ARGONNE NATIONAL LABORATORY

INTRA-LABORATORY MEMO

June 1, 2007

TO: M. C. Billone

FROM: Y. Yan

SUBJECT: Work Plan for the Breakaway Oxidation of ZIRLO Cladding at 800-1015ºC

PURPOSE

Use this work plan to conduct the breakaway oxidation tests in steam at 800-1015ºC with unirradiated ZIRLO cladding samples. The tests are to determine the breakaway oxidation time and to generate a reliable data set for the increase in oxidation rate (i.e., weight gain rate) and the associated hydrogen pickup that causes embrittlement. The criterion for breakaway oxidation is 200-wppm hydrogen pickup due to breakaway oxidation of the outer-surface oxide layer.

GENERAL DESCRIPTION

In accordance with the current NRC-LOCA program plan, oxidation tests will be conducted on unirradiated ZIRLO cladding samples to characterize the evolution with time at temperature of the oxygen and hydrogen pickup and of the oxide thickness and morphology.

The conditions for the planned tests are given in Table 1. The minimum times for breakaway oxidation of Zry-4 occur at oxidation temperatures of 800ºC and 1000ºC [1]. In terms of hydrogen pickup, 1000ºC-oxidation gives the minimum breakaway time. Therefore, tests are to be conducted at 950-1015ºC and 800ºC under near saturated steam conditions. The test samples will be 1”-long segments of cladding tube with the ends ground flat and square. Extensive benchmark oxidation tests in steam have been conducted. Three Type S thermocouples (TCs 1-3) were spot welded onto the Inconel specimen holder (120°C apart and 1/4” above the sample) and two Type S thermocouples (TCs 4-5) were spot welded onto the 1”-long ZIRLO sample (see Fig. 1). These benchmark results allow additional tests to be conducted without welding TCs onto the samples. A temperature history of the benchmark test with a ZIRLO sample in the as-received condition is shown in Fig. 2. The calculated weight gain K is obtained by Cathcart-Pawel (CP) equations for Zry-4

$$K^2 = \delta^2 t \qquad (1)$$

$$\delta^2/2 = 0.1811 \exp(39940/RT) \qquad (2)$$

where the parabolic rate constant $\delta^2/2$ is given by Cathcart et al. [2] in $(g/cm^2)^2/s$. Based on previous ANL studies, the weight gain for ZIRLO oxidized for long times at 1000°C is expected to be lower than the CP-predicted value for Zry-4.

Table 1 Test Matrix for Breakaway Oxidation Tests with ZIRLO Supplied by Westinghouse in 2006; tests conducted with ZIRLO supplied in 2003 are also included

ZIRLO Lot	T °C	Test Time[a] s	CP Wg mg/cm^2
2006	1015	4000	15.6
2006	1000	1500	8.63
2003	1000	2440	11.1
2003	1000	3480	13.0
2006	1000	3600	13.5
2006	1000	4000	14.2
2006	1000	4200	14.5
2006	1000	5000	15.9
2006	985	3400	11.9
2006[b]	**985**	**3400**	**11.9**
2006	985	3600	12.3
2006	985	4000	12.9
2006[b]	**970**	**2600**	**9.5**
2006	970	3000	10.2
2006	970	3400	10.8
2006	950	3000	8.9
2006	800	4000	---

[a]Includes time from beginning of ramp at 300ºC to end of hold time at oxidation temperature.

[b]Samples with machined scratch, ≈20-μm deep into the outer surface.

The purpose of this memo is to document the procedure for conducting breakaway oxidation tests with ZIRLO samples. These tests are to be conducted in the out-of cell LOCA Integral Test Apparatus under near saturated steam conditions.

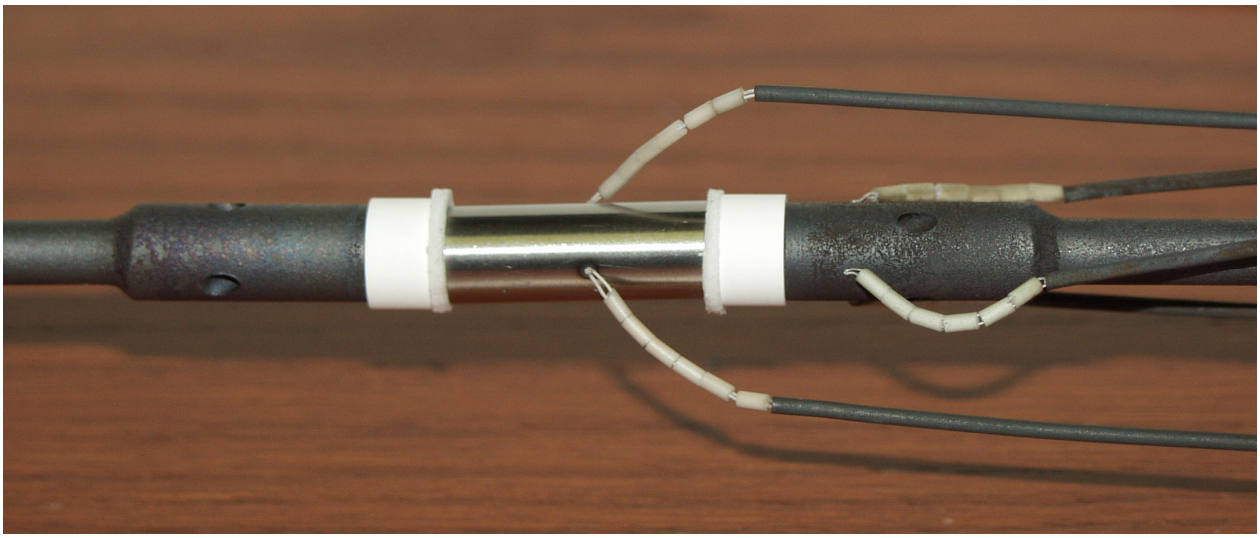

Fig. 1. Test train design for two-sided oxidation tests with three holes drilled into the Inconel holder below the sample (left) for steam ingress and three holes drilled into the holder above the sample for steam egress. Also shown are the three TCs permanently welded to the Inconel holder just above the sample.

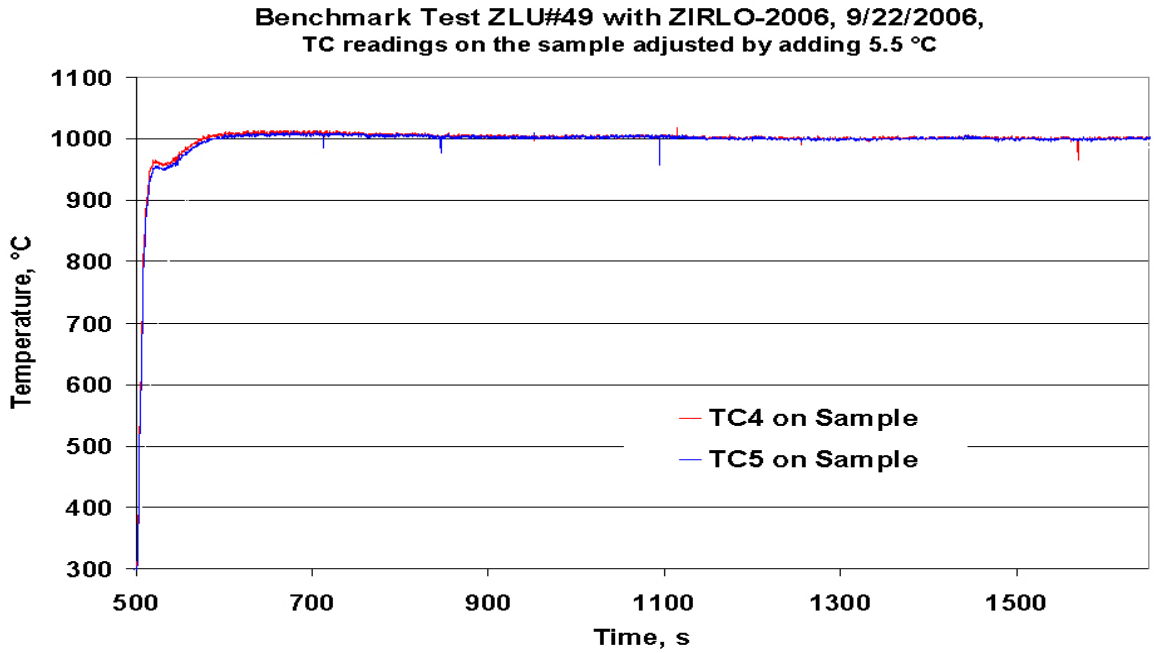

Fig. 2 Thermal benchmark result with two TCs welded onto as-fabricated, 17×17 ZIRLO cladding. The sample hold temperature is 1000±5ºC, where 1000ºC is the average of the two TC readings and ±5ºC is the circumferential variation.

SAMPLES

The as-fabricated oxidation samples shall be cut from a fresh 39"-long ZIRLO cladding tube, received in 2006. Before the oxidation test, the diameter of each sample shall be measured with a micrometer to an accuracy of ±0.001 in. The measurement shall be done at two azimuthal orientations 90° apart at the axial center of the sample. Length measurements are also taken. The sample then will be cleaned with Ethanol and then in distilled water in an ultrasonic bath for 2-3 minutes. Sample weight measurements will be conducted before and after each test with a balance to an accuracy of ±0.0001 gram. Data are recorded on data sheet (see Appendix A; note: the term specimen is used for sample in the datasheet).

For as-received ZIRLO tubing, dimensional characterization has been performed by ANL Central Shop. IPS determined the oxygen and hydrogen content by vacuum extraction (LECO). The results are shown in Table 2 and compared to the results for the ZIRLO received in 2003

Table 2. Materials Characterization of ZIRLO in As-received Condition

	2003	2006
Measured Outer Diameter, mm	9.50	9.484 ± 0.003
Measured Wall thickness, mm	0.57	0.568 ± 0.003
Surface Roughness, μm	0.11± 0.01	0.17 ± 0.03
Measured H Content, wppm	5 ± 0	11± 3
Measured O Content, wppm	1185 ± 30	1164 ± 26
Surface Condition	No scratches observed	No scratches observed

PROCEDURE

A. Sample Cleaning & Loading and Apparatus Assembly

Note: before loading the sample, the apparatus including the quartz tube should be appropriately installed and aligned.

1. Measure mass and length of sample and record data on the datasheet (see Appendix A).
2. Clean sample by using ultrasonic cleaner with Ethanol and then water for 200 s.
   Use rubber or latex gloves to handle sample after cleaning.
3. Place sample and test rig on a table.
4. Assemble sample with ceramic fittings and gaskets to test rig loosely (≈1-mm gap between ceramic fitting and Inconel holder). Avoid any possible damage to Type S TCs welded onto Inconel holder.
5. Place the test rig into quartz tube.
6. Plug extension wires of TCs into S-type TC connectors.
7. Check with PI to ensure that assembly is acceptable.

B. Test Conduct

8. Fill boiler with 1000 ml of distilled water. Pull red scram button on control panel.
9. Close steam control valve **B4** to test chamber.
10. Open by-pass valve **B3**.
11. Start boiler immersion heater at position 72.
12. Open valve to allow circulating water to flow through furnace.
13. Check to ensure that circulating water is flowing through the furnace.
14. Turn on breaker of 480V power. The cable connects to control cabinet, which contains controller for the furnace.
15. Document conduct of the test in experiment datasheet (see Appendix A). Each experiment shall be identified as "ZLU-XX". Record test time and temperature.
16. After boiler thermocouple reads 100°C, turn off by-pass valve **B3.**
17. Open valve **B4** to test chamber.
18. Wait until TE1-3 reading is at ≈30°C in test chamber. Temperatures are monitored by display panels on control cabinet.
19. Start the test program.
    - Double click shortcut of "**Stype.LTC**" on computer screen.
    - Set testing target temperature according to datasheet provided by the PI.
    - Hit "start" box on computer screen. The oxidation program should start to record the data.
    - Wait 10 seconds, and then pull green button on controller panel to start the furnace.
    - Monitor temperature change on controller panel and on DAQ screen. The furnace controller will run test sequence. It will ramp to 300°C and stay at 300°C for 500 s.
20. Use timer inside of window **Block StypeA** to monitor test time.
21. If test time is longer than 20 minutes, add 50 ml water to the boiler every 10 minutes.
22. Maintain boiler-water temperature at 100±0.5ºC.

C. Completion of Test

23. When the time at temperature has been reached, turn off furnace by pressing scram button.
24. Turn off immersion heater in boiler when furnace temperature is <800°C.
25. Open by-pass valve **B3**
26. Close the valve **B4**.
27. Stop test program (Click "File" on menu-bar and the click "Exit" from pull-down menu, or just click on X button at corner of window).
28. Turn off breaker.
29. When furnace temperature is <40°C, open radiant furnace and unplug test rig.
30. Photograph sample in situ if requested by PI.
31. Remove sample from the insert.
32. Weigh sample with balance and record data on the datasheet (see Appendix A).
33. Store sample in labeled vial provided by PI.

Metallographic examination, oxygen analysis and hydrogen analysis may be requested by the PI. The step-by-step instructions for metallographic examinations of unirradiated ZIRLO

cladding are given in IPS-335-01-02. The data summary and results of the post-test examinations will be reported separately in IPS-490-01-xx.

References

[1] S. Leistikow and G. Schanz, Nuclear Engineering and Design 103 (1987) 65-84.
[2] J. V. Cathcart et al, ORNL/NUREG-17 (1977).

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NRC Program File
IPS Document File

Appendix A

Data Sheet for NRC Oxidation Tests

Date: _____ Operator_____

Specimen No. _____ Test No._____

Material Information:

Heat/Composition_____ Irradiation Conditions _____

Testing Conditions:

Target Temperature (°C)_____ Test Duration (s) _____

Benchmark Test ID / PID =_____ Test Train # _____

ID Argon Pressure =_____psi/cfh OD Argon Purge = _____psi/cfh

Control/Set-point TC _____ Other TCs_____

Sample Information	Pre-test	Post-test	Measured Difference
Weight (g)			
Length (inch)			
OD (inch)			
Std. Mass (5.0000 g)			

CP WG (mg/cm^2) _____ CP ECR (%):_____

Comments:

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