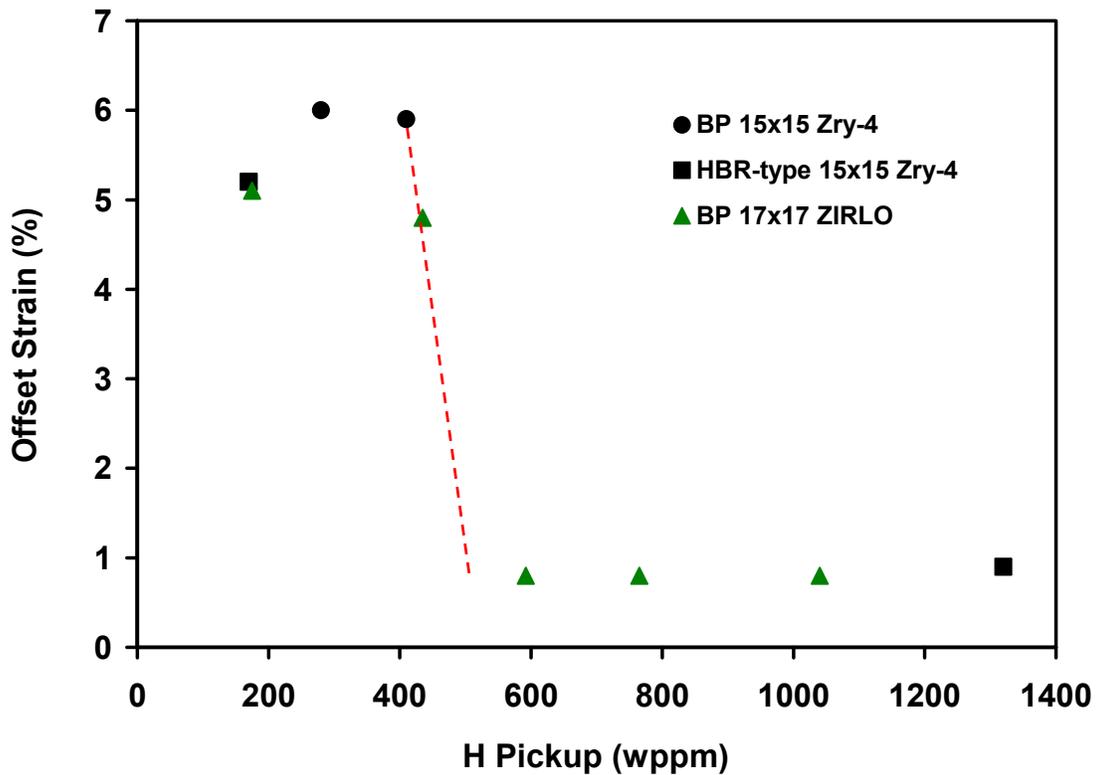


Figure B-1. Ductility (from ring compression tests at 135 degrees C) vs. hydrogen pickup for breakaway oxidation samples oxidized at 970–1,000 degrees C. Ductile-to-brittle transition occurs at \approx 500 wppm hydrogen pickup. “BP” refers to “belt polished” cladding and HBR-type refers to cladding comparable to H.B. Robinson vintage (i.e., old) cladding.

APPENDIX B REFERENCES¹

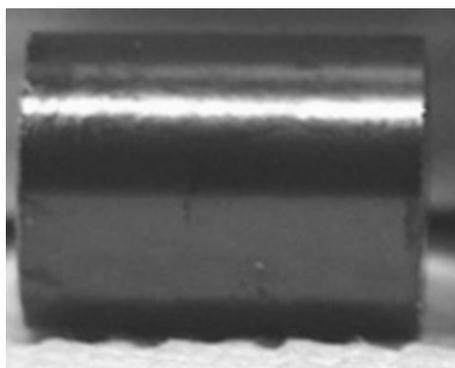
- B-1. U.S. Nuclear Regulatory Commission (NRC), NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," Washington, DC, July 2008.

¹ All NRC documents that are publicly available may be accessed through the Electronic Reading Room on NRC's public Web site at <http://www.nrc.gov/reading-rm/doc-collections/> and through the NRC's Agencywide Documents Access and Management System (ADAMS) at <http://www.nrc.gov/reading-rm/adams.html>. The documents can also be viewed online or printed for a fee in the NRC's Public Document Room (PDR) at 11555 Rockville Pike, Rockville, MD. For problems with ADAMS, contact the PDR staff at 301-415-4737 or 800 397-4209; fax 301 415-3548; or e-mail pdr.resource@nrc.gov.

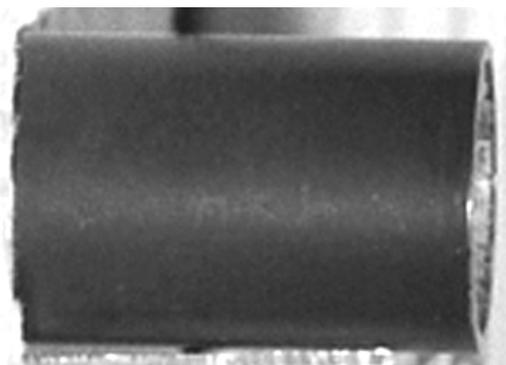
APPENDIX C

NEGATIVE EFFECTS OF ETCHING WITH HYDROFLOURIC-CONTAINING ACID AS PART OF SAMPLE CLEANING

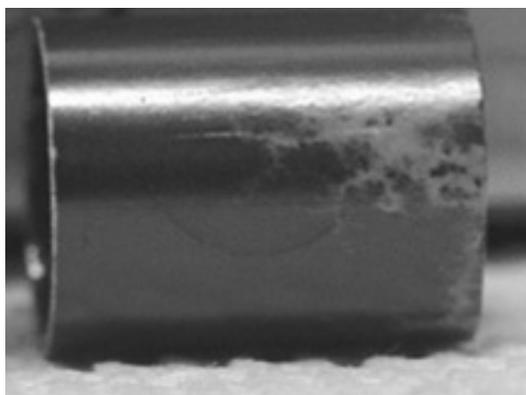
As part of the work in NUREG/CR-6967, “Cladding Embrittlement during Postulated Loss of Coolant Accidents” (Ref. C-1), 17×17 low-tin Zircaloy-4 (Zry-4), 17×17 ZIRLO[®], and 17×17 M5[®] alloy cladding samples were subjected to etching for 180 seconds (s) in a hydrofluoric (HF)-containing solution (3.5 percent-HF + 45 percent-HNO₃ + 51.5 percent-H₂O) before ultrasonic cleaning with ethanol and water. The samples were then oxidized for 2,400 s at 1,000 degrees Celsius (C) (1,832 degrees Fahrenheit (F)). The cladding materials showed different sensitivity to etching based on visual observation, with the inner surface showing more discoloration than the outer surface for each material. Hydrogen-content measurements were not performed because of the likely hydrogen pickup from inner surfaces. The outer cladding surfaces for the three oxidized materials are shown in Figure C-1. Pre-etched Zry-4 and M5[®] exhibited lustrous-black outer-surface oxides, while ZIRLO[®] showed signs of discoloration indicative of tetragonal-to-monoclinic transformation and breakaway oxidation.



(a) Zry-4



(b) M5[®]



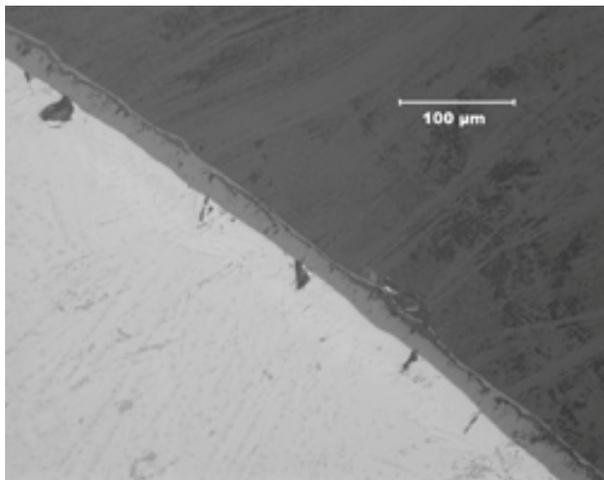
(c) ZIRLO[®]

Figure C-1. Outer surfaces of samples etched for 180 s in a 3.5%-HF acid mixture before oxidation at 1,000 °C for 2,400-s hold time: (a) Zry-4, (b) M5[®], and (c) ZIRLO[®]. (Note: The surface of M5[®] was lustrous-black, but the quality of the photograph is not high enough to show it.)

For the spent nuclear fuel program, ZIRLO[®] samples were etched in a 1 percent-HF acid solution for 180 s before hydriding. This worked well for the spent nuclear fuel application, for which relevant cladding temperatures are less than or equal to 400 degrees C (752 degrees F) and the cladding is in a non-oxidizing environment (helium-filled storage, transport, or storage-and-transport casks). However, HF-etching before hydriding caused breakaway oxidation for samples oxidized for only 280 s total test time with a hold time of 180 s at 1,200 degrees C (2,192 degrees F). Figure C-2a shows the appearance of the outer cladding surface after oxidation, and Figures C-2b and C-2c show regions of breakaway and intact oxide layers, respectively. The surface discoloration is significant. Some of the discoloration may be caused by impurities picked up during the hours of argon purging and exposure to Ar+30 percent H₂ at 400 degrees C (752 degrees F). Additional studies were performed with lightly etched samples exposed to the 1 percent-HF acid mixture for 60 s, 30 s, and 15 s. These samples were not exposed to the hydriding-furnace environment, so the only source of impurity was from the acid etching. The 15-s sample was cleaned in 80-degrees C (176-degrees F) distilled water before the standard ultrasonic cleaning in ethanol and distilled water. Figure C-3 shows that surface discoloration persists even for the 15-s-etch sample following oxidation at less than or equal to 1,200 degrees C (2,192 degrees F) for 280 s.



(a)



(b)



(c)

Figure C-2. Appearance and morphology of outer-surface oxide following etching for 180 s in 1%-HF acid bath, exposure to flowing argon (Ar) and Ar+30%H₂ for <10 hours at 400 degrees C and oxidation for 280 s with a 180-s hold time at 1,200 degrees C: (a) appearance of outer surface, (b) metallographic image showing breakaway oxidation under area of discoloration, and (c) metallographic image of intact oxide layer under black surface region.



Figure C-3. Outer-surface appearance of ZIRLO® sample that was etched for 15 s in a 1%-HF acid mixture, rinsed in 80 degrees C distilled water, ultrasonically cleaned in ethanol and water baths, and heated in steam from 300 degrees C to 1,200 degrees C in 100 s and held at 1,200 degrees C for 180 s. The hydrogen pickup was 510 ± 30 wppm.

APPENDIX C REFERENCES¹

- C-1. U.S. Nuclear Regulatory Commission (NRC), NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," Washington, DC, July 2008.

¹

All NRC documents that are publicly available may be accessed through the Electronic Reading Room on the NRC's public Web site at <http://www.nrc.gov/reading-rm/doc-collections/> and through the NRC's ADAMS at <http://www.nrc.gov/reading-rm/adams.html>. The documents can also be viewed online or printed for a fee in the NRC's Public Document Room (PDR) at 11555 Rockville Pike, Rockville, MD. For problems with ADAMS, contact the PDR staff at 301-415-4737 or 800-397-4209; fax 301-415-3548; or e-mail pdr.resource@nrc.gov.

APPENDIX D

CORRELATION BETWEEN CLADDING OUTER-SURFACE APPEARANCE AND HYDROGEN PICKUP

The breakaway oxidation tests documented in NUREG/CR 6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents" (Ref. D-1) were conducted with a furnace equipped with a viewing port. The window allowed viewing of about half the sample outer surface. Initial scoping tests were conducted for a fixed oxidation time. This process was refined such that tests were terminated when discoloration was observed to initiate on the cladding outer surface. As a result, a considerable database was generated for outer-surface appearance versus hydrogen content and hydrogen pickup. Examples from the work of Y. Yan et al., "Progress Report on Breakaway Oxidation of Bare and Prefilmed ZIRLO" (Ref. D-2) are presented here to guide investigators on what to expect from small discoloration spots and from larger areas of surface discoloration. These examples are from test samples exposed to higher steam oxidation temperatures (970–1,000 degrees Celsius (C) (1,778–1,832 degrees Fahrenheit (F))). For these samples, small areas of discoloration correlated with hydrogen pickups in the range of 50–250 weight parts per million (wppm), while larger areas of discoloration correlated to greater than 400 wppm of hydrogen. At lower oxidation temperatures (e.g., 800 degrees C) with corresponding lower hydrogen generation rates, significant surface discoloration may precede 200-wppm hydrogen pickup.

For Zircaloy-4 (Zry-4) cladding materials, the surface discoloration (indicative of breakaway oxidation and high hydrogen pickup) progresses from lustrous-black to dull-black to gray. Figure D-1 shows pre-breakaway H.B. Robinson (HBR)-type 15×15 Zry-4 following oxidation at about 1,000 degrees C (about 1,832 degrees F) for 3,600 seconds (s). The sample is lustrous-black but the hydrogen pickup is 40 wppm, indicating that breakaway is likely to occur within a few hundred seconds beyond 3,600 s. The other two samples were oxidized for long test times (5,400 s and 7,200 s). The outer surface of these samples is completely gray and the hydrogen pickup values are high. For Zry-4, by the time that the outer surface transforms from lustrous-black to gray, the sample is well beyond breakaway initiation.

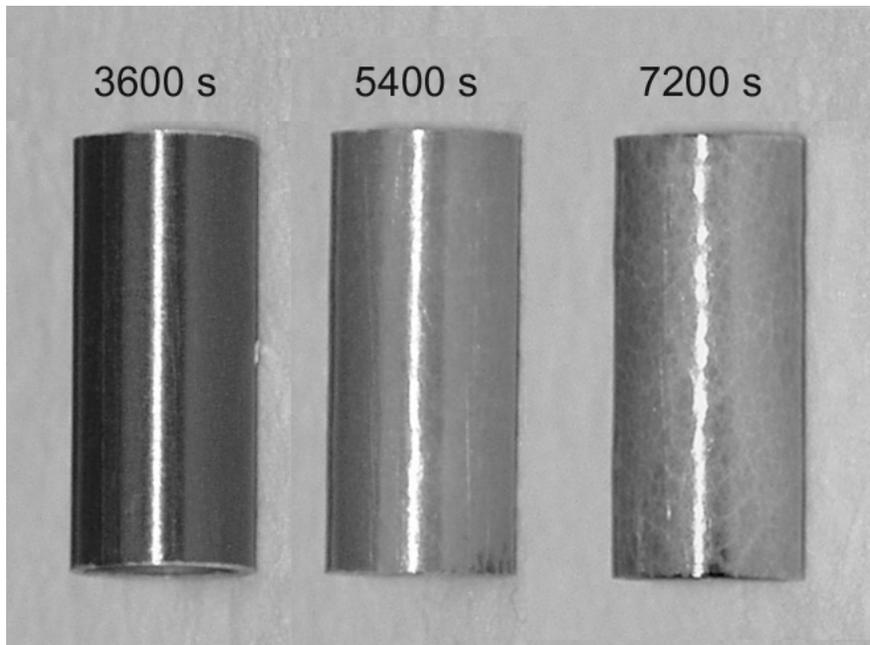
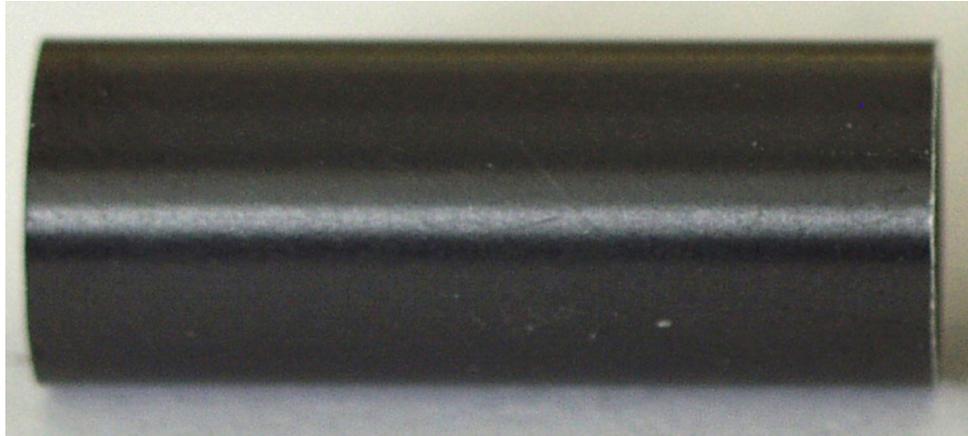


Figure D-1. Outer-surface appearance of an older vintage (HBR) of 15×15 Zry-4 following oxidation at $\approx 1,000$ °C for 3,600 s (lustrous-black with 40-wppm hydrogen pickup), 5,400 s (gray with 2,300-wppm hydrogen pickup), and 7,200 s (with 3,100-wppm hydrogen pickup).

Similar results were obtained for 17×17 ZIRLO® oxidized at 1,000 degrees C (1,832 degrees F). However, for ZIRLO®, the color change of the outer surface was from lustrous-black to yellow (or tan). Figure D-2 shows the transformation of colors from lustrous-black to lustrous-black with yellow spots to yellow.



(a) 1,500 s at 1,000 degrees C; 5-wppm hydrogen pickup



(b) 3,600 s at 1,000 degrees C; 60-wppm hydrogen pickup



(c) 5,000 s at 1,000 degrees C; 1,350-wppm hydrogen pickup

Figure D-2. Outer-surface appearance and hydrogen pickup for ZIRLO® samples oxidized at 1,000 °C: (a) lustrous-black at 1,500 s, (b) lustrous-black with yellow spots at 3,600 s, and (c) yellow at 5,000 s.

For polished 15x15 Zry-4, the minimum breakaway oxidation time is about 5,000 s and occurs at a long-time oxidation temperature of 985 degrees C (1,805 degrees F). Figure 38a in NUREG/CR-6967 shows the appearance of the outer surface of the sample oxidized at 985 degrees C for 5,000 s (it is included below as Figure D-3 for the convenience of the reader). The sample exhibited a gray line along the axial direction. Metallography (Figures 38b and c in NUREG/CR-6967) confirmed that the outer-surface oxide under this gray region was in breakaway, while the inner-surface oxide was still intact. Also, the circumferential variation of hydrogen was significant, with a peak in hydrogen concentration under the gray layer. The sample picked up 280-wppm hydrogen, which is just beyond the 200-wppm criterion.

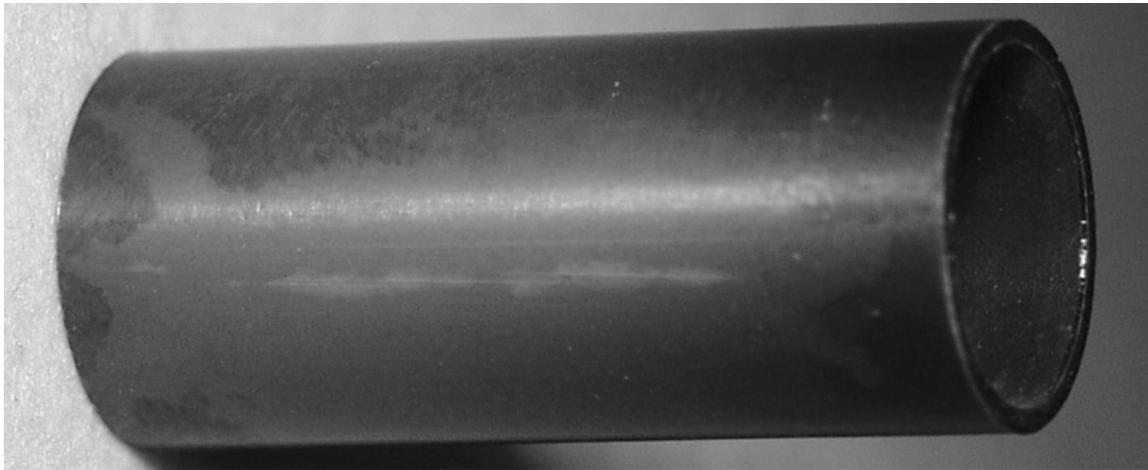


Figure D-3. Polished 15x15 Zry-4 cladding oxidized at 985 °C for 5,000 s. The gray line along about two-thirds of the sample length is the region under which breakaway oxidation had occurred. Circumferentially averaged hydrogen pickup was 280 ± 160 wppm. Hydrogen pickup under the gray streak was >460 wppm.

Figures D-4 to D-9 show ZIRLO[®] samples with surface discoloration and the corresponding hydrogen pickup. It is clear from these photographs that any visual evidence of breakaway oxidation, even small spots, is indicative of initiation of local breakaway oxidation and hydrogen pickup. Figures D-4 to D-6 correspond to Figures 81 to 83 in NUREG/CR-6967. Figure D-7 is taken from Figure 2 of Y. Yan, T. Burtseva, and M. Billone, "Update on Breakaway Oxidation of Westinghouse ZIRLO Cladding (Ref. D-3), and Figures D-8 and D-9 are taken from Figures 2 and 4 of Y. Yan, T. Burtseva and M.C. Billone, "Progress Report on Breakaway Oxidation of Bare and Prefilmed ZIRLO (Ref. D-2).

Figure D-10 is from Y. Yan, T.A. Burtseva, and M.C. Billone, "Breakaway Oxidation of ZIRLO Exposed to Transient Temperature Histories (Ref. D-4). The sample was oxidized at an isothermal temperature of 980 degrees C (1,796 degrees F) for 2,000 s. The temperature was cycled five times from 1,030 degrees C (1,886 degrees F) to 930 degrees C (1,706 degrees F) for 400 s before an additional 400-s isothermal oxidation at 980 degrees C. The surface-discoloration pattern is different from those obtained from isothermal tests, and the color is a mixture of yellow and gray.

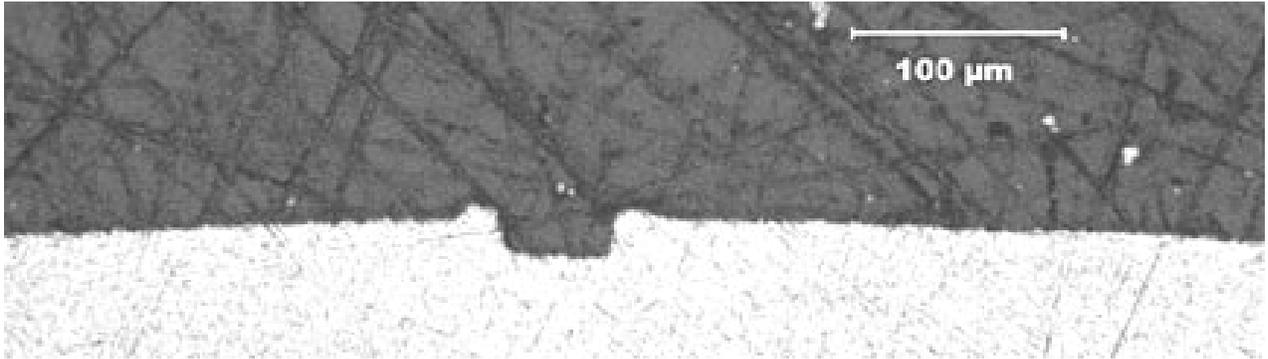


Figure D-4. Cross section of ZIRLO[®] cladding with machined scratch \approx 20-micrometers deep into outer surface

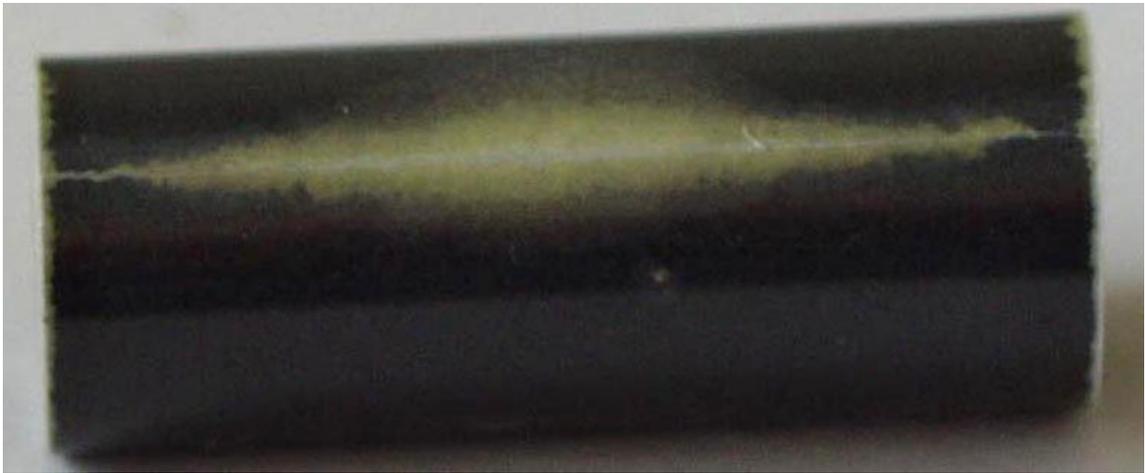


Figure D-5. Outer surface of scratched ZIRLO[®] sample following oxidation at 985 degrees C for 3,400 s. Local hydrogen pickup under the yellow surface was 440 wppm; average pickup was 175 wppm.

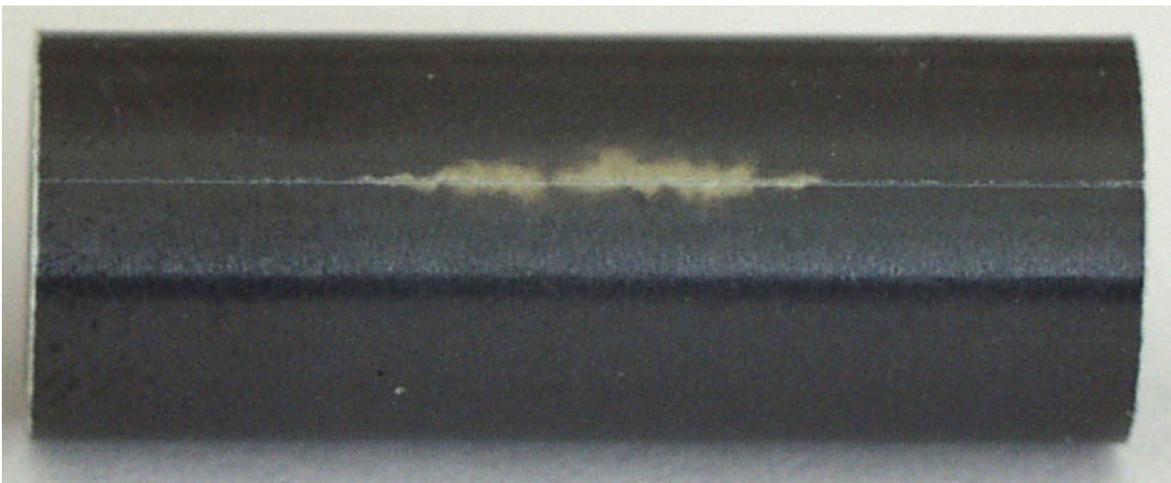


Figure D-6. Outer surface of scratched ZIRLO[®] sample following oxidation at 970 degrees C for 2,600 s. Local hydrogen pickup under the yellow surface was 120 wppm; average pickup was 44 wppm.

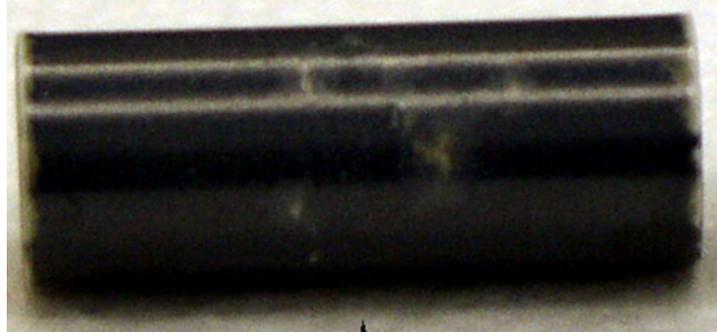


Figure D-7. Outer-surface appearance for ZIRLO® sample oxidized at 1,000 degrees C for 4,000 s. Hydrogen pickup was 120 ± 110 wppm with >280 wppm under the yellow spots.

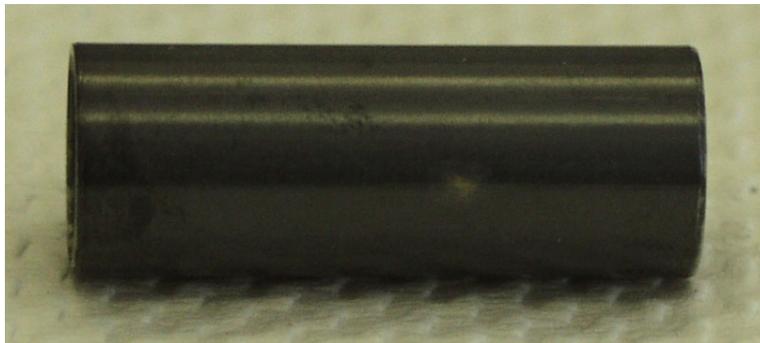


Figure D-8. Outer surface of prefilmed ZIRLO® oxidized at 985 degrees C for 3,000 s. One yellow spot can be seen just to the right of the sample midplane. Hydrogen pickup in a 2-mm-long ring including the yellow spot was 50 ± 40 wppm.

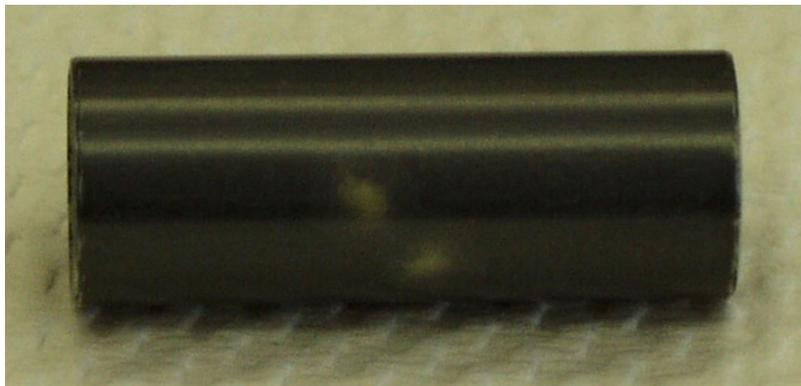
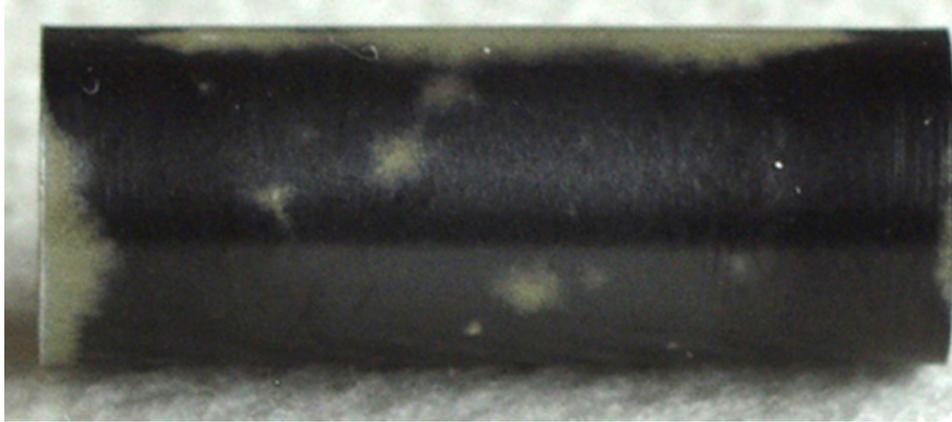
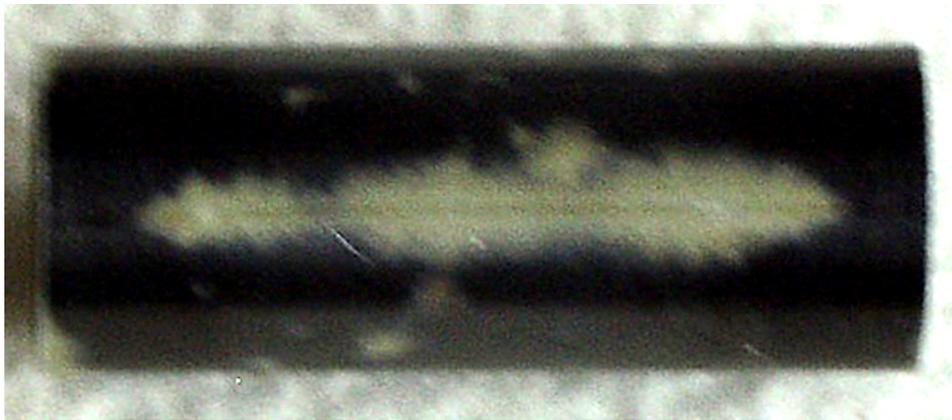


Figure D-9. Outer surface of prefilmed ZIRLO® oxidized at 980 degrees C for 3,200 s. Two small yellow spots can be observed. Hydrogen pickup in a 2-mm-long ring sectioned to include a yellow spot was 120 ± 120 wppm, with 300-wppm hydrogen under the spot. For a sibling sample tested under the same conditions, the local hydrogen content under the yellow spot was 470 wppm.



(a)



(b)

Figure D-10. Outer-surface appearance of as-fabricated ZIRLO[®] sample oxidized for a total test time of 2,800 s: 2,400 s at 980 degrees C and 400 s with five temperature cycles from 930 to 1,030 degrees C. Hydrogen content was measured to be 230 ± 80 wppm, indicating breakaway oxidation for a total test time of 2,800 s.

APPENDIX D REFERENCES¹

- D-1. U.S. Nuclear Regulatory Commission (NRC), NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," Washington, DC, July 2008.
- D-2. Yan, Y., T. Burtseva and M.C. Billone, "Progress Report on Breakaway Oxidation of Bare and Prefilmed ZIRLO," Argonne National Laboratory (ANL) letter report to the NRC, May 29, 2007. (ADAMS Accession No. ML080800314).
- D-3. Yan, Y., T. Burtseva, and M. Billone, "Update on Breakaway Oxidation of Westinghouse ZIRLO Cladding," ANL letter report to the NRC, Jan. 8, 2009. (ADAMS Accession No. ML091330334).
- D-4. Yan, Y., T.A. Burtseva, and M.C. Billone, "Breakaway Oxidation of ZIRLO Exposed to Transient Temperature Histories," ANL letter report to the NRC, April, 2009. (ADAMS Accession No. ML092710523).

¹

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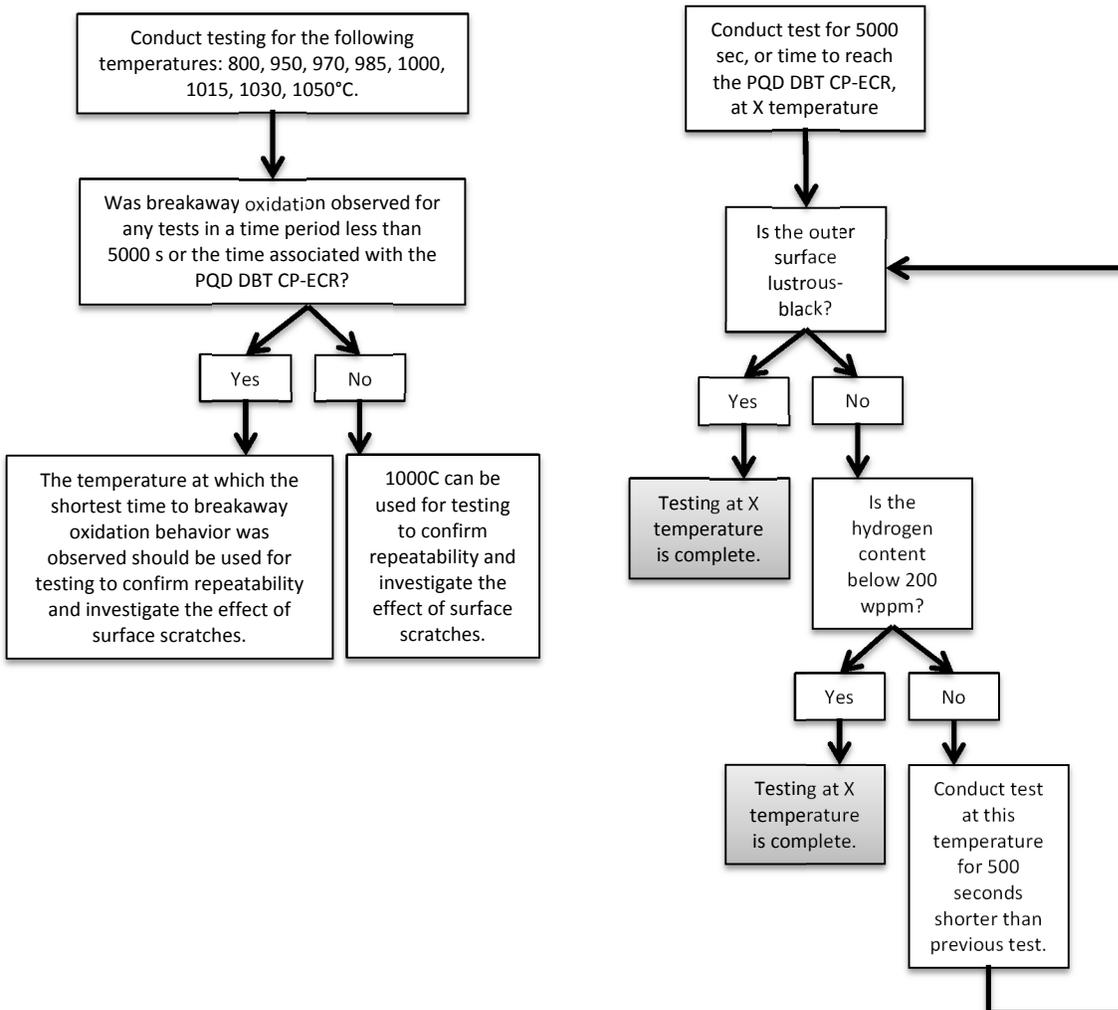
APPENDIX E

OVERVIEW AND LOGIC DIAGRAM TO ILLUSTRATE SAMPLE TEST MATRICES

Establishing the susceptibility to breakaway oxidation for a zirconium cladding alloy

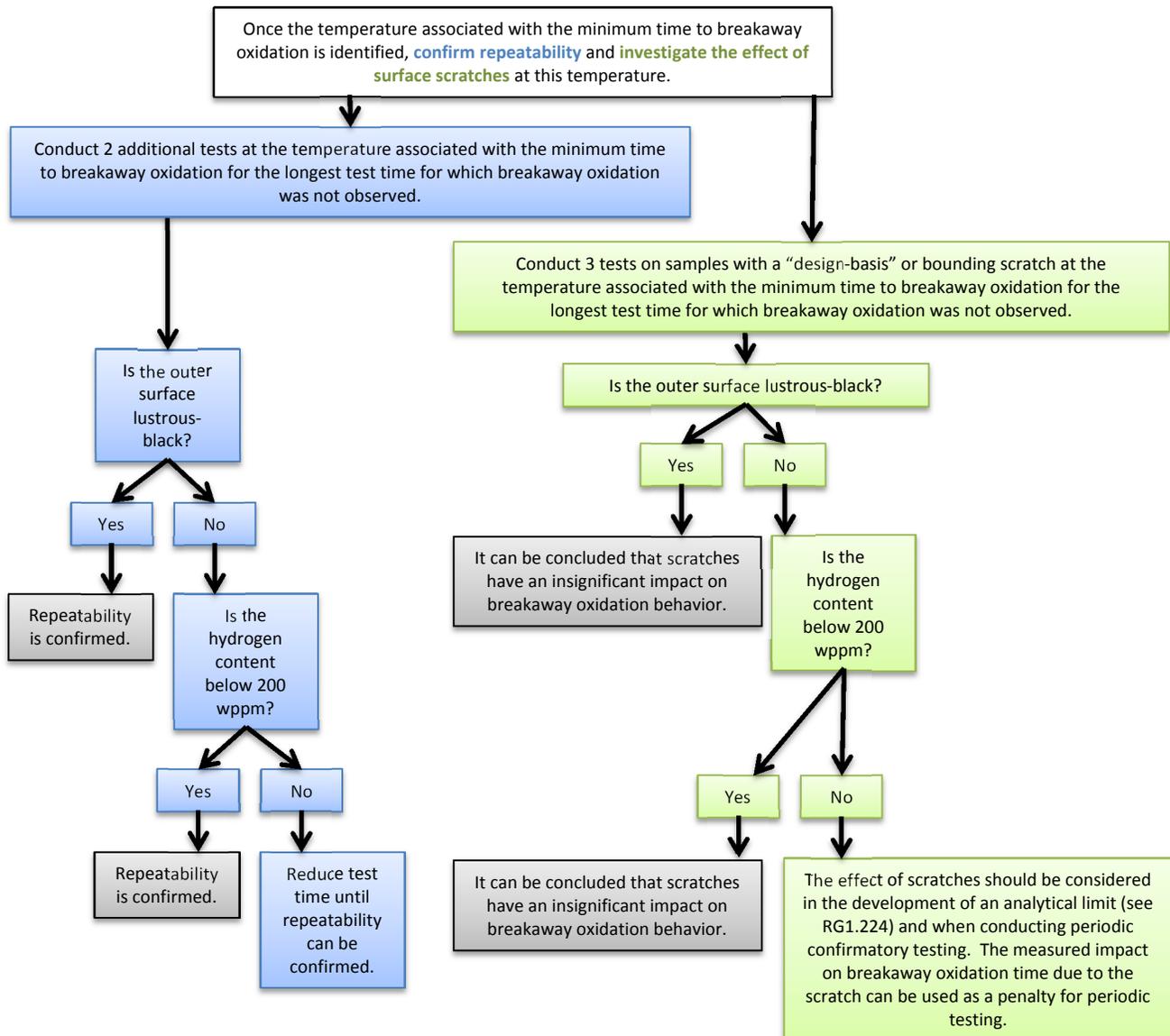
The diagram below is provided to illustrate the test matrix described in Section A-10, “Test Temperatures,” of Appendix A to this regulatory guide for initial characterization of a cladding alloy’s breakaway oxidation behavior. The test matrix begins with eight tests, conducted incrementally within the range of temperature at which breakaway may occur.

The logic diagram can be repeated for each reduction in time increment. Time reduction increments of 500 seconds are recommended as a practical increment to search for a reduced time scale at which breakaway oxidation does not occur.



Once each temperature has been tested with a logic diagram conclusion of “Testing at X temperature is complete,” additional tests should be conducted to demonstrate repeatability and to characterize the influence of a surface scratch.

Two additional tests should be conducted at the temperature at which the minimum test time was recorded (if none of the initial test series resulted in observation of breakaway behavior, two tests at 1,000 °C should be conducted). To characterize the influence of a surface scratch, three repeat tests, at the conditions (time and temperature) of the minimum observed breakaway behavior, should be conducted on samples with a bounding or design-basis scratch.



To elaborate on the two possible breakaway criteria within the logic diagram, it is useful to refer to Figure D-2b in Appendix D to this regulatory guide. In this image, yellow spots are observed on the surface of the cladding. This observation would lead to the “No” tree of the logic diagram above, which asks if the outer surface is lustrous-black. The logic tree then calls for a hydrogen content measurement.

In this case, 60-wppm hydrogen was measured. This observation would lead to the “Yes” tree of the logic diagram above and therefore complete testing for a particular temperature with the conclusion that breakaway oxidation had not occurred for the test temperature and time combination.

Periodic Testing for breakaway oxidation behavior

In the case of periodic testing, it is acceptable to measure the breakaway oxidation behavior of the specified sample population or test frequency for only the temperature at which the minimum time to breakaway oxidation was measured, or at 1000°C, if all temperatures show no breakaway oxidation by 5,000 seconds, and to demonstrate that breakaway oxidation is not experienced within the time of the established analytical limit. The test matrix below illustrates the reduced test matrix described in Section C of this regulatory guide.

