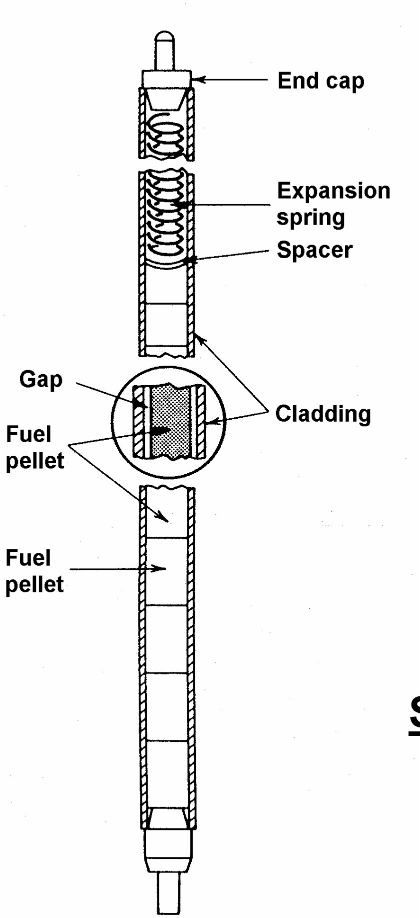
Dual phase MgO-ZrO_2 ceramics for use in LWR inert matrix fuel

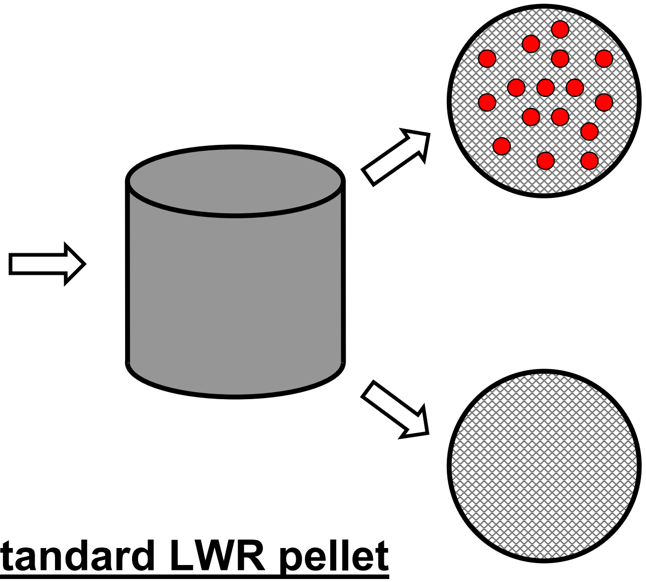
**Medvedev P. G., Frank S. M.,
Lambregts M. J., Maddison A. P.,
O'Holleran T. P., Meyer M. K.**

Idaho National Laboratory

LWR Inert Matrix Fuel Concept



Standard LWR pin



Standard LWR pellet geometry:

Diameter ~ 8.2 mm
Height ~ 12 mm

Macrodispersion:

Inert matrix and dispersed plutonium inclusions 0.1- 1.0 mm diameter

Microdispersion:

Inert matrix and plutonium intimately mixed

IMF advantage: efficient Pu disposition

Research needs: find a suitable matrix material

Background

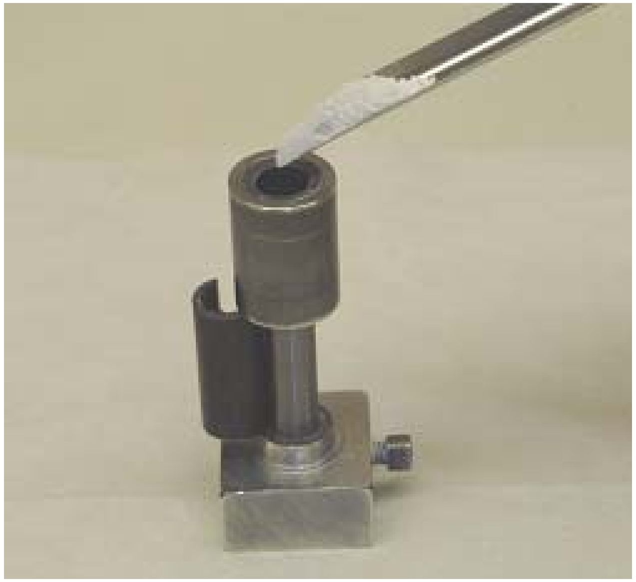
- Currently YSZ is a #1 IMF candidate
- Yet YSZ -based IMF suffers from low thermal conductivity, difficult to reprocess
- MgO is attractive, but unstable in water
- We propose MgO-ZrO_2 ceramics for use in LWR IMF
  - MgO
    - efficient heat conductor
    - easily dissolved in acids (reprocessing)
  - ZrO_2
    - protection from LWR coolant attack
- Intent to develop a better performing IMF matrix

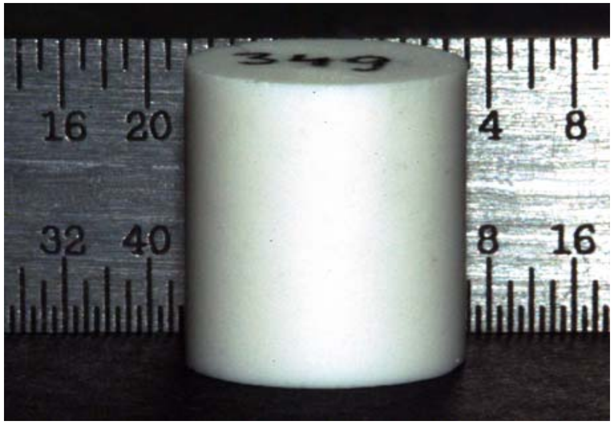
Description of actual work

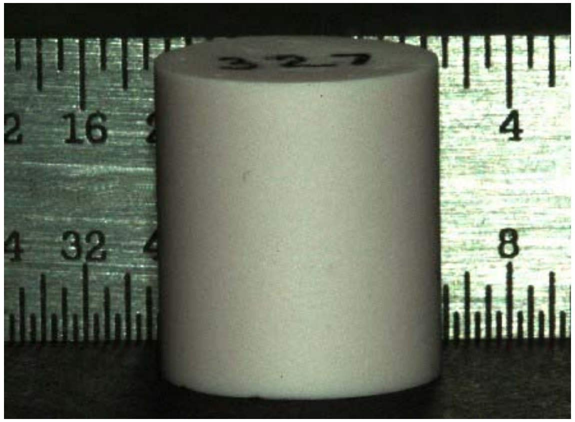
- MgO-ZrO_2 ceramics fabrication
- Product characterization
  - microscopy, XRD
- Performance assessment
  - hydration resistance
  - thermal transport properties
  - solubility in HNO_3
- Establish whether the product is feasible for use in LWR inert matrix fuel
- Current focus: fabrication of Pu-bearing MgO-ZrO_2 ceramics

Fabrication

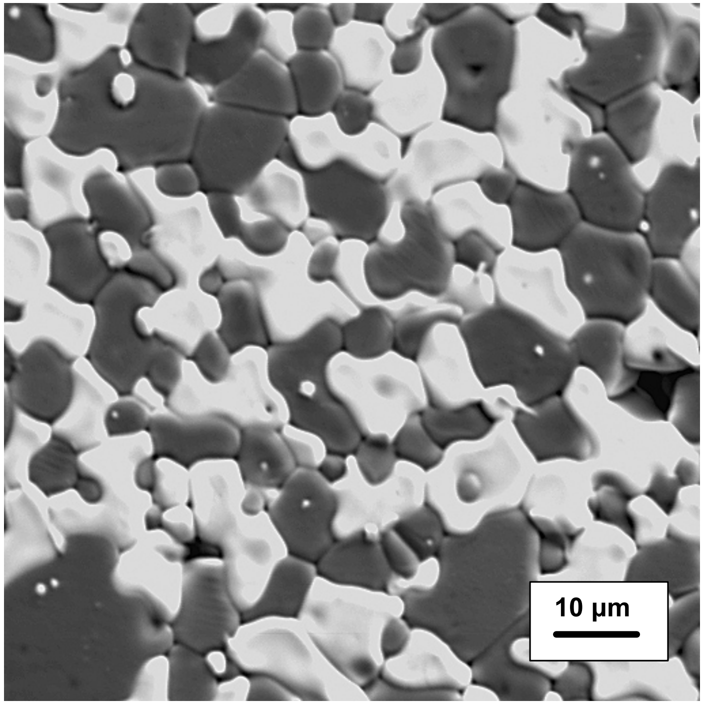
- MgO-ZrO_2 powder mixture
- pre-conditioned
- cold-pressed
- sintered in air
  - 1700°C
  - 7.5 hrs



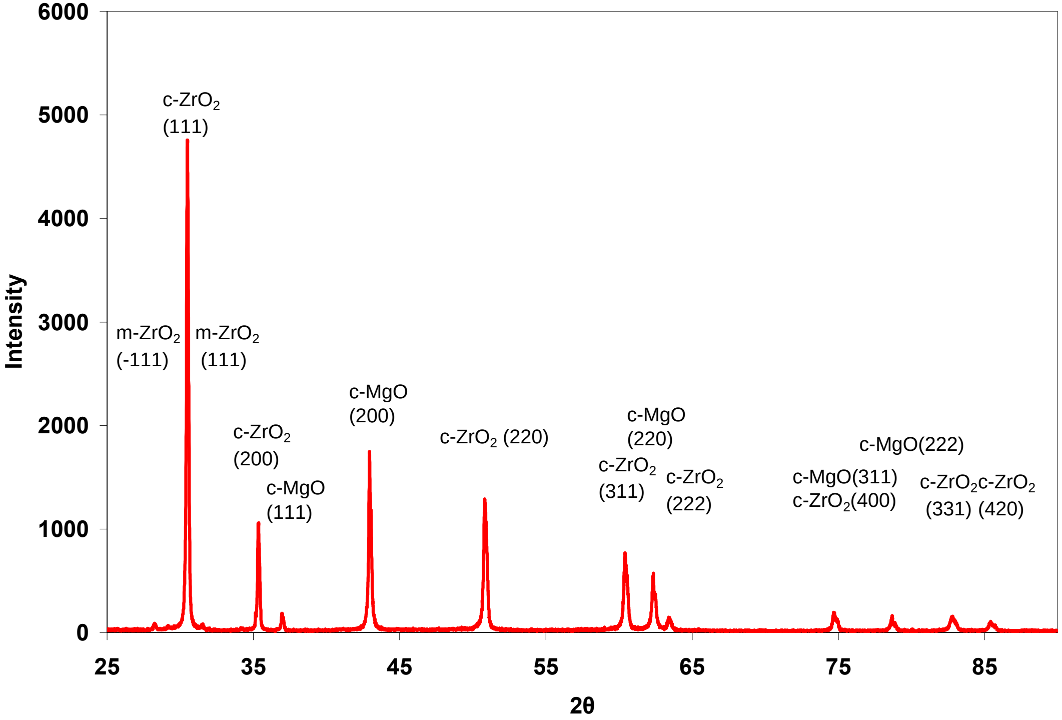




Microstructure



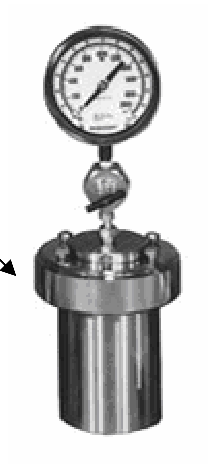
50/50



- Bright phase: $Mg_{0.160}Zr_{0.840}O_{1.840}$
- Dark phase: MgO
- Grain size 10-20 µm

Experimental investigation of hydration resistance

- Performed in de-ionized and borated (13000ppm H_3BO_3) water
- Parr pressure vessel
- Up to 700 hours, T=300^{o}C, saturation pressure
- Post-exposure examination: microscopy and x-ray diffraction
- Monitored pellet mass as a function of time
- Used mass loss rate per cm^2 sample surface area to quantify hydration resistance



Parr pressure vessel

Temperature controller

Heating mantle

Hydration resistance: remarkable contrast with MgO

MgO pellet
after 3 hr in boiling water

$MgO-ZrO_2$ pellet
after 700 hours in de-ionized water at 300°C

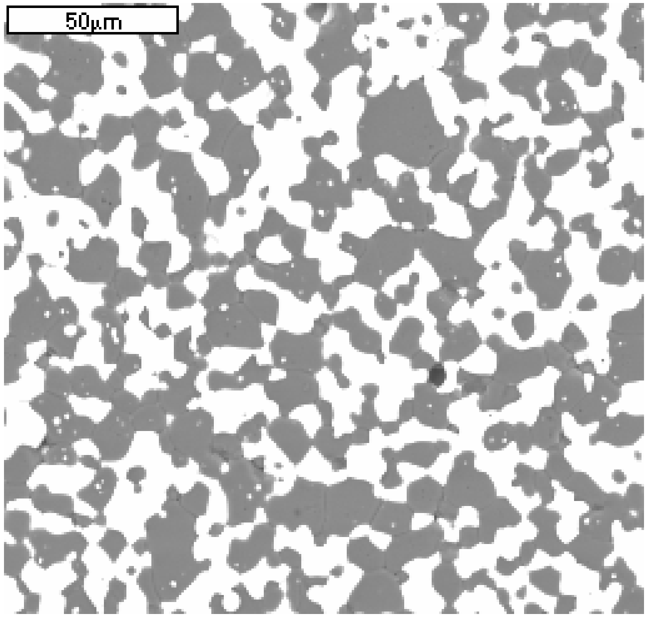
Idaho National Laboratory

AFCI

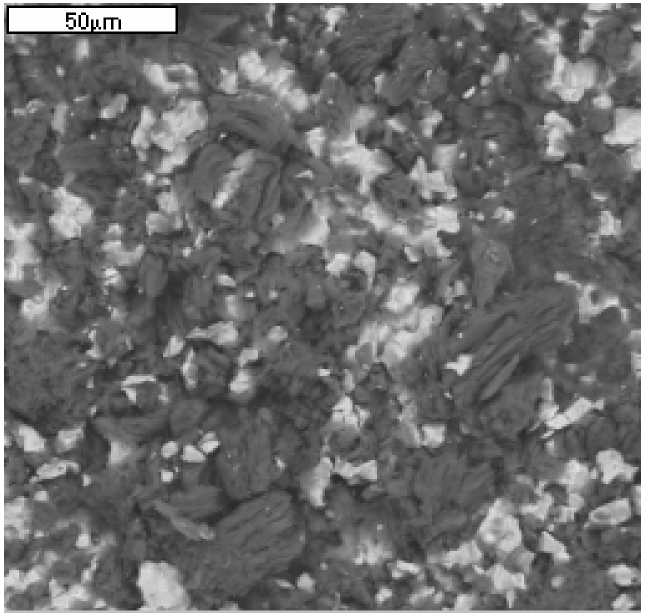
Microstructure before and after hydration attack

As-fabricated, polished and etched surface

Surface after 700 hr in deionized water at 300°C

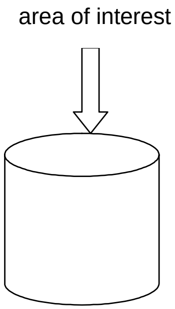


White phase: ZrO_2-MgO(ss); grey phase: MgO

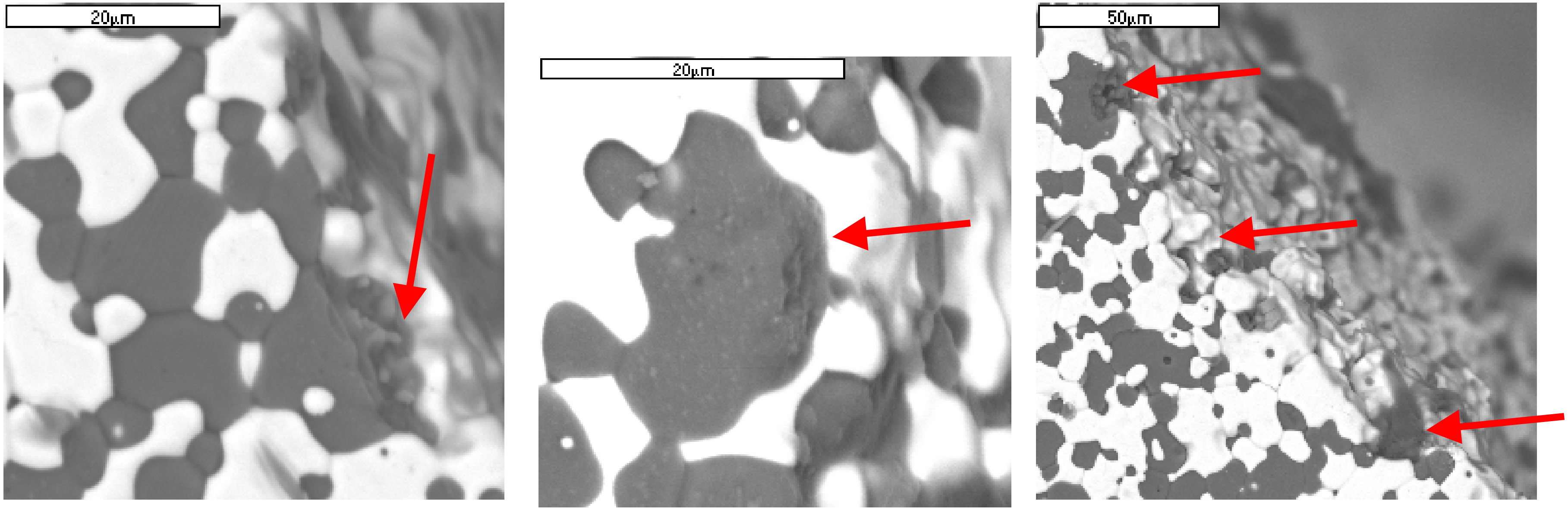


White phase: ZrO_2-MgO(ss); grey phase: $Mg(OH)_2$+MgO

Pellet cross-section after exposure



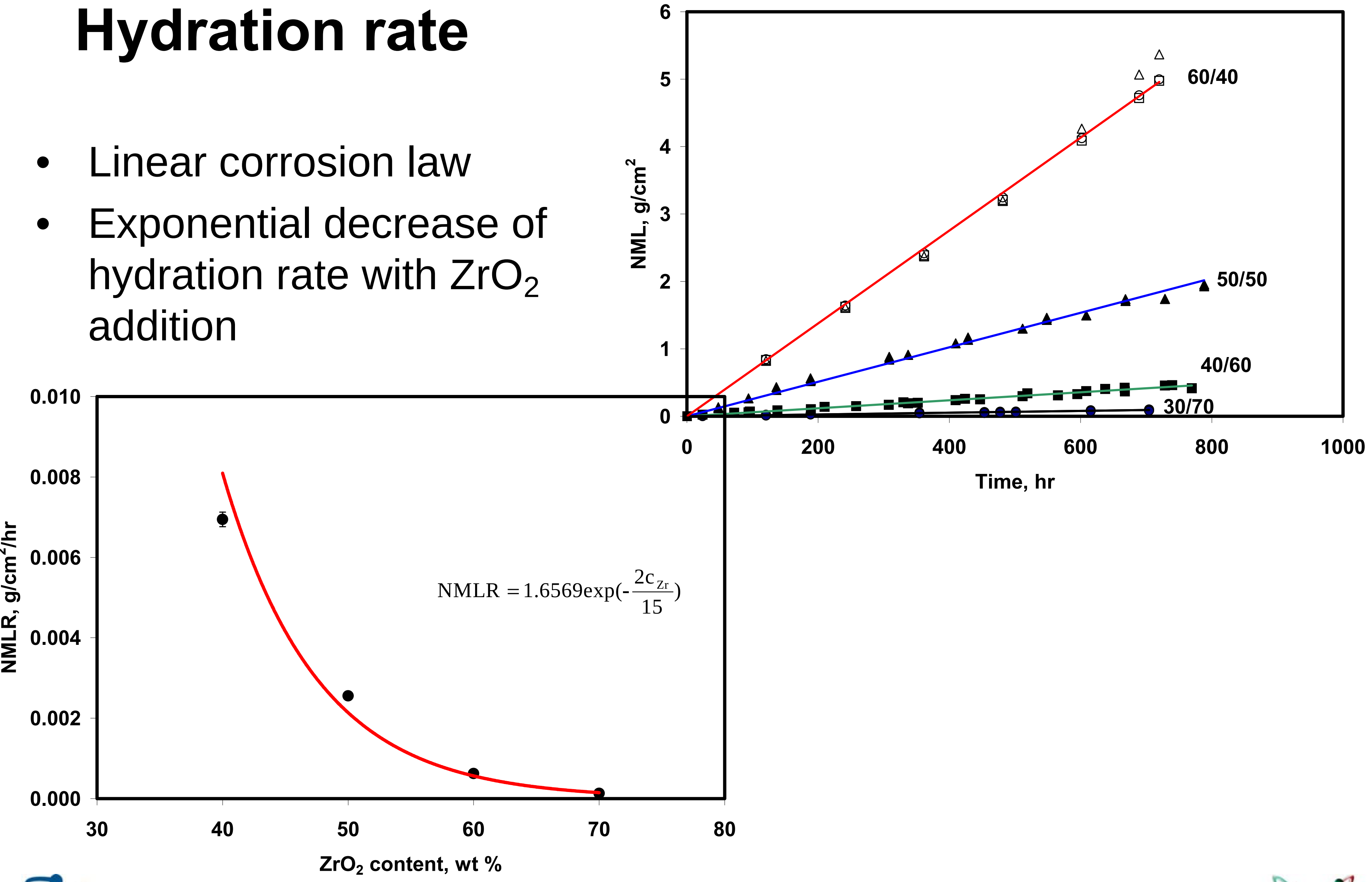
Hydration reaction is confined to the surface layer
Bulk of the MgO is encapsulated by ZrO_2



$MgO-ZrO_2$ ceramics after 700 hr in deionized water at 300°C
White phase: ZrO_2-MgO(ss); grey phase: MgO

Hydration rate

- Linear corrosion law
- Exponential decrease of hydration rate with ZrO_2 addition

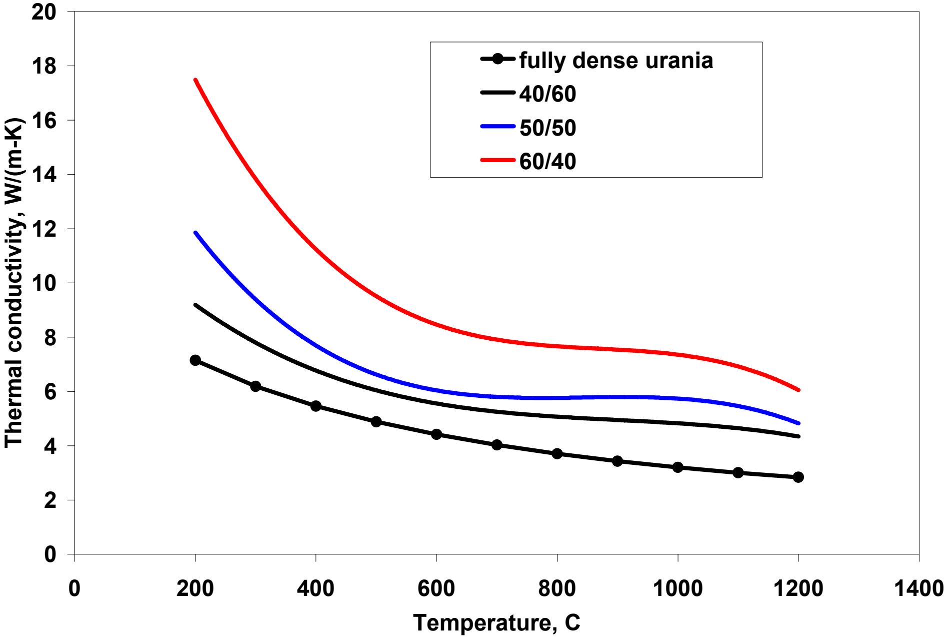


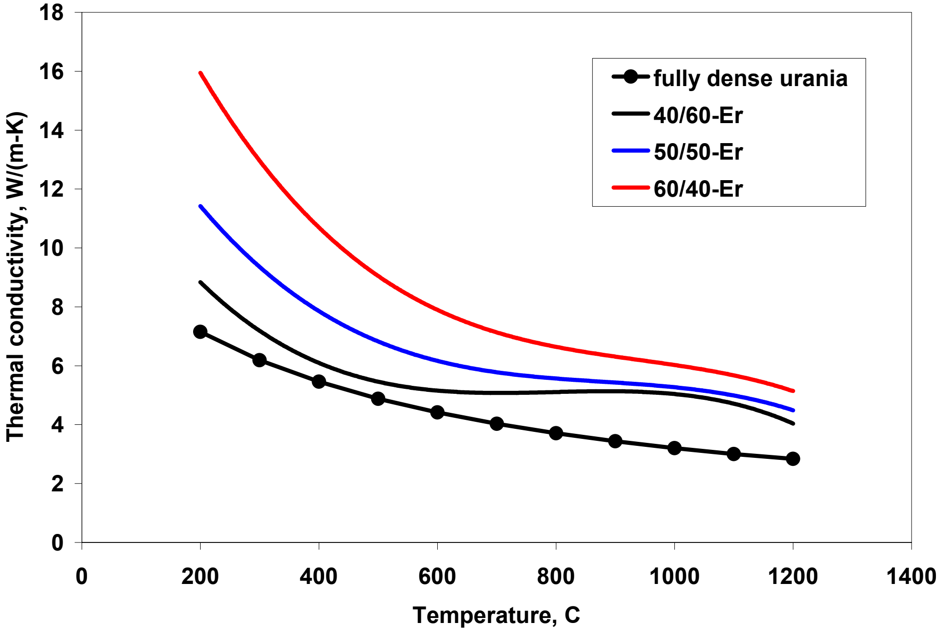
$$\mathrm{NMLR} = 1.6569\exp\left(-\frac{2c_{Zr}}{15}\right)$$

Thermal Analysis

- Goal
  - assess expected fuel centerline temperature
- Strategy:
  - Measure thermal diffusivity (*a*, s/m^2) using laser flash technique
  - Calculate heat capacity (*C*, Joule/kg C) from literature values for MgO, ZrO_2, and Er_2O_3
  - Calculate thermal conductivity as a product of *a*, *C*, and density (*r*, g/cm^3)
  - Solve the steady-state heat conduction problem for the infinite rod with uniformly distributed heat sources and temperature dependant thermal conductivity

Results of Thermal Conductivity Determination



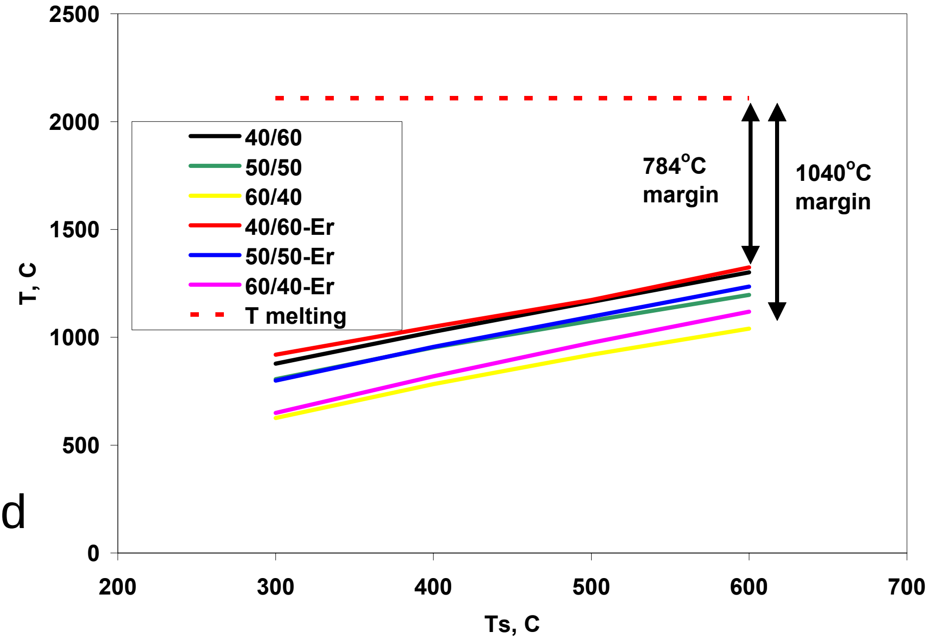


Idaho National Laboratory

Fuel Centerline Temperature Calculation

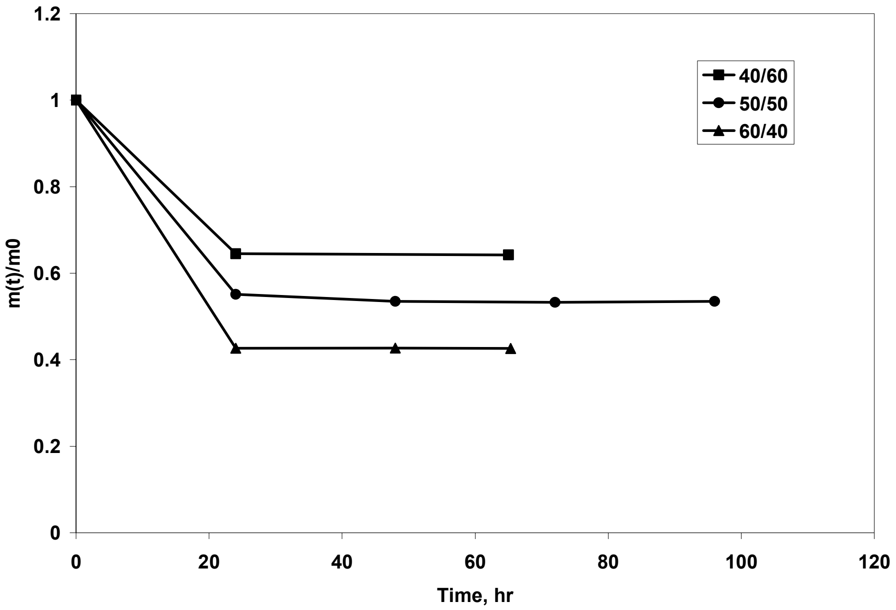
- $$\int_{Ts}^{Tcl} k(T)dT = \frac{q'r^2}{4}$$
  - *k(T)* temperature dependent thermal conductivity
  - *Tcl* pellet centerline temperature
  - *Ts* pellet surface temperature
  - *q'* volumetric heat generation
  - *r* fuel pellet radius
- Assumptions
  - pellet radius 4.095 mm
  - pellet height 10 mm
  - linear power density of 426 W/cm
  - pellet surface temperature 300-600°C
- 784°C-1040°C margin between T_{cl} and $T_{melting}$
  - Current Westinghouse PWR: 1068°C (T_{cl} = 1788°C and $T_{melting}$ =2878°C)

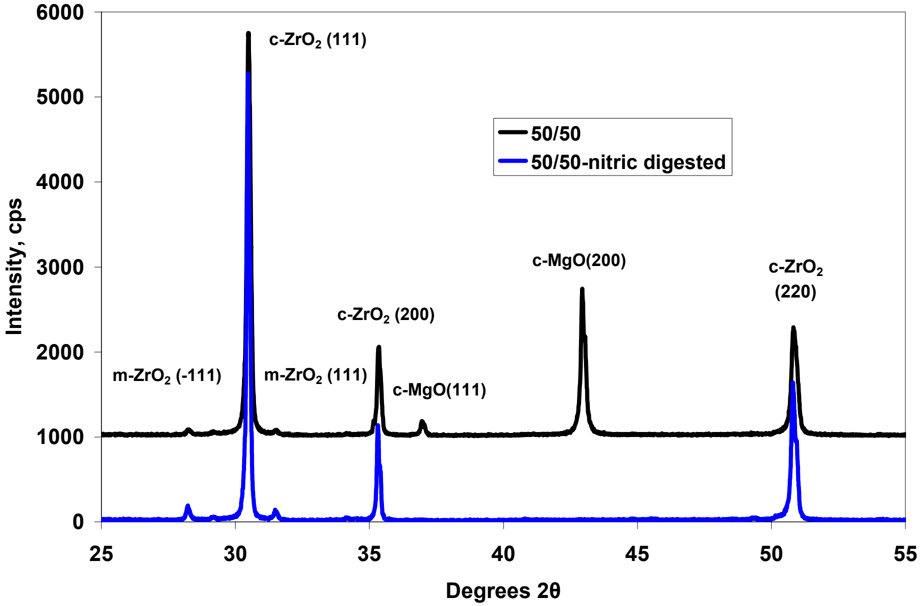
Results:



Dissolution in Nitric Acid

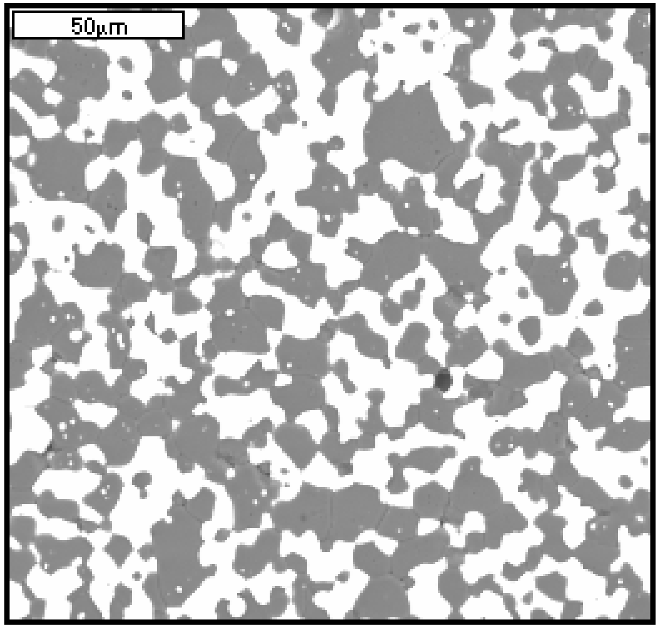
- Samples exposed to concentrated HNO_3 at ~55°C
- Sample mass monitored as a function of time
- Samples appeared intact despite mass loss
- Mass lost equaled mass of the MgO phase present in samples
- XRD confirmed dissolution of MgO phase





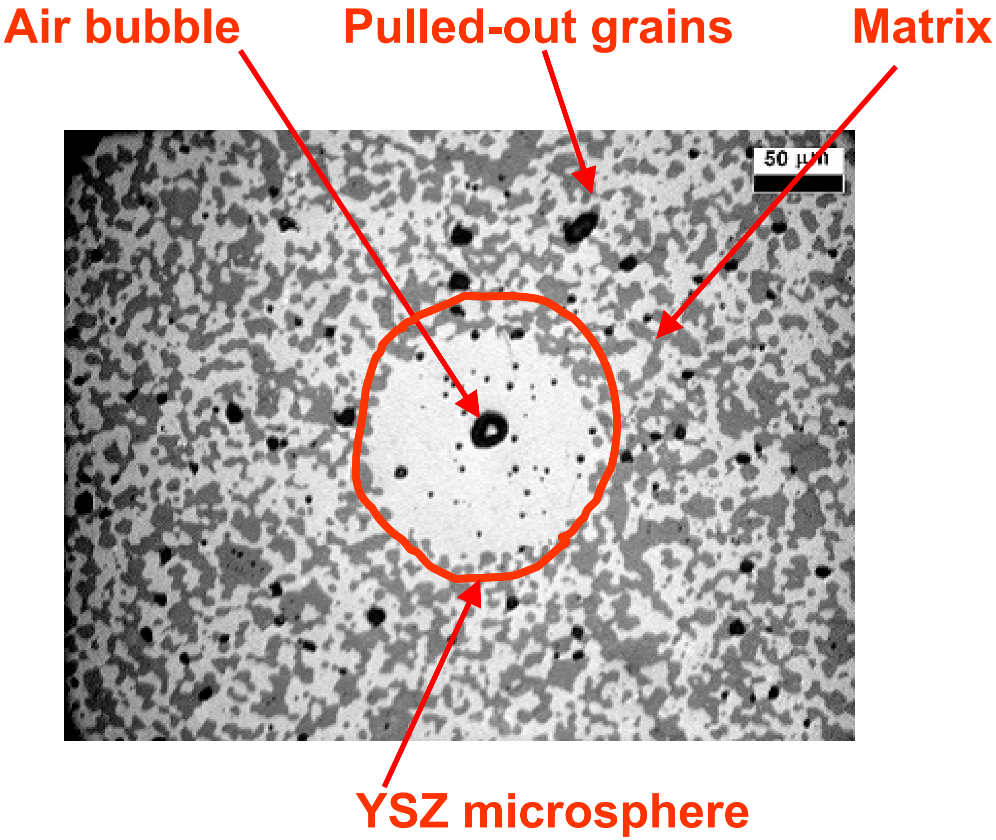
Reprocessing possibility

- Dissolution of MgO phase will allow acid to penetrate inside the pellet and dissolve fission products
- Insolubility of ZrO_2-ss in HNO_3 provides an opportunity for easy separation of Zr
- ZrO_2-ss can be further dissolved in HF
  - Use of HF implies departure from current reprocessing technology



Simulation of dispersion-type fuel fabrication

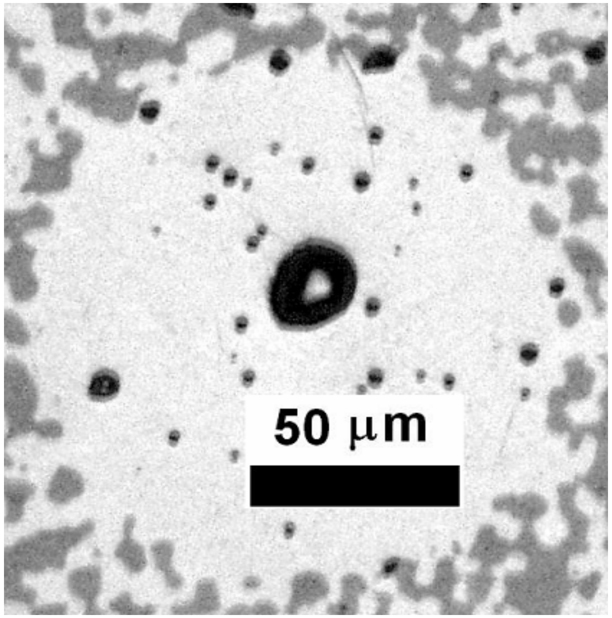
- Used 100 µm ceramic microspheres to simulate fissile phase
- Successfully incorporated microspheres into the matrix


Air bubble

Pulled-out grains

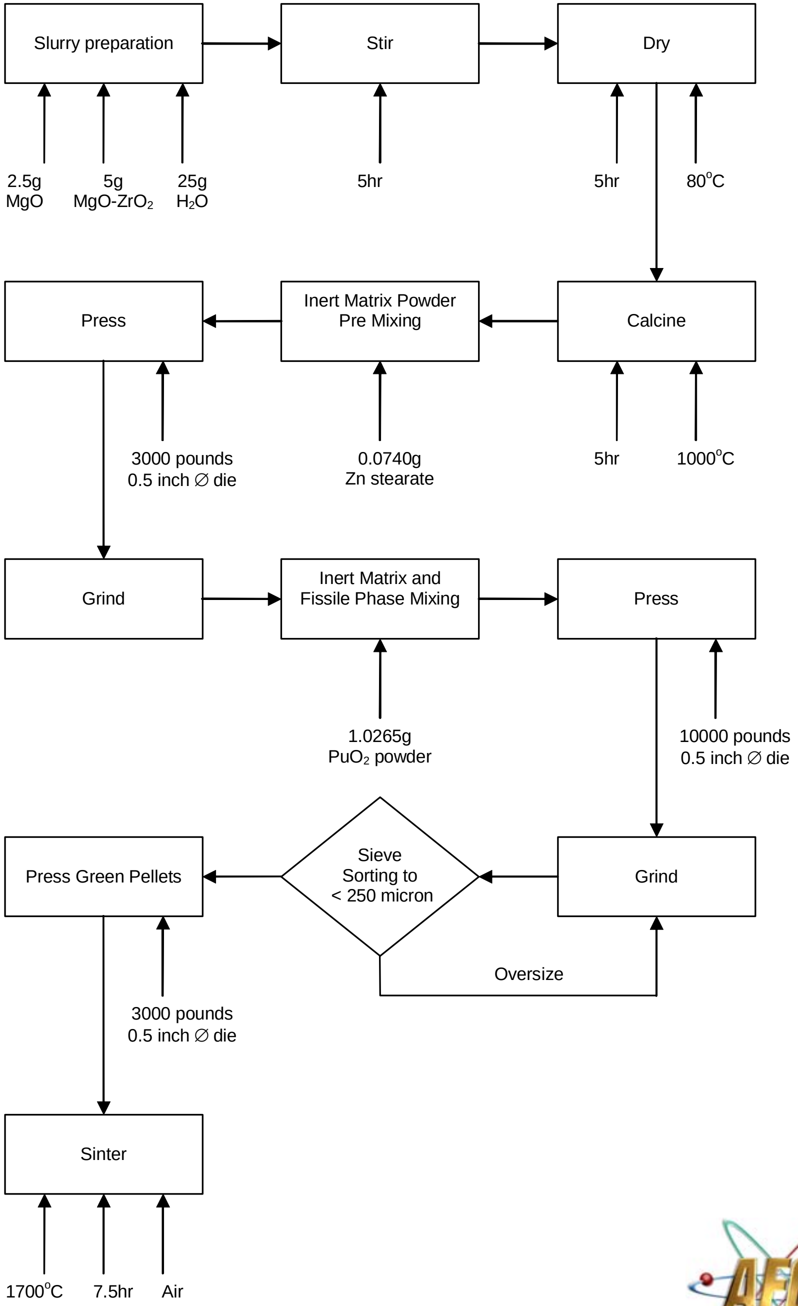
Matrix

YSZ microsphere



Current focus: fabrication of Pu-bearing MgO-ZrO_2 ceramics

- Previously developed MgO-ZrO_2 ceramic fabrication flowsheet modified to add PuO_2 powder or microspheres
- Target Pu concentration 1g/cm^3 in the ceramic
- Possible Er doping 0.35 g/cm^3



Slurry preparation

2.5g MgO

5g MgO-ZrO_2

25g H_2O

Stir

5hr

Dry

5hr

80°C

Calcine

5hr

1000°C

Inert Matrix Powder Pre Mixing

0.0740g Zn stearate

Press

3000 pounds 0.5 inch ∅ die

Grind

Inert Matrix and Fissile Phase Mixing

1.0265g PuO_2 powder

Press

10000 pounds 0.5 inch ∅ die

Grind

Sieve Sorting to < 250 micron

Oversize

Press Green Pellets

3000 pounds 0.5 inch ∅ die

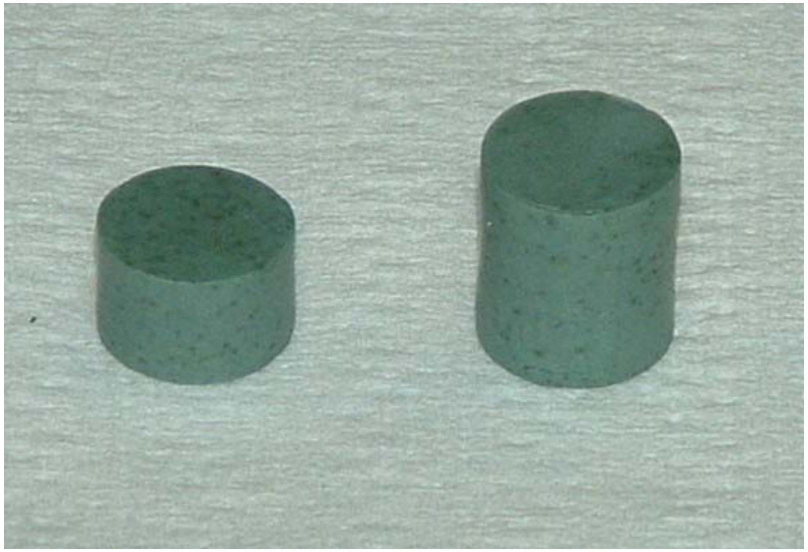
Sinter

1700°C

7.5hr

Air

First batch of MgO-ZrO_2-PuO_2 ceramics fabricated



MgO	43.5 wt.%
ZrO_2	43.5 wt. %
PuO_2	13 wt. %

powder from
weapons grade Pu

Conclusions

- Developed novel IMF fuel concept capitalizing on the known advantages of the product's precursors: MgO and ZrO_2
- MgO acts as an efficient heat conductor while ZrO_2 provides protection from the reactor coolant attack
- Documented significant performance gains
  - Hydration resistance
  - Thermal conductivity
  - Possibility of reprocessing

Idaho National Laboratory

Conclusions

- Results of this study encourage further development of this technology
- Currently pursued as a part of the DOE Advanced Fuel Cycle Initiative’s effort to evaluate transmutation in LWRs
  - Fabrication of actual fuels
  - Irradiation in Advanced Test Reactor at INL