Update on GIF LBL Round Robin

John Hunn
Fred Montgomery
Chuck Baldwin
Tyler Gerczak
Grant Helmreich

Advanced Gas Reactor
TRISO Fuels Program Review

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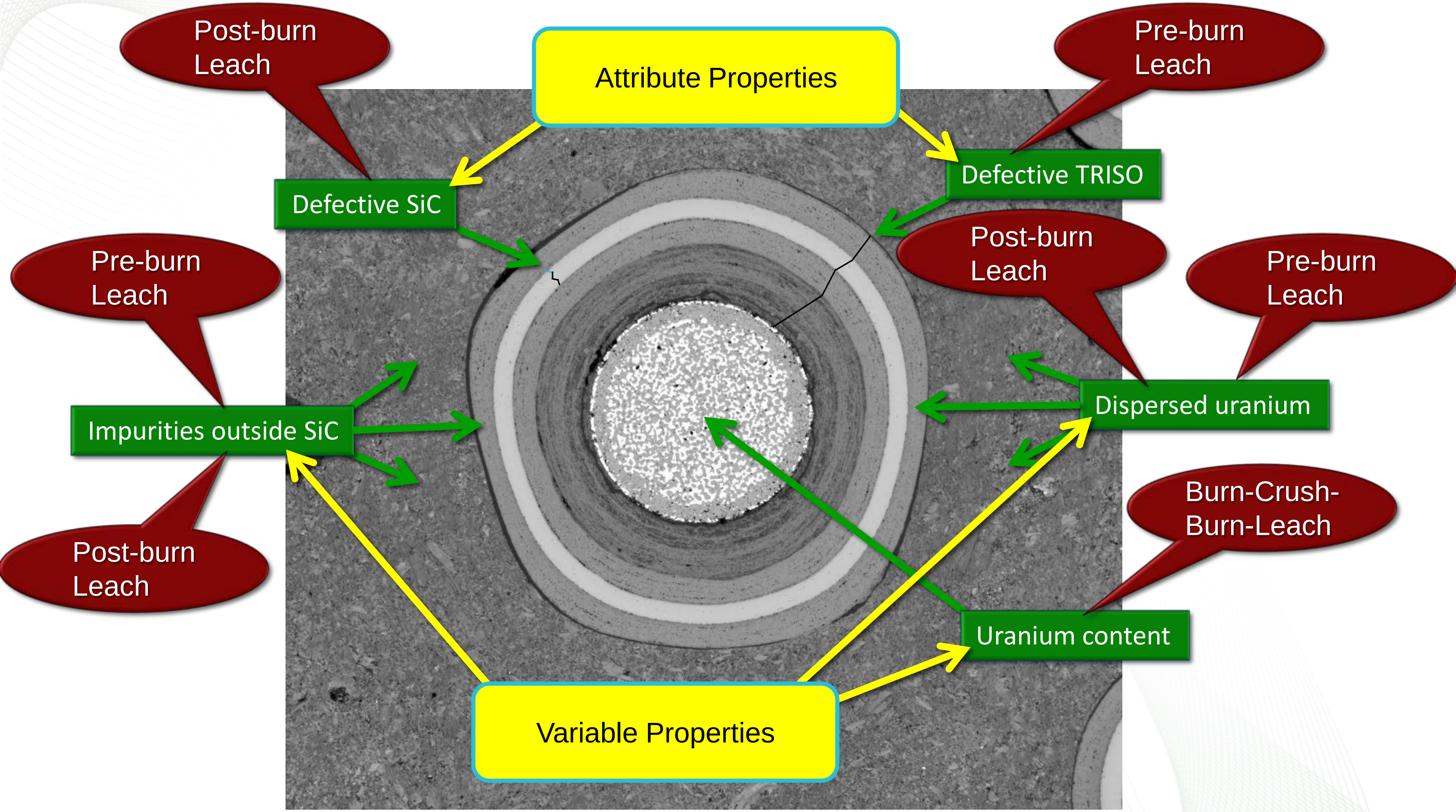
Outline

- Background and summary of the cooperative LBL benchmark exercise
- Review of the general approach for the round robin experiment
  - measured properties
  - sample preparation
  - measurements to be performed
  - fabrication of simulated pre-burn leach defects
  - fabrication of simulated post-burn leach defects
- Results of ORNL measurements

Background

- The Generation IV International Forum (GIF) Very High Temperature Reactor (VHTR) Fuel and Fuel Cycle Project Management Board (FFC-PMB) is coordinating a cooperative round robin experiment to benchmark the Leach-Burn-Leach (LBL) process that is a key Quality Control (QC) measurement used to measure defect fractions in tristructural isotropic (TRISO) particle fuel.
- This benchmarking exercise is unique from previous GIF-VHTR-FFC-PMB QC benchmark projects in that it has involved the exchange of depleted uranium bearing TRISO particles.
- Because LBL defects fractions are typically very low (10^{-5} range), very large samples would be required to reduce the statistical sampling error to a level that would allow useful round robin comparison of LBL analysis on random samples from a single TRISO composite.
- To improve the accuracy of the LBL benchmarking exercise, the use of simulated LBL defects was chosen so that the defect fraction would be known in each sample.
- ORNL completed fabrication and analysis of the simulated LBL defects in 2016 using depleted urania (DUO_2)-TRISO (see ORNL/TM-2015/722-R2).
- Samples with simulated LBL defects were shipped from ORNL to the Korean Atomic Energy Research Institute (KAERI) in January 2017 and approval for receipt of samples at the Institute of Nuclear and New Energy Technology (INET) is nearing completion.
- INET is preparing to ship larger (~95,000-particle), representative samples of DUO_2 -TRISO.

Properties and defects of interest



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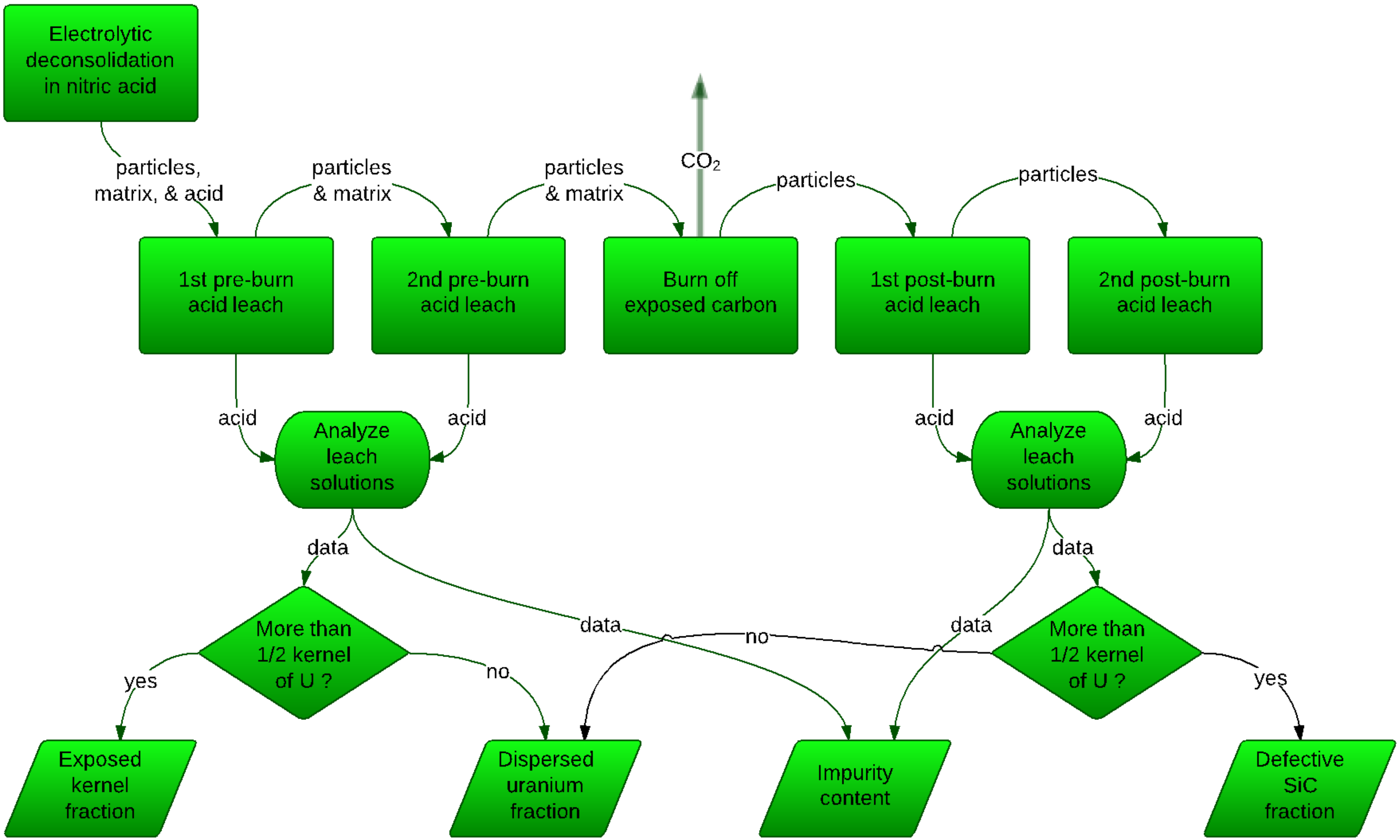
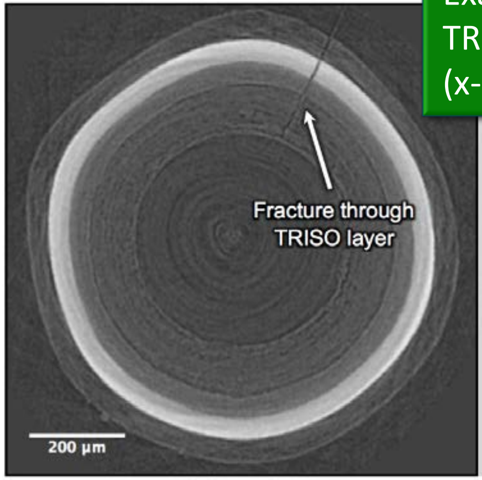
ORNL LBL flow diagram

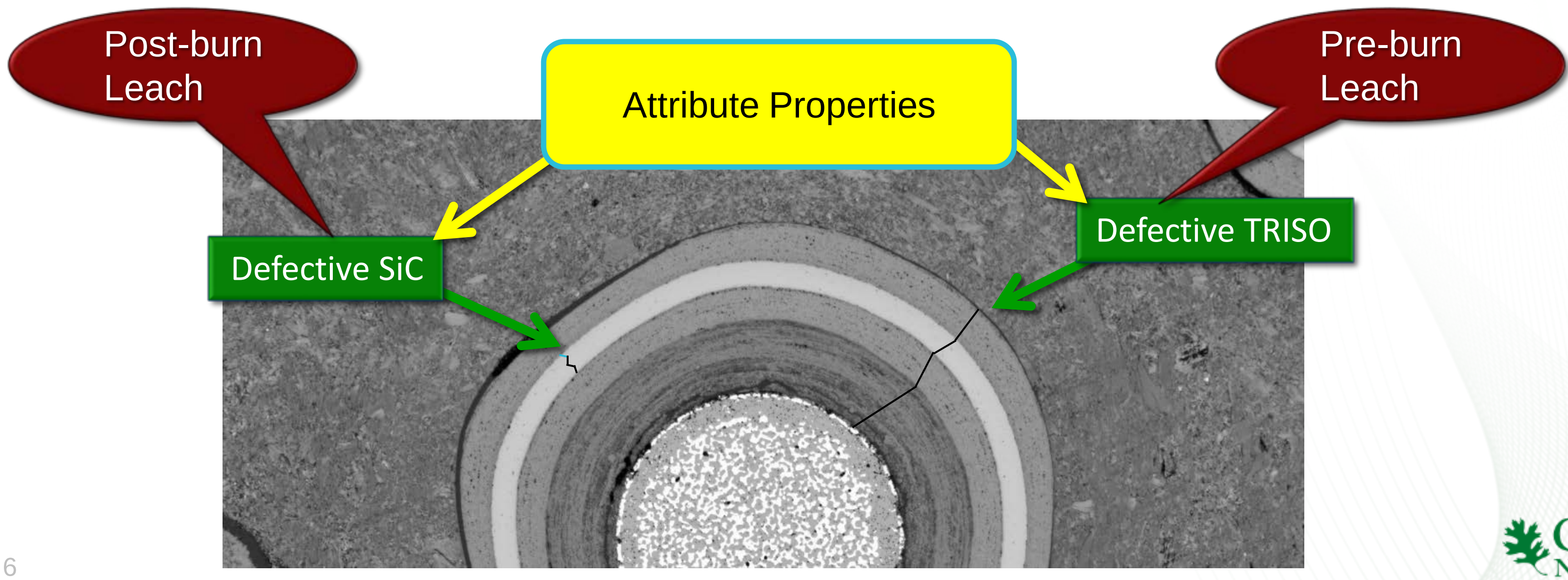


General approach for LBL benchmark – Attribute properties

- Measure **attribute** properties using ORNL samples containing particles with simulated LBL-defects
  - (a) TRISO defect
    - simulate a failed TRISO coating
  - (b) SiC defect
    - simulate a failed SiC (IPyC must be intact)



Example of a TRISO defect (x-ray image)



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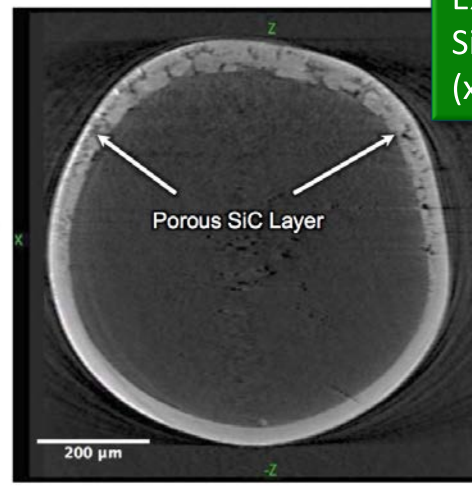
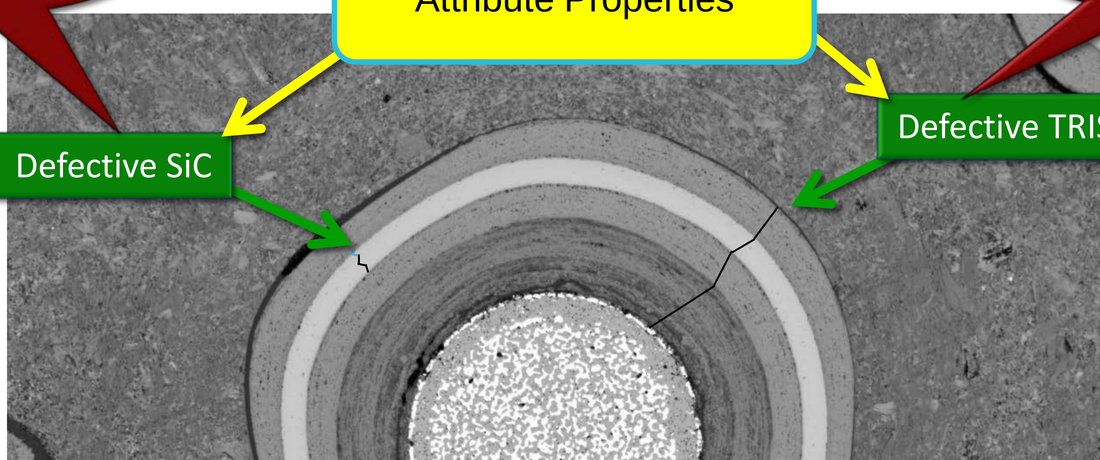
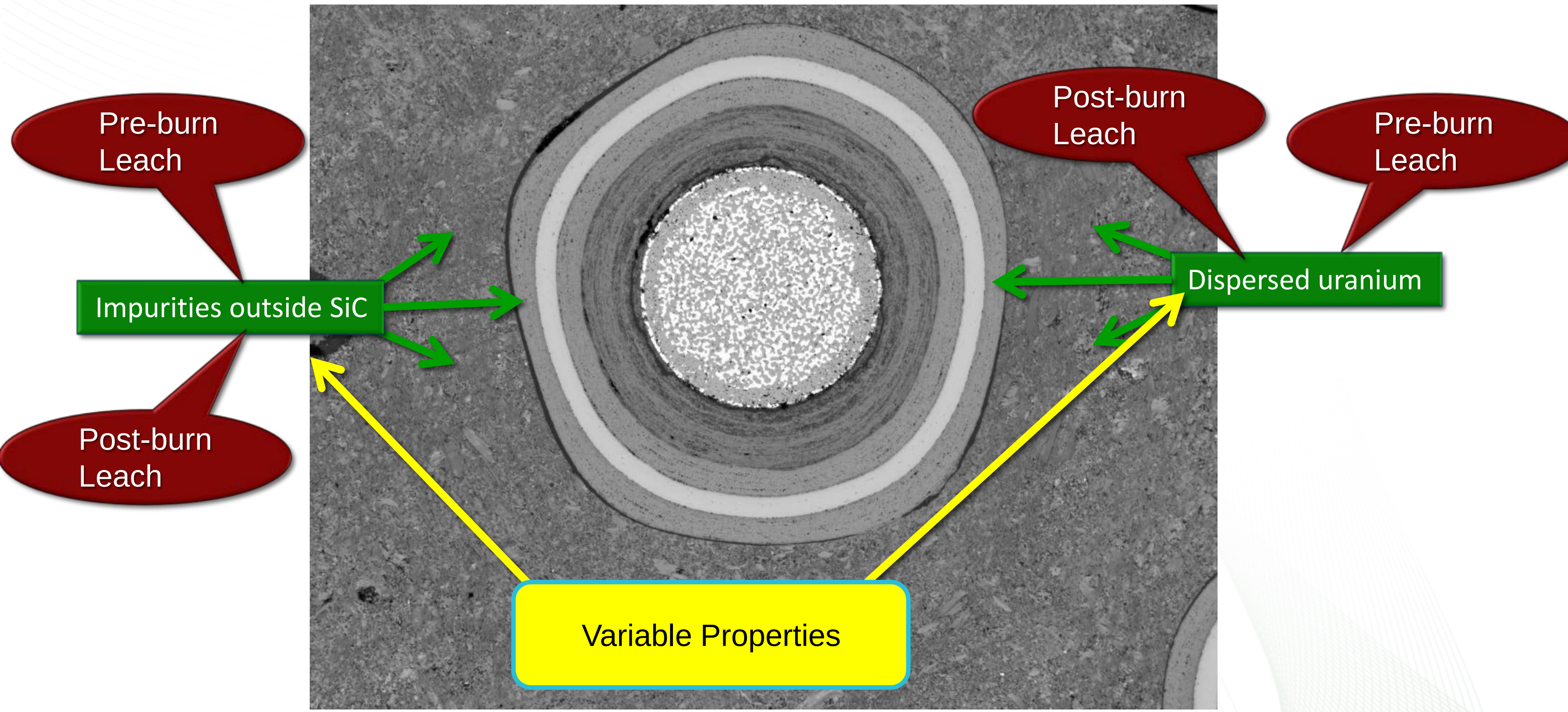


Example of a SiC defect (x-ray image)



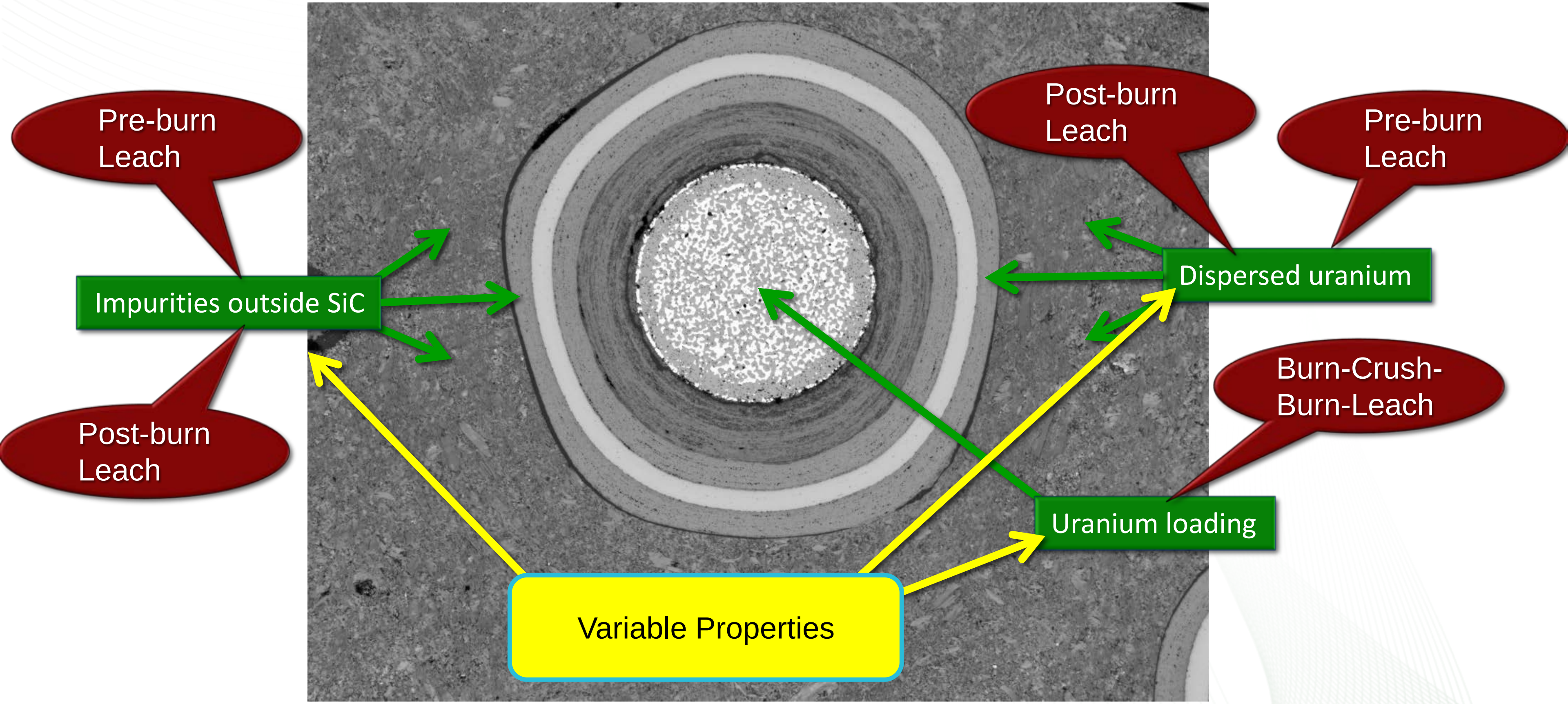
General approach for LBL benchmark – Variable properties

- Include known amount of an impurity standard in ORNL samples to provide round robin data on impurity analysis



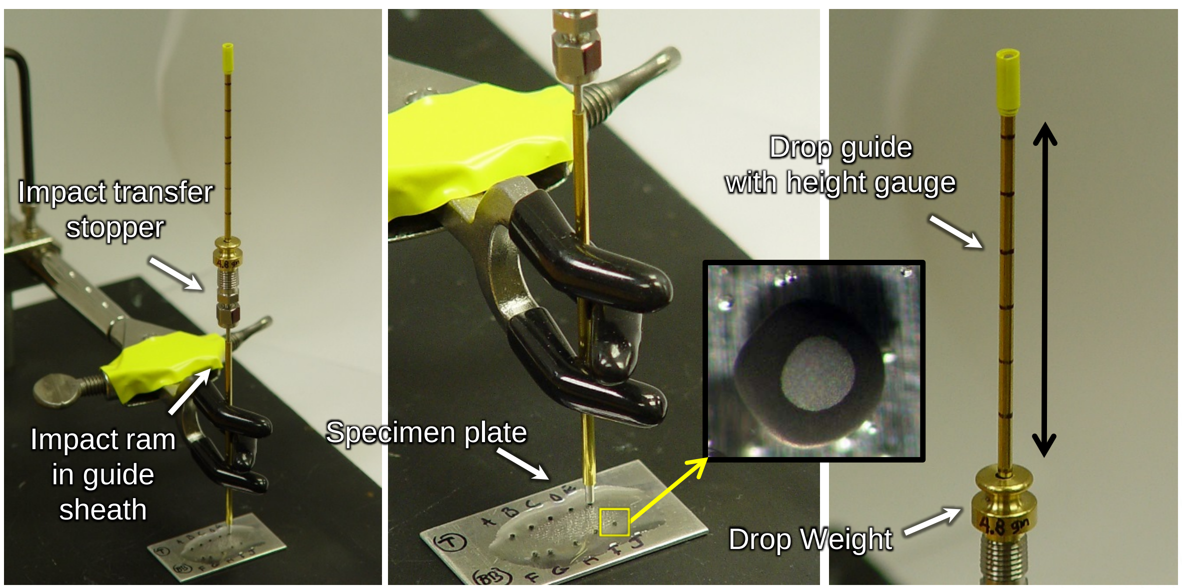
General approach for LBL benchmark – Variable properties

- Use samples of representative DUO_2-TRISO provided by INET for measurement of impurities and uranium loading

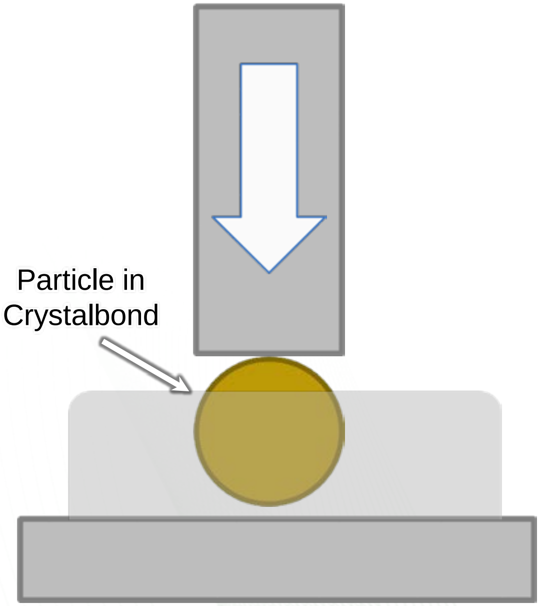


Fabrication of simulated pre-burn leach defects

- A simple impact process was used to crack the TRISO coating on DUO_2-TRISO particles.
- Details were reported in ORNL/TM-2015/722-R2.



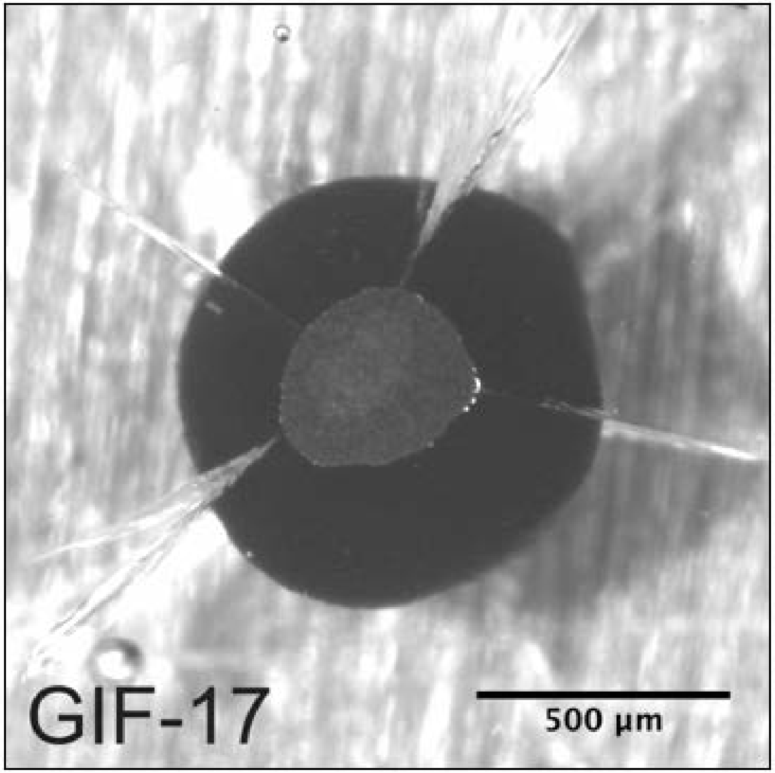
Mechanical fracture apparatus

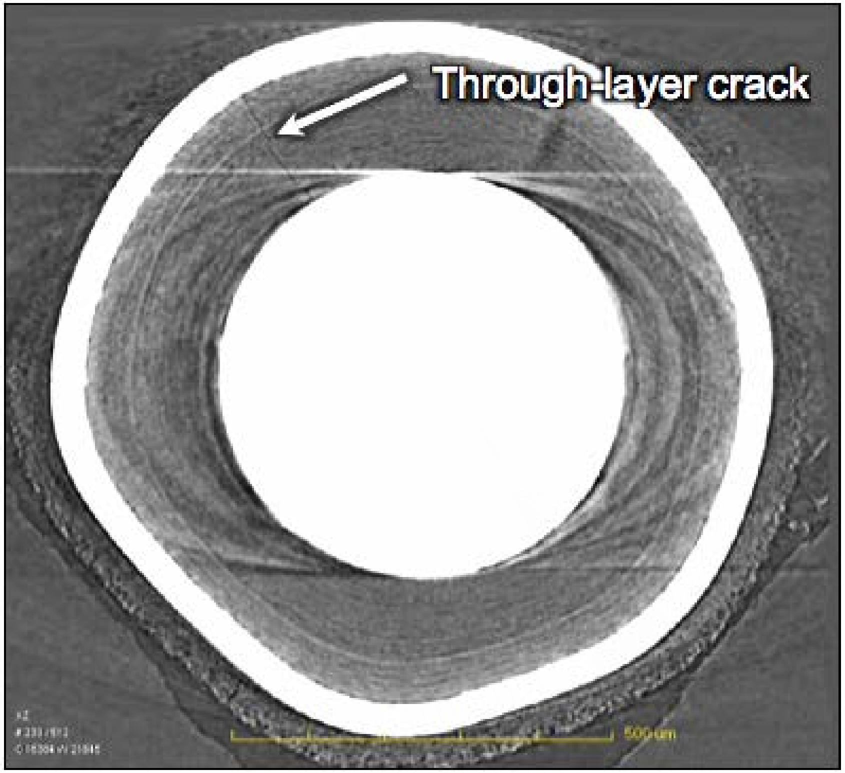


Schematic of impact area

Characterization of simulated pre-burn leach defects

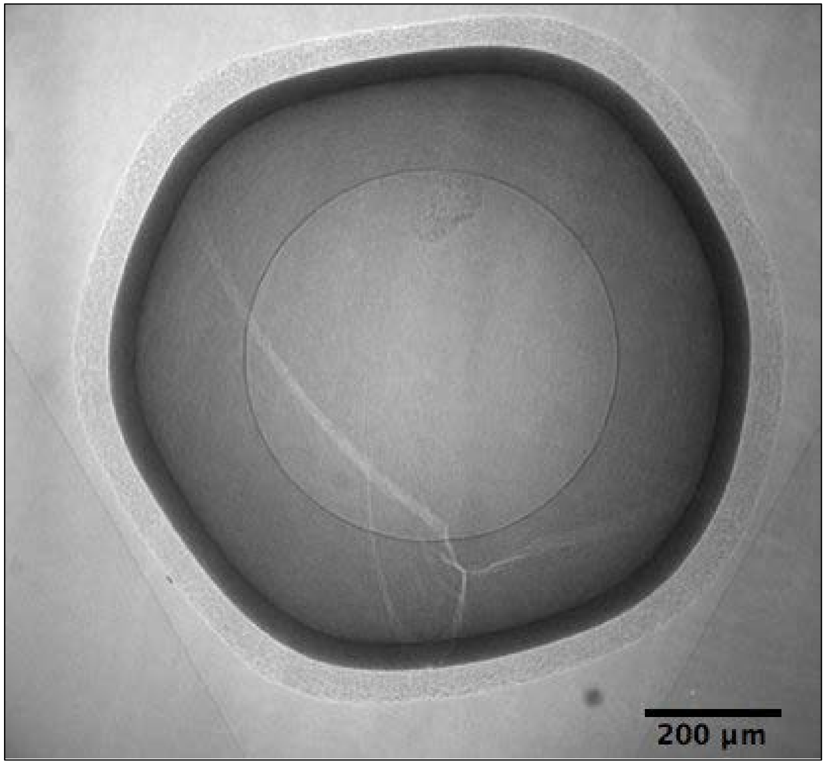
- Each particle was imaged while still in the Crystalbond epoxy to characterize the impacted surface; 3–5 cracks propagating out from the point of impact into the surrounding epoxy provided a favorable preliminary selection criteria.
- After removing each particle from the epoxy, x-ray tomography was used to confirm that all TRISO coatings had through-layer cracks resulting in an exposed kernel.

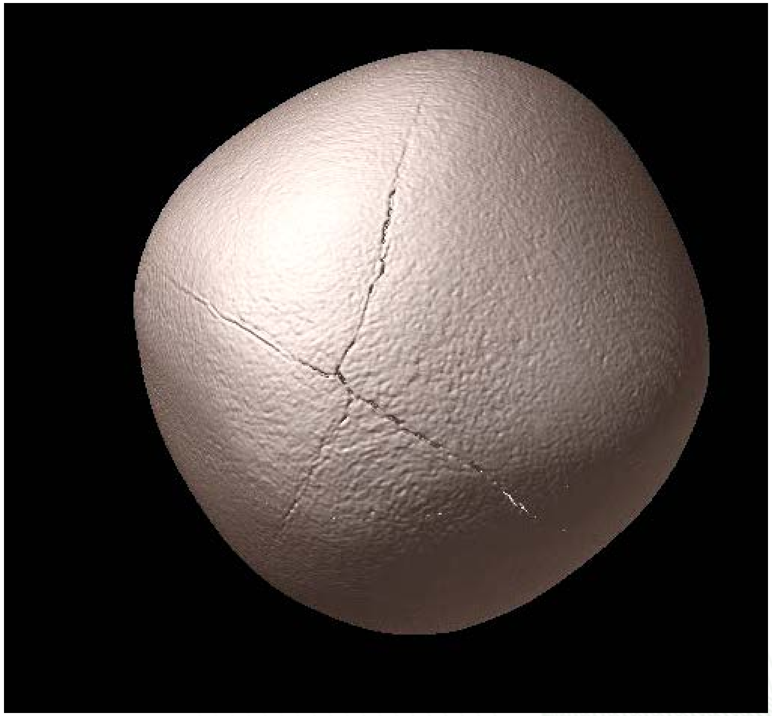




Verification of simulated pre-burn leach defect behavior

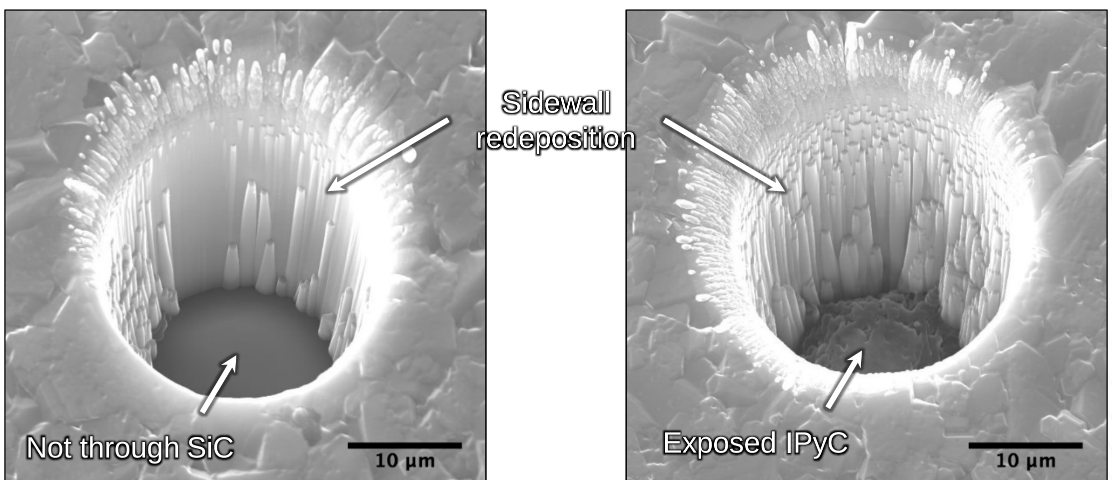
- Pre-burn leaching was performed to verify that the simulated defects behaved as designed.
- Uranium in the kernel was essentially completely dissolved after 24-hour leach in boiling acid, with negligible uranium detected in second leach.
- After pre-burn leaching, x-ray tomography was used to image the leached particle; all TRISO coatings remained intact and the kernel was gone.





Fabrication of simulated post-burn leach defects

- A scanning electron microscope (SEM) with a focused ion beam (FIB) attachment was used to mill holes through the SiC layer of the DUO_2-TRISO particles.
- Details were reported in ORNL/TM-2015/722-R2.
  - Minimum hole size was limited due to re-deposition during milling and need for reliable and reproducible results.
  - The outer pyrocarbon (OPyC) of the DUO_2-TRISO particles was first removed to reduce the required crater depth by burning it off in air at 750°C.
  - A larger diameter defect was produced to allow for direct confirmation of the through layer nature by SEM imaging of the simulated defect crater bottom and reduce the influence of redeposition.
  - A mottled crater bottom indicated the inner pyrocarbon (IPyC) layer was exposed.



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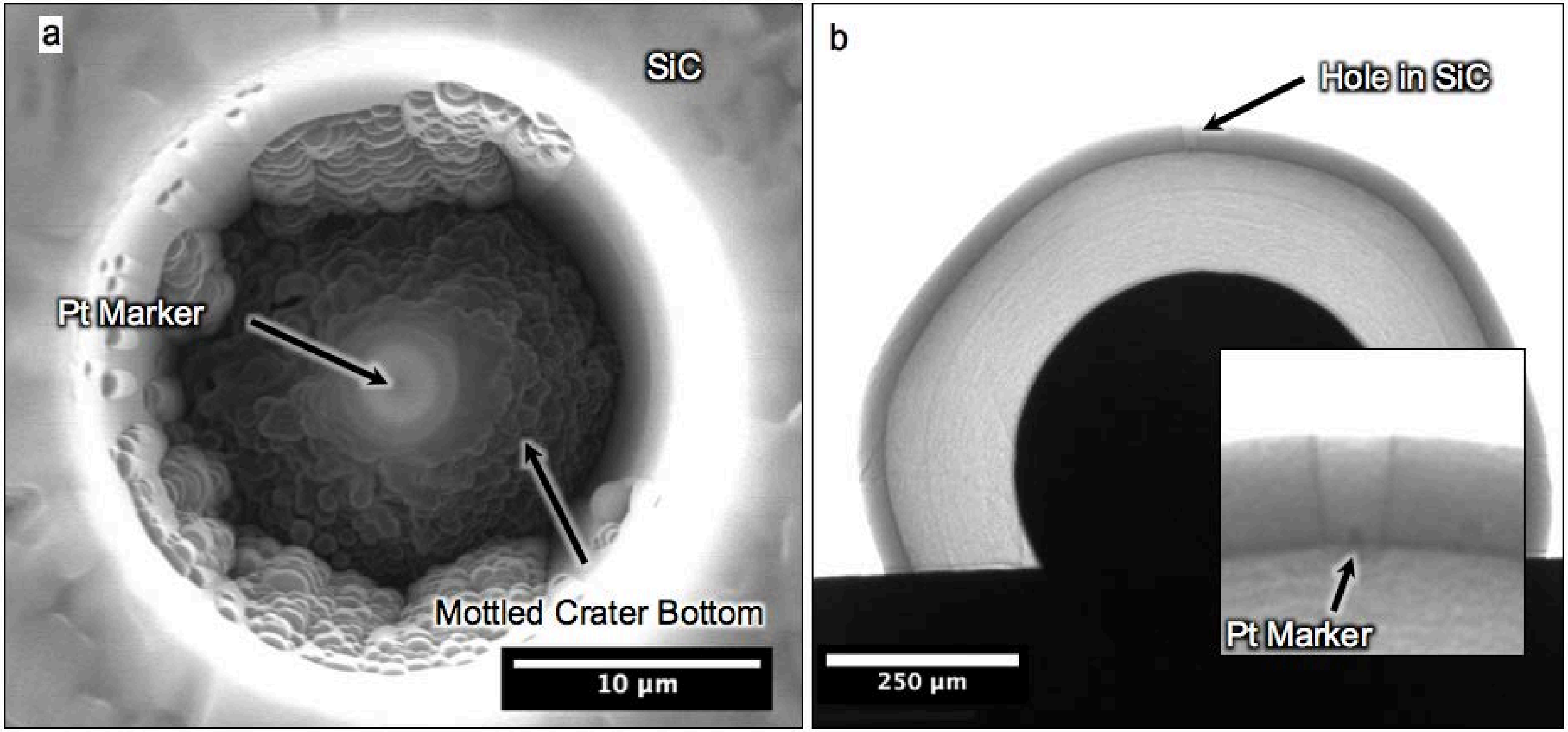
Characterization of simulated post-burn leach defects

- SEM imaging of every simulated defect was used to verify the IPyC was exposed.
- X-ray imaging was used to verify the crater did not extend more than 10 µm into the IPyC so as to minimize pre-burn leaching.
  - a Pt marker was deposited after FIB milling to help with x-ray contrast

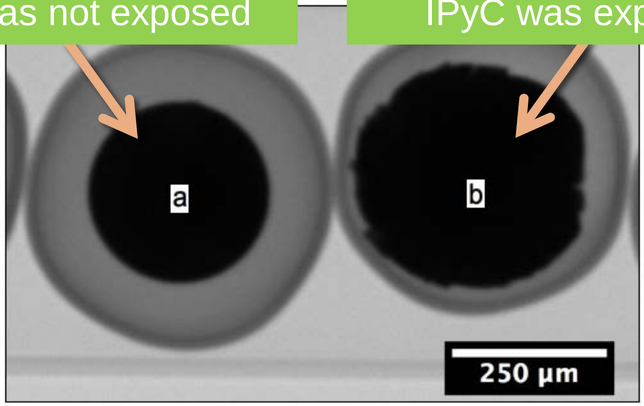


Verification of simulated post-burn leach defect behavior

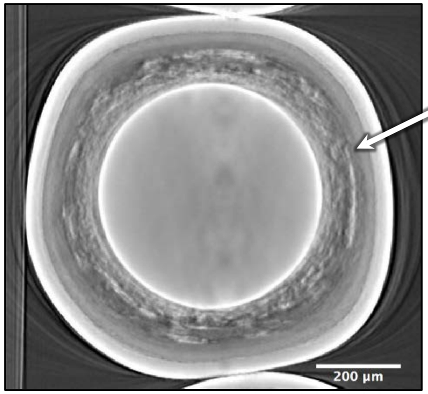
- Successfully-exposed IPyC was verified by performing the burn step of the LBL process and using x-ray radiography to confirm removal of buffer/IPyC and oxidation of kernel.
- LBL was performed on 10 particles to verify that the simulated defects behaved as designed.
- A small fraction of uranium (4–5%) was detected in second 24-hour pre-burn leach solution indicating intact IPyC was not 100% impermeable to the boiling nitric acid; this was not expected to impact benchmark experiment.
- Uranium in kernel was essentially completely leached during first 24-hour post-burn leach in boiling acid, with negligible uranium detected in second leach.

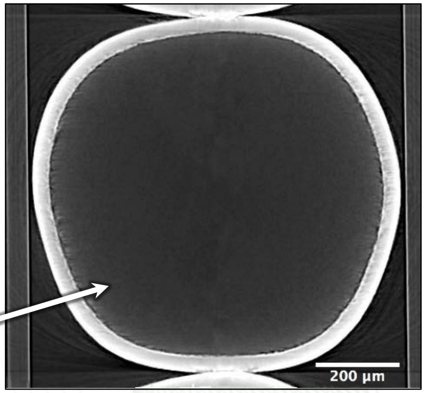
Particle with smooth crater bottom indicating IPyC was not exposed

Particle with mottled crater bottom indicating IPyC was exposed



U-dispersion in buffer indicates acid infiltration





Kernel is gone

Preparation of LBL benchmark round-robin samples

- A known number of DUO_2-TRISO with simulated pre-burn or post-burn LBL defects were added to ZrO_2-TRISO particle sets.
- A known mass of coal powder impurity standard (NIST SRM-1632d) was also added to each round-robin sample.
- Each round-robin sample (1–7) was randomly assigned a blind sample ID (A-G).

Round-robin sample ID	Number of simulated pre-burn leach defect DUO_2-TRISO particles	Number of simulated post-burn leach defect DUO_2-TRISO particles	Number of ZrO_2-TRISO surrogate particles	Mass of SRM-1632d impurity standard
1	0	0	~9,000	~0.5 g
2	1	0	~9,000	~0.5 g
3	2	0	~9,000	~0.5 g
4	4	0	~9,000	~0.5 g
5	0	1	~9,000	~0.5 g
6	0	2	~9,000	~0.5 g
7	0	4	~9,000	~0.5 g

LBL benchmark round-robin samples

- Average DU content of simulated LBL defect particles was measured
  - Needed for shipping and to calculate the number of defects from the LBL measurement of DU
  - **Data measured by ORNL on three 5-gram samples**
    - $(7.003 \pm 0.017)\times10^{-4}$ grams U per particle (average ± standard deviation)
    - $(2.17 \pm 0.03)\times10^{-3}$ grams ^{235}U per gram U (average ± standard deviation)
- Samples packaged for shipment to INET and KAERI (labeled A–G)

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LBL measurements of ORNL round-robin samples

- Each participant will perform LBL on all seven samples provided.
  - track ID of each sample and do not combine
  - transfer entire contents of vial into leaching vessel
    - rinse any residual powder into vessel to promote accurate impurity analysis
  - pre-burn leach analysis
    - measure exposed U from TRISO defects
    - also analyze leachates for non-uranium impurities (Fe, Cr, Mn, Co, Ni, Al, Ti, V)
  - post-burn leach analysis
    - measure exposed U from SiC defects
    - also analyze leachates for non-uranium impurities (Fe, Cr, Mn, Co, Ni, Al, Ti, V)
- After completion of analysis, ORNL will provide sample details needed for the round robin analysis.
  - a list of the number and type of simulated defects in each sample
  - the identification number of each simulated defect particle
  - the mass of NIST SRM-1632d powder in each sample

ORNL analysis of the seven ORNL round-robin samples

- ORNL has completed analysis of the seven ORNL round robin test samples prepared for their portion of the experiment.
- ORNL typically tests up to four LBL samples as an analysis set.
  - Samples A, B, and C were run through LBL with a simultaneous control blank (i.e., an empty vessel with just acid in it to provide a background value).
  - Samples D, E, F, and G were run through LBL with a second simultaneous control blank.
- Samples were subjected to ORNL's standard leach-burn-leach analysis procedure.
  - two 24-hour pre-burn leaches in boiling nitric acid
  - a 72 hour burn in flowing air at 750°C
  - two 24-hour pre-burn leaches in boiling nitric acid
- Additional leaches are typically performed if a successive leach detects uranium at a level >10% of the previous leach.
  - Samples D and G required four leaches to pass the <10% criterion.

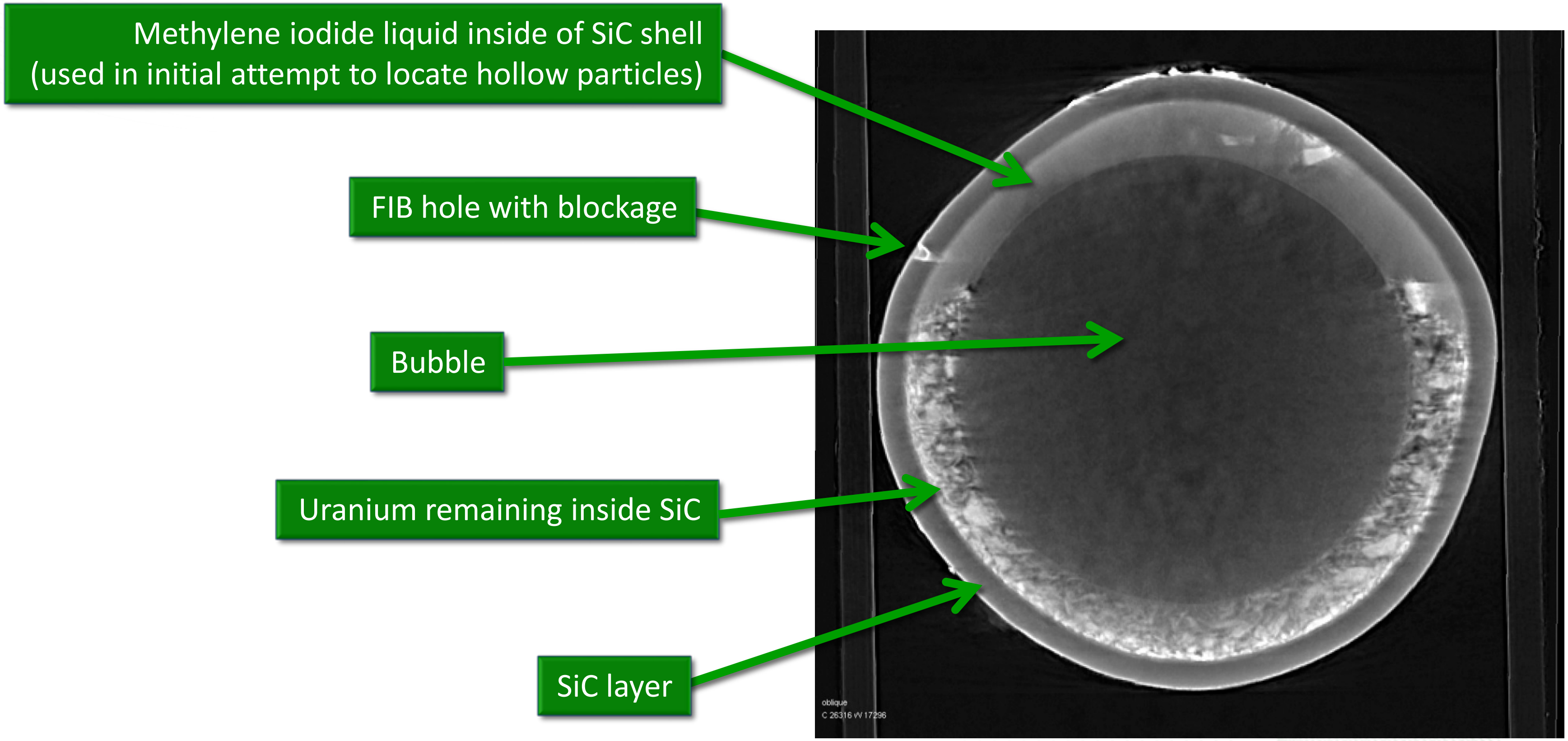
Results for Exposed Uranium Content

- The equivalent number of exposed kernels in each leach was determined by dividing the measured uranium in the leachates by the average uranium content in the DUO_2-TRISO particles (7.003×10^{-4} g U) .
- The results correlated to the expected round-robin sample sets (1–7).
- Results were within analysis uncertainty of expected values except for sample ORNL-D, which should have had an exposed-kernel value near 2.

Blind sample ID	Equivalent number of exposed kernels in pre-burn leach	Equivalent number of exposed kernels in post-burn leach	Predicted sample ID (ORNL/TM-2015/722 Appendix A)
ORNL-A	1.79 ± 0.18	0.00027 ± 0.00003	ORNL-3 (2 pre-burn)
ORNL-B	0.00034 ± 0.00004	0.000157 ± 0.000017	ORNL-1 (no defects)
ORNL-C	0.94 ± 0.09	0.000019 ± 0.000005	ORNL-2 (1 pre-burn)
ORNL-D	0.00051 ± 0.00005	**1.40 ± 0.08**	ORNL-6 (2 post-burn)
ORNL-E	0.0069 ± 0.0006	0.91 ± 0.09	ORNL-5 (1 post-burn)
ORNL-F	4.0 ± 0.4	0.00053 ± 0.00005	ORNL-4 (4 pre-burn)
ORNL-G	0.0103 ± 0.0010	3.7 ± 0.3	ORNL-7 (4 post-burn)

Incomplete Leaching in One Particle in ORNL-D

- Burn-leach particles were x-rayed after LBL to find the defective particles and then these particles were images with x-ray tomography.
- Tomography revealed incomplete leaching in one ORNL-D particle.



Results for Impurity Content

- Impurity content was determined for the typically specified impurities (Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni).
- After blind sample analysis was complete, data was compared to the expected impurity concentrations.

- Excellent agreement for Al, Ca, V, Cr, Mn, Fe, Co
- Ti was slightly low
- Ni was high, but Ni mass fraction in the standard was an “information only” value (low-confidence and no reported uncertainty)
- Al and Ni had significant fraction in post-burn leach

Impurity element	Percent recovery in pre-burn leach	Percent recovery in post-burn leach	Total percent recovery
Al	64.1 ± 12.3%	32.3 ± 8.5%	96.4 ± 14.9%
Ca	89.9 ± 24.7%	1.2 ± 3.4%	91.1 ± 24.9%
Ti	71.6 ± 17.3%	4.7 ± 1.5%	76.2 ± 17.4%
V	92.2± 22.7%	5.1 ± 1.3%	97.3 ± 22.7%
Cr	98.0 ± 24.8%	8.2 ± 2.2%	106.2 ± 24.9%
Mn	98.0 ± 26.3%	3.4 ± 2.1%	101.4 ± 26.4%
Fe	102.6 ± 27.6%	1.2 ± 0.4%	103.7 ± 27.6%
Co	101.3 ± 27.1%	2.5 ± 1.1%	103.8 ± 27.1%
Ni	102.1% ± >27.7%	48.2% ± >14.3%	150.3% ± >31.2%

Results for Impurity Content

- Impurity content was also determined for additional impurities included in the coal powder impurity standard, some of which are relevant to LBL of irradiated fuel (e.g., Sr, Cs, Ce, Eu).

National Institute of Standards & Technology

Certificate of Analysis

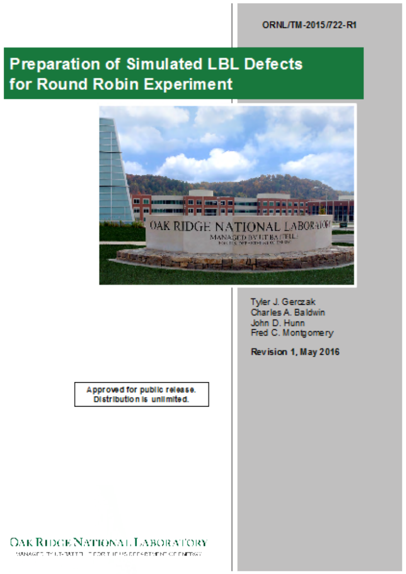
Standard Reference Material® 1632d

Trace Elements in Coal

- After blind sample analysis was complete, data was compared to the expected impurity concentrations.
- Most impurities were within 1 σ of 100% recovery
  - Na, Al, K, Ca, Sc, V, Cr, Mn, Fe, Co, Cu, Zn, As, Rb, Sr, Cd, Cs, Ba, Ce, Eu, Pb, Th
- A few impurities were within 2 σ of 100% recovery
  - B, Mg, Ti (large measurement uncertainty for B)
- Sb had very poor recovery (5-10%)

Summary

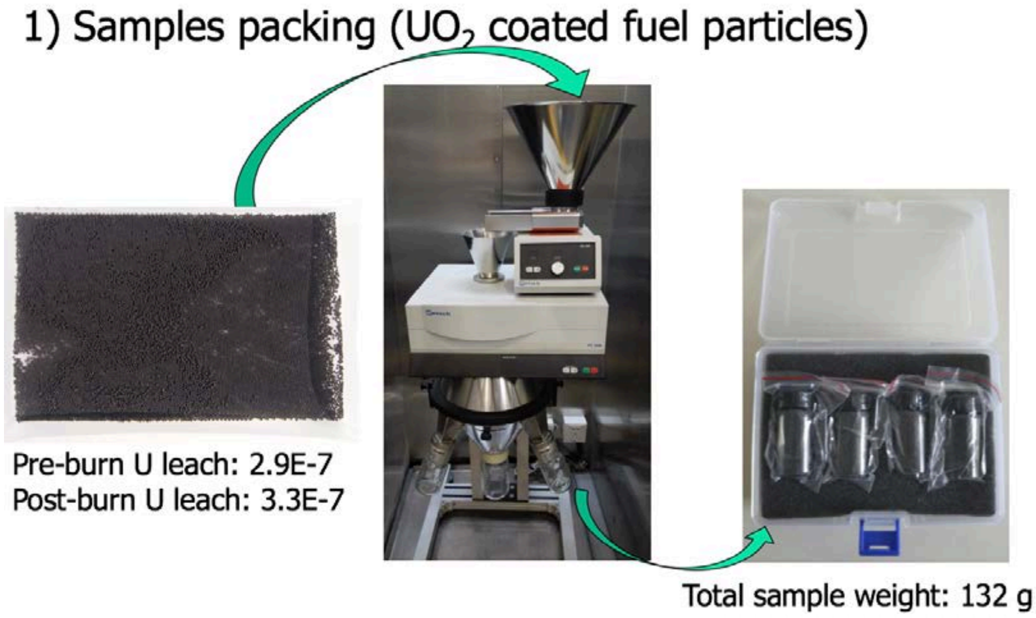
- ORNL has completed fabrication and analysis of the simulated LBL defects using depleted urania (DUO_2) TRISO.
- Samples shipped to KAERI and ready to ship to INET.
- ORNL has published a report describing the preparation of simulated LBL defects for the round robin experiment (ORNL/TM-2015/722-R2).



- ORNL has completed analysis of their set of round robin samples with simulated LBL defects.
- Defect detection and enumeration was successful on six of the seven samples measured by ORNL.
- One of the simulated post-burn LBL defects did not completely leach in Sample ORNL-D, and Sample ORNL-G required four 24-hour leaches.
  - may be related to nitrate formation from nitric acid intrusion through IPyC
- Recovery of typically-specified metal impurities was excellent overall.

China and Korea Status

- China
  - 132-gram samples of representative DUO2-TRISO have been prepared.
  - INET analysis of their samples is complete.
  - INET is acquiring approval for shipments.



- Korea
  - KAERI LBL procedure is being verified before measuring US samples.

Thank you for your attention

John Hunn

hunnjd@ornl.gov

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US Department of Energy
Office of Nuclear Energy –
Advanced Reactor Technologies

Advanced Gas Reactor Fuel
Development and Qualification Program