Capabilities for Spent Fuel Characterization at Argonne National Laboratory*

by

L. A. Neimark and R. V. Strain
Argonne National Laboratory
Argonne, Illinois 60439-4838

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INTRODUCTION

Summaries of the status of spent nuclear fuel (SNF) owned by the Department of Energy (DOE)\(^1,2\) have highlighted the need to obtain a better understanding of the current physical and chemical condition of the SNF as a foundation for establishing a clear path forward for the fuel's eventual geologic disposal in a long-term repository. Specific issues include the feasibility of dry storage for fuels currently stored in a wet condition, whether the fuel requires stabilization treatment before it can be stored in even an interim facility, and whether the fuels would remain in a safe geometry and chemical state under an off-normal condition. If stabilization is required, characterization of the end product would also be required.

Because much of the currently stored fuel has not been adequately characterized for physical, chemical, and nuclear properties, current information on these attributes will be necessary before the fuel would be accepted in either an interim or long-term storage facility. The query sent last year to the holders of SNF requested information on such items as cladding condition, chemical test results, actinide content by isotope, fuel burnup, and heat generation rate. In most cases, for fuel stored about 30 or more years, such information was not obtained when storage began, and the current condition of the SNF is only now becoming a salient issue to be addressed.

To initiate obtaining the required information, the DOE has generated an SNF Characterization Plan\(^3\) based on the needs for characterizing the materials stored at the individual major DOE storage sites. This plan emphasizes the current state of the SNF, as the physical and chemical state of much of the SNF has deteriorated during storage owing to the environmental conditions at each site. The principal focus of the plan, therefore, is to characterize those fuel attributes that are key to the safe handling, transportation, and storage of the SNF. The drivers for specific attributes are regulatory requirements, resolution of technical issues, or a design need.\(^3\)

Argonne National Laboratory's facilities in Illinois and Idaho possess capabilities that can be used to address many of the characterization issues that have been raised. This paper will describe these capabilities and attempt to
relate them to the characterization needs as they are now perceived. Two companion papers\textsuperscript{4,5} describe the facilities at ANL-W more fully.

**CHARACTERIZATION CONSIDERATIONS**

The type and degree of SNF characterization that is needed and possible is dependent upon a number of considerations. These include fuel type, present condition, amount of material, location in the DOE complex, and the intended interim or final disposition.

The fuel type and its composition, including the cladding, effectively prescribes one sub-set of characterization issues. The fuel geometry will dictate how it must be handled, where it can be handled, possible examination tools, and the feasibility of it being transported in available shipping casks. The composition establishes the past and future chemical reactions with the environment that likely should be characterized and the tools to do it. The present condition of the SNF has the same set of issues as the fuel geometry, with probably a greater emphasis on handling and transportation.

From the large amount of SNF that is stored in the DOE complex, it can be concluded that not all of the SNF will be "characterized". Some will receive only visual inspection, some of these will receive more intensive non-destructive characterization, and only a fraction of these will receive the more in-depth destructive examinations and testing that require hot-cell techniques that could be classed as "sophisticated". Thus, disciplined sampling plans will be needed to assure that the characterization activities truly envelop the SNF populations and focus the limited resources on characterizing those units that will provide the most significant information.

The current location of the SNF raises two important issues. The first is, does the storage site have the hot-cell capabilities that will be necessary to satisfy the examination and testing needs of that site's SNF? If the answer is no, the second issue is whether the representative samples of the SNF can be transported to a hot-cell facility that does have the capabilities. Transportation issues are beyond the scope of this paper, but they could be germane to the future use of off-site facilities for fuel characterization. The transportation of research quantities of materials which have programmatic value, which materials for examination and testing have, is vastly different than the shipment of large amounts of valueless SNF between interim storage facilities or to the eventual geologic repository.

Finally, the intended interim or final disposition of the SNF will determine the characterizations necessary to satisfy the requirements and their drivers for safe handling, transportation, and the storage period itself. A corollary to this will be the need to perform similar characterizations and testing of SNF that has undergone any stabilization or treatment to establish that it can meet the same requirements.

It can be concluded that not all of the SNF in the DOE complex will be characterized and not all in the same manner or degree. For those materials that do require in-depth examinations or testing, the Argonne facilities are aptly suited to perform many of them.

**DESCRIPTION OF FACILITIES**

The Alpha-Gamma Hot Cell Facility (AGHCF) at Argonne's Illinois Site (AIS) is a multi-program facility for the examination, characterization, and testing of irradiated nuclear fuel and structural materials. Activities at
AIS have included the development of nuclear fuel systems for fission reactors such as the Advanced Neutron Source and the Liquid Metal-Cooled Reactor; the characterization of fuel and structural materials from DOE-owned and commercial fission reactors, e.g., Three Mile Island Unit II and components from LWRs to investigate irradiation-assisted stress corrosion cracking; the testing of fuel and fuel pins under off-normal, accident-type conditions (e.g., the foaming characteristics of Al-clad alloy and dispersion fuels); and the long-term testing of LWR fuel in an environment to simulate faulted dry storage. The AGHCF can handle up to 10,000 Ci of 1 MeV gamma radiation in units measuring up to 6 ft. in length and 4 in. in diameter. Truck-transported casks up to 20,000 lbs are unloaded dry.

The AGHCF consists of the kilocurie hot cell (AGHC) and an associated electron beam laboratory (EBL) that contains a shielded electron microprobe, a scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) capability, and a scanning Auger microprobe for surface analyses. In addition, there are two steel-shielded nitrogen atmosphere gloveboxes for small sample preparation or small-scale test setups. The AGHC has two separate environmental areas, both having nitrogen atmosphere, one with 100 ppm O₂ and ~200 ppm moisture and the other with 0.25 wt.% O₂. Although the principal function of the nitrogen atmosphere is fire suppression, the relatively low levels of oxygen and moisture in a main work area provides a good environment for maintaining the oxidation state of reactive materials such as uranium-base fuels. It is in this area of the cell where fuel sectioning and metallography are done, and it is the location of the cell's two shielded metallographs.

In the other work areas of the AGHC is equipment for gamma spectroscopy, mensuration, fission-gas collection, and macrophotography. A variety of furnaces are also located there for high-temperature testing in controlled environments. These furnaces include the Fuel Behavior Test Apparatus (FBTA) and the Whole-Pin Furnace (WPF).

Located in the same building as the AGHC is the Irradiated Materials Laboratory (IML). This air-atmosphere, centicurie hot cell is used for mechanical property tests (tensile and creep-rupture, slow-strain-rate tensile testing up to 300°C in a monitored water environment, and instrumented Charpy impact to 300°C) of non-fueled materials.

The ANL Electron Microscopy Center (EMC) is available for the examination of low-activity-level structural materials. Such specimens could be examined by a 1.2-MeV transmission electron microscope, a 100-KeV scanning transmission electron microscope, and an advanced analytical electron microscope. The EMC is also located in the same building as the AGHC and IML. Transmission electron microscopy of irradiated fuel is also available in the Chemical Technology Division facilities which are currently evaluating the characteristics of high-level waste forms. And finally at ANL-E, the Intense Pulsed Neutron Source (IPNS) is available for interrogation of small fuel samples by neutron diffraction techniques.

Supplementing these ANL-E capabilities are those of the new Analytical Chemistry Laboratory (ACL) at ANL-W in Idaho. The ACL offers state-of-the-art analytical chemistry capabilities for irradiated fuels and materials. These include inductively coupled plasma/atomic emis-
sion spectrometry, isotope-dilution mass spectrometry, and X-ray diffraction. Of particular importance is the capability for fuel burnup analyses, a significant need in SNF characterization.

RELATIONSHIP OF CAPABILITIES TO NEEDS

Any listing of characterization capabilities would be incomplete without relating them to the expected programmatic needs. This relationship establishes the role the ANL facilities could play in the SNF characterization efforts.

It is assumed that only small segments of large fuel elements or small single-fuel elements would be transported to the AGHCF for detailed examination or specific tests. The initial screening examinations of large numbers of fuel elements or assemblies would be done in the pools where they now reside or in large hot cells on or near the storage sites. This initial screening would identify areas that deserved detailed interrogation or which would be suitable for specific testing. Cutting these large units down to the desired size would be accomplished at the site's hot cell. This would minimize the transportation requirements for shipping this now programmatically valuable material to the AGHCF.

A typical examination or testing plan at the AGHCF could include the following activities.

a. Initial Inspections

The item would be visually inspected for physical integrity and chemical state. The appearance would be documented with macrophotography, including color and stereo photographs. Samples of surface reaction layers would be removed for analysis by X-ray or electron diffraction or Auger scanning microscopy to identify the reaction product and establish the state of the chemical reaction, i.e., its completeness.

b. Fission-Product Identification and Location

Gamma spectroscopy would be used to determine the spatial distribution of the principal remaining fission-product isotopes. Such a determination would yield information on the leaching characteristics of the fuel, if surfaces that had been exposed to water were part of the sample. A more detailed evaluation of the fission-product inventory could be obtained by obtaining samples for Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), a capability that exists at both ANL-E and ANL-W.

c. Effects of Corrosion

Samples of the parent unit would be examined by optical microscopy, SEM, and Auger microscopy to determine the extent and nature of fuel and/or cladding corrosion that had occurred during storage. Corrosion mechanisms and kinetics could be evaluated from the data obtained. Such an evaluation would be one basis for projecting what may occur to fuel units during future storage especially if a primary containment barrier breached. These methods and evaluations are relevant to all cladding types now in storage. The extent of hydriding in the fuel and cladding would be evaluated by quantitative stereology to obtain the distribution and amount of the hydride phase. A detailed phase analysis could be obtained from either X-ray, electron, or neutron diffraction, all available at the ANL-E site. Evaluations of existing corrosion could be supplemented by in-cell corrosion studies in either air or limited volumes of water (limited by criticality issues). A thermogravimetric apparatus could be set up in available space in the AGHC.
d. Particulate Characterization

If the material to be characterized is a wet sludge or dry particulate, one apparent concern is its potential pyrophoricity. Attributes of interest that could be characterized at ANL-E are drying rates, particle size distribution, surface area, and composition, by the methods previously described.

e. Fission-Product Behavior During Off-normal Events

While the ICP-MS will provide a comprehensive total inventory of potentially available radionuclides that could escape under any conceivable or inconceivable condition, there is a need to provide more realistic potential source term values that take into account the mitigating factors from inherent containment, such as fuel form, composition, and cladding. Because temperature will be the principal driving force for fission-product or actinide release, exposure of fuel segments to elevated temperatures under controlled environments would provide data on the physical behavior of the fuel and the manner in which it releases its fission products. The FBTA and WPF systems in the AGHC have the capability to monitor the release of gaseous fission products while viewing and recording the physical behavior of the fuel. A relatively simple modification of the FBTA for the collection of volatile species would provide data on both their release and transport. The numerous analytical techniques described previously could be used to identify the migrating species.

f. Mechanical Properties

A good indicator of the state of a material's mechanical properties is its microhardness. Microhardness measurements of the fuel and cladding would provide an indication of the material's ductility and its potential for failing during handling. This initial screening could be supplemented by simple bend tests to qualitatively assess the unit's brittleness. More sophisticated tensile and Charpy-impact tests could be difficult to conduct because of the need to use ASTM-prescribed specimen geometries.

The above examination and testing plan leaves open the possibilities for more specific tests for specific fuel types. Whether they could be accommodated within the large envelope of ANL capability would depend upon the specific requirements.

RESULTS OF A CURRENT CHARACTERIZATION

A recent physical inventory of all accountable materials stored in the AGHC resulted in the finding of an EBR-II Mk-IA fuel pin that had undergone a significant interaction with the high-purity (=100 ppm O₂) hot-cell environment. This sodium-bonded, U-5 wt.% fissium alloy fuel pin, clad with Type 304 stainless steel, had arrived in 1974 with a suspected pinhole breach that had not been found. It went into storage in a closed (screw-cap) tube shortly thereafter. It remained in the in-floor storage hole in the high-purity area of the cell for 19 yrs. When removed last year, the pin appeared as if it had been cut open lengthwise with an old-fashioned can opener, as shown in Fig. 1. The only fuel that remained was a fragmented piece at the bottom, also shown in Fig. 1. The rest had powdered and fallen out into the containment tube. There was no evidence of the sodium bond. The crack adjacent to what would have been the top of the fuel column was straight and then changed to the ratcheted appearance down to the bottom. The top end of the crack is approximately at the end of the fuel column, and the cladding shows an abrupt decrease in diameter at this
point. This suggests that the top end of the fuel reacted with the little moisture and oxygen that entered through a cladding defect in this region. Over time the volume expansion of the reaction product stressed the cladding to rupture resulting in the straight crack region. Subsequent reaction between the environment and the exposed fuel resulted in its powdering and falling out of the cladding. As fresh fuel surfaces reacted with the environment, the reaction/expansion/powdering process continued and the cladding was incrementally ratcheted open. The remaining fuel at the bottom apparently had not yet reacted to the point of powdering and remained essentially in place.

Figure 2 shows a cross section of the remaining fuel. The topochemical outlines in the fuel fragments indicate an incomplete gas/solid reaction, which is occurring inward from the free surfaces of the particles. In general, the reaction appears to be occurring from the outer surface of the fuel slug inward, indicating a likely role for the sodium that was once between the fuel and the cladding. Figure 3 shows an SEM image of a topochemical boundary between reacted and probably only somewhat reacted fuel areas.

The results obtained to date indicate only the initial steps in determining how this fuel reacted with the environment. Auger analysis will be used to obtain data on oxygen levels, and EMP analysis will be used to assess the involvement of sodium and the migration of fission products. Electron diffraction may be used to further characterize the powdered reaction product and the unreacted fuel if necessary to understand the end-state of the reaction. SEM fractography will be used to obtain information on the cladding ratcheting mechanism.

The behavior of this pin in what is usually considered a benign environment potentially typifies what may be possible for similarly failed pins now in storage, or pins that may fail in future storage for as yet undefined causes.

SUMMARY

The analytical and testing capabilities for irradiated fuels at ANL in both Illinois and Idaho are extensive and could be used to resolve significant issues in the DOE SNF program. The facilities and expertise are available to do just that.

REFERENCES


Figure 1. Cladding of Metal-fueled Pin that Split Open during Storage. ET 285205; 285207
Figure 2. Optical Photograph of Cross Section through Retained Fuel. ET 287107
Figure 3. SEM Photographs Showing Apparent Chemistry-related Microstructural Changes Near Edge of Fuel Particles. ET 320843; 320845