

# HOT CELL FACILITIES FOR FABRICATION OF MATERIALS FOR TRANSMUTATION OF MINOR ACTINIDES: (Pu,Am)-MgO CERAMIC/CERAMIC COMPOUNDS

***Frederic Jorion\***, **Christophe Maillard**, **Francois Desmouliere**, **Xavier Genin**, **Louis Donet***

CEA/Marcoule DEN/VRH/DRCP/SE2A, BP 17171, 30207 BAGNOLS SUR CEZE

## ABSTRACT

The transmutation of minor actinides continues to be investigated under the international FUTURIX/FTA program with the participation of the US Department of Energy (DOE), the Institute for Transuranium Elements (ITU) in Karlsruhe, the Japan Atomic Energy Research Institute (JAERI) and the French Atomic Energy Commission (CEA), with the fabrication of eight rods scheduled for irradiation beginning in 2007 in the Phenix reactor (CEA Marcoule). The resources necessary for fabricating (Pu,Am)Ox-MgO materials are now available in the laboratories of the ATALANTE research complex at Marcoule. After reviewing the data relevant to synthesizing actinide compounds and fuel fabrication, the article focuses on the main equipment used (press, furnace, XRD and SEM) and discusses the results obtained to date.

**KEYWORDS** americium, plutonium, press, furnace, hot cell, x-ray diffraction.

## 1. INTRODUCTION

The purpose of the FUTURIX/FTA (**FU**els for **T**ransmutation of trans**UR**anium elements in phen**IX** / “**F**ortes **T**eneurs en **A**ctinides” [high actinide content]) international irradiation program is to demonstrate the feasibility of burning minor actinides in dedicated reactors: critical electricity-generating transmuters or hybrid systems (ADS) according to the double strata concept. The program is being pursued by the CEA jointly with the US Department of Energy (DOE), the Institute for Transuranium Elements (ITU) in Karlsruhe, and the Japan Atomic Energy Research Institute (JAERI). For the CEA, this program follows experiments previously carried out or currently in progress within the scope of the 1991 radioactive waste management act. The FUTURIX/FTA experiment addresses the technical feasibility of transmuting minor actinides in fast neutron reactors, mainly from the standpoint of fuel behavior [1].

The international cooperation implied several basic decisions. While the Europeans and the CEA favor actinide oxide composites with which they have acquired expertise, the Americans and Japanese have focused on fuel with high thermal conductivity operating at low temperatures, i.e. metal and nitride fuel, respectively. These initial orientations constitute reference routes, with the others generally reserved as alternatives (nitride for the DOE) or fallback solutions (nitride for the Europeans). The major advantage of FUTURIX/FTA is that it involves a joint irradiation program or the various experimental fuels and will yield comparative data. The FUTURIX/FTA program provides an opportunity to implement new alternative methods rather than the conventional powder metallurgy used to synthesize and prepare oxide fuels. Following developments in recent years in U and Pu coprecipitation [2] and testing for application to other actinides, mixed Pu-Am oxide has been synthesized by oxalate co conversion using protocols developed with surrogates [3].

Specific fabrication and analysis techniques for glove box and hot cell use had to be developed to produce these compounds. For example, a chemical reactor was nuclearized to allow coprecipitation of americium and plutonium controlled by telemanipulators. Uniaxial press compaction technology suitable for use in shielded cells was developed, as well as a high-temperature sintering furnace. Several characterization techniques are implemented, including X ray diffraction analysis to determine the phases present in the material and scanning electron microscopy for microstructural characterization. This article details the techniques implemented for the FUTURIX program, substantiating the technological orientations and illustrating them with the results obtained.

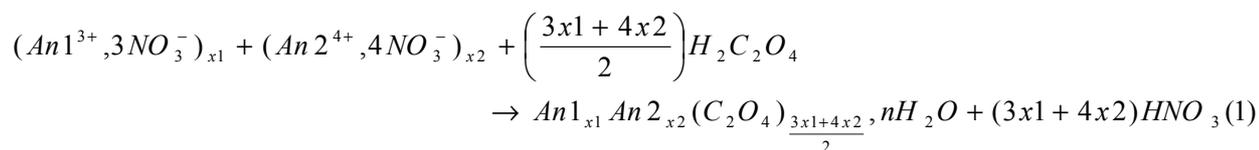
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\* telephone no. : 33 166791613, fax no. 33 166791649, email : jorionf@amandine.cea.fr

## 2. SYNTHESIS OF ACTINIDE COMPOUNDS

### 2.1. SYNTHESIS TECHNIQUE AND EQUIPMENT

Oxalate co conversion of actinides in aqueous phase was selected for preparing the precursors in the FUTURIX program. Oxalate coprecipitation consists in precipitating several actinides present in solution by adding an oxalic acid ( $H_2C_2O_4$ ) solution. The precipitate is heat-treated to obtain a compound or mixture of compounds [4]. Theoretically, the oxalate coprecipitation of a mixture of trivalent and tetravalent actinides occurs according to the following reaction:



Calcining the multiphase oxalate precipitate in oxidizing atmosphere yields the single-phase oxide  $An1_xAn2_{(1-x)}O_2$ . The fundamental parameters ( $[HNO_3]$ ,  $[H_2C_2O_4]_{\text{excess}}$ ) were selected on the basis of the americium and plutonium oxalate solubility curves versus  $[HNO_3]$  and  $[H_2C_2O_4]$  [5]. Two  $(Pu_{(1-x)}Am_x)O_2$  compounds (where  $x = 0.8$  and  $0.5$ ) were synthesized in this way by co conversion in a shielded line. Figure 1 shows the chemical reactor installed in an operational shielded cell.



Figure 1. Co conversion device in a shielded line

It comprises:

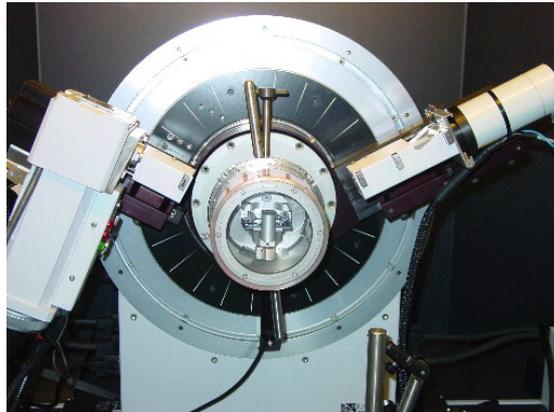
- a 250 mL jacketed overflow reactor containing a PTFE-coated magnetic stirring bar,
- a stirrer,
- two peristaltic pumps,
- a fritted glass filter tube (porosity 10–16  $\mu\text{m}$ ),
- a filtration flask maintained under negative pressure by a pump.

Considering the quantities of nuclear material implemented (about 50 g), no additional criticality precautions were required. The shielded cell is dedicated to chemical experiments, and standard safety procedures were observed. Large volumes of liquid effluents ( $V_{\text{acid}}$  and  $V_{\text{base}} > 10$  L) are managed in another dedicated shielded line; small volumes must be contained in suitable PTFE vials. Vials containing significant quantities of radioelements are vented to air to prevent bursting by overpressure due to radiolysis. The reagents necessary for the experiments transit via a dedicated glove box behind the shielded line. Small quantities of acid are transferred in La Calhène containers with or without radiological shielding depending on the measured dose rate.

### 2.2. ANALYSIS METHODS AND EQUIPMENT

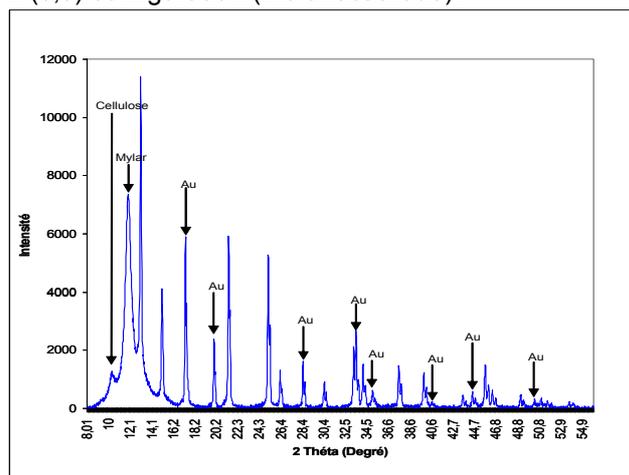
Both  $(Pu_{(1-x)}Am_x)O_{(2-y)}$  compounds (where  $x = 0.8$  and  $0.5$ ) have been extensively characterized. One of the techniques used is X ray diffraction analysis of the powder to characterize the crystal structure. This analysis uses

a Bruker D8-Advance powder diffractometer with an X ray tube having a molybdenum anticathode and a nuclearized sample holder for examining radioactive solids. The sample holder (Figure 2) was developed specifically for this application.



**Figure 2.** Nuclearized X ray diffraction unit

The powder sample is diluted in cellulose to limit the quantity and thus the dose rate; 30 mg is generally sufficient for analysis purposes, to which gold is added as an internal measurement standard. The sample is encapsulated in Mylar film to prevent material dispersal during transport, and placed in a leaktight container with a beryllium window; the container connects to the preparation glove box by means of a La Calhène docking flange. The connector is then attached to the XRD goniometer for the measurement. The X ray spectrum is acquired with the goniometer operating in  $(\theta, \theta)$  configuration (Mo anticathode).

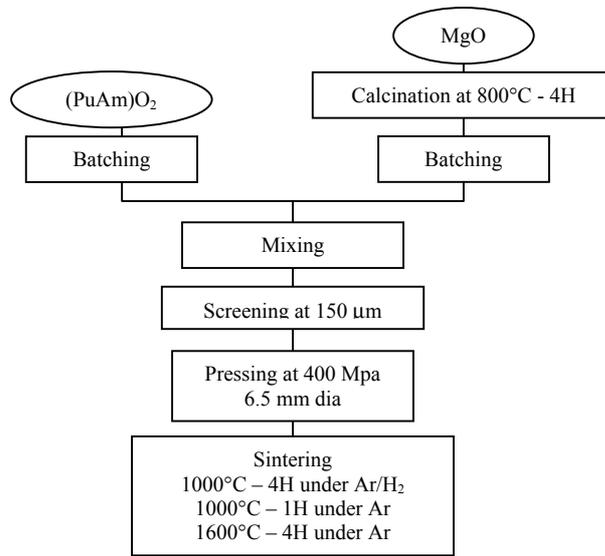


**Figure 3.** X ray diffraction diagram of  $\text{Am}_{0.5}\text{Pu}_{0.5}\text{O}_2$  compound

The crystalline phase is determined by comparison with diffraction diagrams referenced in an ICDD crystallographic database (136 895 records, 83% of which are for inorganic materials). Figure 3 shows the X ray diffraction diagram for one of the two  $(\text{Pu}_{0.5}\text{Am}_{0.5})\text{O}_{(2-y)}$  compounds synthesized, confirming the synthesis of a single-phase CFC structure compound.

### **3. FABRICATION OF $(\text{Pu}_{1-x}\text{Am}_x)\text{O}_2$ -MGO COMPOSITES**

The composites are fabricated by powder metallurgy from a mixture consisting mainly of magnesia (MgO) and a  $(\text{Pu,Am})\text{O}_2$  solid solution; green pellets are produced by press compaction followed by a densification heat treatment. Two formulations were studied:  $(\text{Pu}_{0.5}\text{Am}_{0.5})\text{O}_2 + 70 \text{ vol}\% \text{ MgO}$  and  $(\text{Pu}_{0.2}\text{Am}_{0.8})\text{O}_2 + 65 \text{ vol}\% \text{ MgO}$ . The fabrication process and parameters are indicated in Figure 4.



**Figure 4.** Fabrication process for FUTURIX pellets

### 3.1. MILLING PROCESS

The materials are mixed in an oscillating mixer-mill to ensure satisfactory homogeneity and dispersion of any aggregates. It consists of a 25 mL stainless steel screw-on mixing jar containing the oxide mixture and one or two balls, operated at an adjustable frequency ranging from 3 to 30 Hz. The type of container is of fundamental importance. Standard grinding jars are made of corundum (alumina), tungsten carbide, zirconia, agate, or stainless steel, together with the grinding elements. Resilient containers are generally adopted for hard materials. We chose to use stainless steel grinding jars at relatively low frequency (15 Hz) with an average mixing time of 30 minutes. Two 9 mm balls were used rather than a single 20 mm ball to ensure ball-to-ball contact and stirring rather than jar-to-ball contact. Dry mixing was sufficient, and allowed easier handling in a shielded cell environment.

We selected this type of mixer-mill as a tradeoff between nuclear operating constraints and milling effectiveness. Although oscillating mixer-mills are less efficient than planetary or attrition mills, they are capable of handling smaller quantities (as little as 5 mL useful volume) with a recovery yield near 95%. They thus limit material losses and the production of active waste. In addition, they are highly compact and easier to nuclearize, and the sealed stainless steel grinding jar provides very effective biological shielding. Figure 5 shows a mixer-mill installed in a glove box. They can also easily be installed in a shielded cell and operated by telemanipulator.



**Figure 5.** Nuclearized oscillating mixer-mill

### 3.2. COMPACTION PROCESS

Green fuel pellets are generally produced with a uniaxial hydraulic press. The pelletizing tools comprise an upper and a lower punch sliding inside a die. Several variants are available: floating die, relative motion between punches, etc. In most techniques, retention pressure is applied on the pellet to prevent radial cracking as it is

ejected from the die. The advantage of these presses, which are widely used in the industry, is their very high rate—up to several tens of compacts per minute.

From a research and development perspective we preferred another technology more suitable for use in glove boxes or shielded cells. The press comprises a conventional hydraulic cylinder supplied by a hydropneumatic pump and gooseneck. The compact hydropneumatic pump makes it unnecessary to transfer any oil to or from the shielded cell: the compaction force is generated by compressed air, which is available in the cell. The pump generates an oil pressure of 700 MPa applied to the actuator. This is sufficient for a 50–100 kN (5–10 metric ton) press. Moreover, only a small quantity of contaminated oil (1 to 2 liters) is produced; it is treated by a specific process developed by the CEA [6].

The compaction tooling comprises a petalized die (i.e. a multipiece unit) to allow removal of the pressed compact without applying any ejection pressure. This avoids the need for applying retention pressure during ejection, and simplifies the hydraulic system.

### 3.3. SINTERING PROCESS

#### 3.3.1. Specifications

The research and development phase of the FUTURIX program [7] has led to the specification of an advanced, robust cycle capable of loading very different actinides. The maximum temperature reached is 1600°C in argon + 4% hydrogen atmosphere. We therefore had to design and build a specific furnace meeting the following performance criteria:

- routine operating temperature: 1700°C (maximum temperature: 2000°C),
- loading capacity: at least 20 pellets with PWR geometry (8.19 mm dia × 10 mm high),
- compatible with any type of atmosphere (oxidizing, neutral or reductive),
- suitable for entry into an existing hot cell via a 250 mm dia La Calhène flange,
- furnace assembly and maintenance entirely using telemanipulators.

#### 3.3.2. Furnace design

The main design difficulty with this type of furnace is the dimensional limitation to allow the components to be transferred into the hot cell. A feasibility study oriented our choice of a water-cooled furnace capable of high-temperature operation with suitable loading capacity and meeting the safety standards for use in a hot cell (outer wall temperature < 50°C).

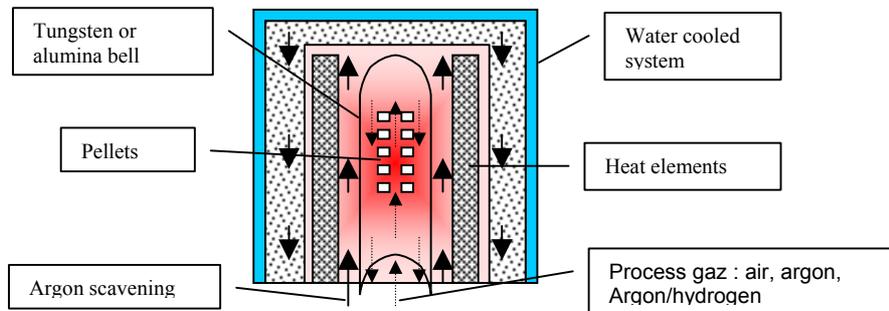


Figure 6. "Osmose" furnace schematic

The "double bell" furnace design (Figure 6) and the selected materials represented a tradeoff among several criteria:

- high-temperature behavior in oxidizing, neutral and reductive atmosphere;
- the existence of a strong temperature gradient (200°C.cm<sup>-1</sup>);
- material compatibility;
- furnace power and robustness (high currents inside a shielded cell);
- manufacturing and maintenance cost.

#### 3.3.3. Heating element and power supply

Another difficulty involved the design of the heating system. The electrical resistance must not be too low, which would require the use of a high current intensity (400 to 800 A) that would complicate the hot cell cable

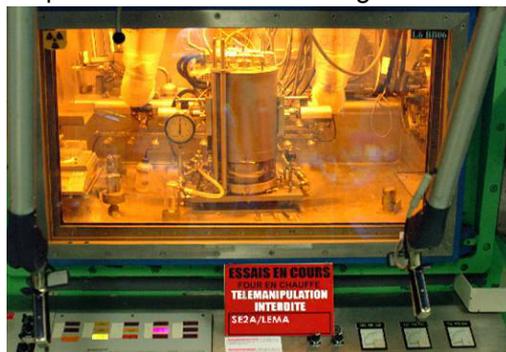
passageways. It is possible to increase the electrical resistance of the material by limiting the thickness of the heating element, but this would diminish its mechanical strength and suitability for remote handling. A tungsten heating element would imply excessive current intensities. We therefore selected a graphite heating element with an effective current limited to 400 amperes; this required the development of a specific electrical feed-through via a 105 mm dia La Calhène flange. The material is protected against oxidation by argon scavenging, requiring a bell device separating the working atmosphere from the inerting stream (Figure 6). Graphite foam insulators (convective heat exchange) are used together with tungsten and carbon deflectors (radiant heat exchange).

### 3.3.3.1. Working bell

A working bell separates the process gas (pellet sintering atmosphere) from the inert gas protecting the heating element. No conventional material is capable of ensuring this function at 2000°C irrespective of the atmosphere. The furnace therefore includes an alumina bell limited to 1700°C for oxidizing atmosphere, and a tungsten bell limited to 2000°C for neutral and reductive atmosphere. The pellet holders consist of small removable wafers available in a range of materials (iridium, rhenium, hafnium, zirconia, etc.) determined by the compound being sintered to prevent the formation of a eutectic detrimental to the final product quality.

### 3.3.3.2. Cooling system

The cooling system comprises a primary system cooling the furnace (7 kW), and a secondary system to separate the primary system from the building chilled water supply. The secondary system is situated outside the shielded cell. The primary system comprises a water/water heat exchanger with substantial thermal inertia (30 L water volume) and a redundant pumping system supplied by the building uninterruptible power supply. In the event of a furnace component failure or the detection of a safety alarm condition, the heating circuit is shut down but the furnace cooling system continues to operate. The secondary system comprises a water/water heat exchanger to prevent contamination of the building chilled water supply. The water in the primary and secondary cooling systems is frequently tested for possible contamination. Figure 7 shows the furnace in operation.



**Figure 7.** Osrose furnace in operation

## 4. ANALYSIS AND CHARACTERIZATION

Several analyses were carried out on fuel pellets from both lots. The characterization methods and equipment are indicated in Table I.

**Table I.** Analysis and characterization of composites

Examinations / Measurements	Equipment
O/M ratio, [Am], [Pu]	Spectrometry: TIMS, ICP-AES and ICP-QMS
Microstructure	Scanning electron microscope
[Am], [Pu] crystal structure	X-ray diffraction
O/M ratio	Thermogravimetric analysis

This article describes only the equipment developed for hot-cell ceramography as part of the microstructure analysis by scanning electron microscopy. This involved the nuclearization of a diamond-impregnated cutoff saw and a polisher. The composite microstructure (size and fissile aggregate distribution) is characterized by electron microscope observation combined with image analysis techniques for quantitative assessment. For electron microscopic characterization, each sample is metallized by gold sputtering (a few nanometers thick) using a nuclearized Polaron SC7640 sputter coater. The \* activity of the actinides prevented examination by elemental analysis equipment associated with SEM: energy-dispersive X ray spectrometry (EDS) (Oxford Instruments "Inca

Energy 200" system). An adjunct to the spectrometer for use in active conditions will soon be available to allow elemental analysis and analysis of the constituents of the composite microstructure.

#### 4.1. HIGH-LEVEL ACTIVE CERAMOGRAPHY

Tools have been developed to prepare the composites under radiological conditions compatible with radiation protection requirements. Commercial equipment is used: a Buehler Minimet polisher and a Buehler Isomet cutoff saw (Figure 8). A specimen preparation method using reversible encapsulation (Figure 9) was developed to simplify waste management. The sample is embedded in Wood's metal (Pb-Bi-Cd-Sn alloy with a low melting point of 72°C), which also provides effective radiation screening on the unpolished faces. Wood's alloy makes polishing difficult because it rapidly clogs the abrasive disks. A special operating procedure was therefore defined. Wood's alloy allows the pellet to be handled in a glove box with dose rates below the detection limit on the coated faces. The irradiation from the upper face can easily be limited by fitting a lead cover during transfers. The cover is removed for optical microscope examination. Figure 10 and Figure 11 show the microstructure determined by SEM after sample preparation.

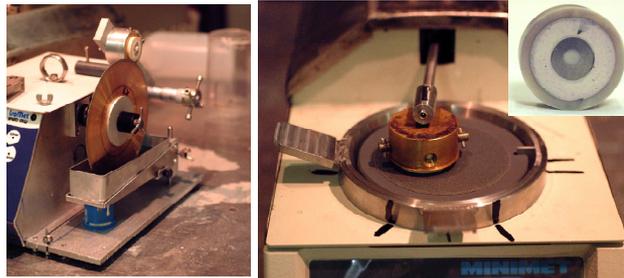


Figure 8. Nuclearized cutoff saw and polisher / Figure 9. Encapsulated, polished specimen in shielded line

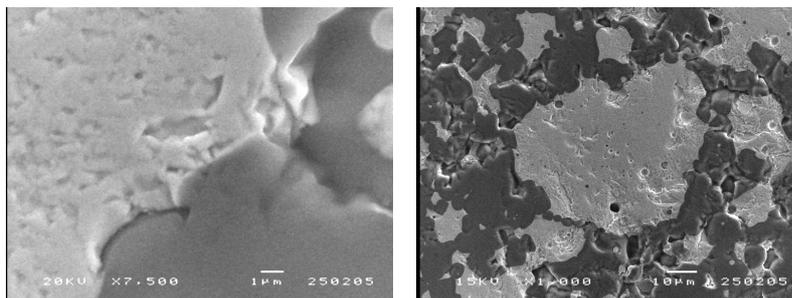


Figure 10. Micrographic images  $(\text{Pu}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$  and constituent interface

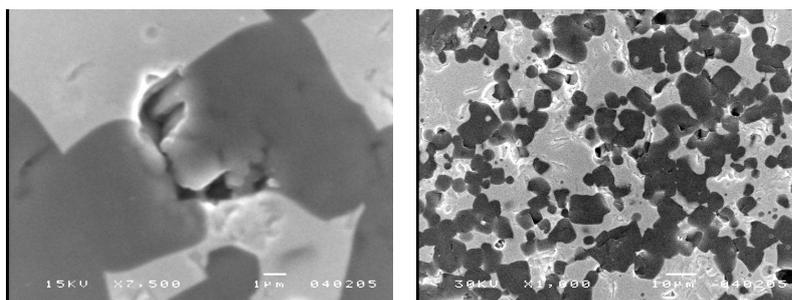


Figure 11. Micrographic images of major solid phases of a  $(\text{Pu}_{0.2}\text{Am}_{0.8})\text{O}_{2-x}$ -MgO cercer

#### 5. CONCLUSION

The CEA laboratories include innovative equipment for synthesizing nuclear materials and fabricating ceramics, as well as the indispensable provisions for characterizing them. This equipment is contributing today to an investigation of mixed actinide oxides  $(\text{Am,Pu})\text{O}_2$  as nuclear burner materials under a major international program, FUTURIX, and the ongoing ECRIX irradiation experiment (1996), currently in progress in the Phenix reactor.

The mixed oxide (Am, Pu)O<sub>2</sub> was synthesized by oxalate co conversion in a shielded line. The chemical reactor designed for this purpose has proved fully satisfactory with regard to the quality of the synthesized material and its suitability for remote handling. The phase synthesized was identified from the X ray diffraction diagram obtained using a nuclearized diffractometer. This characterization was necessary to develop a dedicated measurement cell capable of confining the specimen without interfering with the measurement.

To fabricate the burner pellets we installed dedicated equipment in a shielded cell: an oscillating mixer-mill, a conventional uniaxial press with a "petalized" die set, and a water-cooled double bell sintering furnace. Satisfactory results have been obtained to date.

Nuclearized polishing and cutting devices for use in a shielded cell were also developed for microstructural characterization by scanning electron microscopy. The use of Wood's alloy with a specific protocol allows excellent microstructure images to be obtained.

The CEA is continually developing new means for fabricating and examining advanced nuclear ceramics. These resources will also be particularly well suited for investigating non-oxide nuclear fuels (nitrides, carbides, etc.) and nuclear waste immobilization options, and for characterizing fuel cycle materials.

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