Water Sorption and Radiolysis Studies for Uranium Oxides

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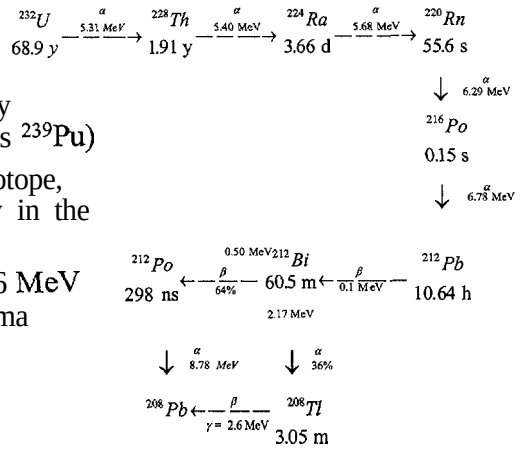
Overview

- $^{233}U/^{232}U$ characteristics
- Experimental facilities
- Experimental studies
  - Gamma radiolysis of fluoride impurities
  - Water sorption on uranium oxides
  - Gamma radiolysis of water sorbed on uranium oxides
  - Alpha radiolysis experiments

Characteristics of ^{233}U



- Relatively high alpha activity (-5000 times ^{235}U, -0.2 times ^{239}Pu)
- ^{233}U contains an impurity isotope, ^{232}U (concentrations typically in the range lo-1500 ppm)
- A daughter of ^{232}U (^{208}Tl, 2.6 MeV gamma) results in high gamma radiation fields

^{233}U storage at ORNL

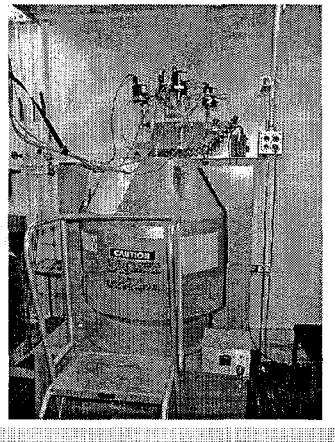
- ORNL serves as the national ^{233}U repository
- ^{233}U removed from the MSRE (as UF, or UF,) will be converted to uranium oxide and placed in storage at ORNL
- ^{233}U Storage Standard issued in July 2000 (DOE-STD-302% *2000, Criteria for Packaging and Storing Uranium-233-Bearing Materials)*
- Experimental studies needed to establish basis for some requirements in the ^{233}U storage standard

^{233}U storage standard laboratory studies

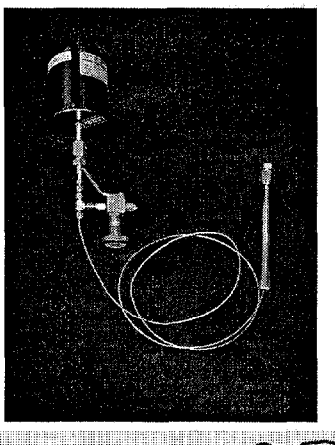
- Moisture content of UO,
  - amount of sorption/desorption
  - rate
  - types of water (sorbed, hydrate)
- Radiolysis
  - moisture on UO,
  - impurities (e.g., fluoride) in UO,

^{60}Co irradiations

ORNL ^{60}Co irradiator
~10^5 rad/h

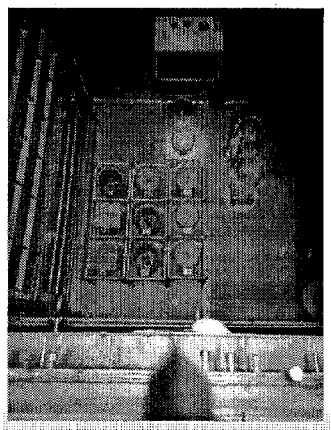


Sample container and
pressure transducer

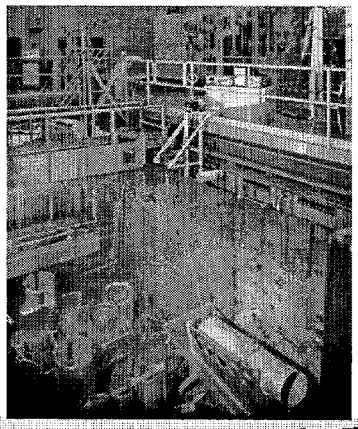


High Flux Isotope Reactor Spent Nuclear Fuel irradiations

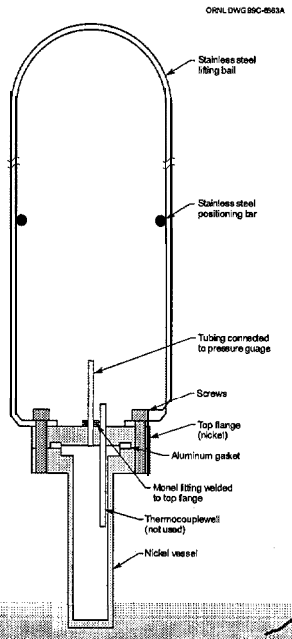
HFIR SNF elements
~10^7– 10^8 rad/h

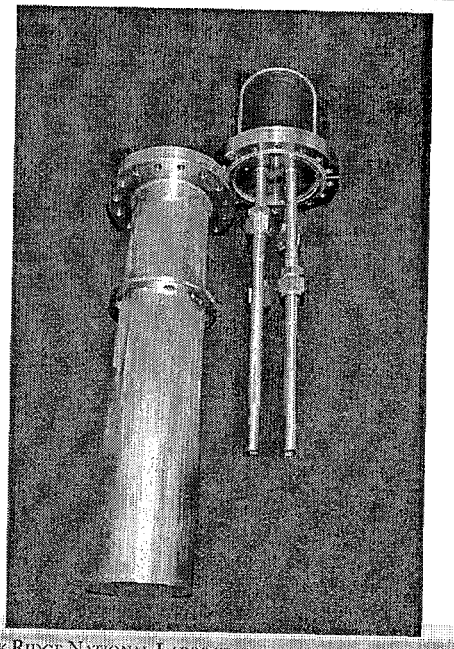


HFIR SNF pool

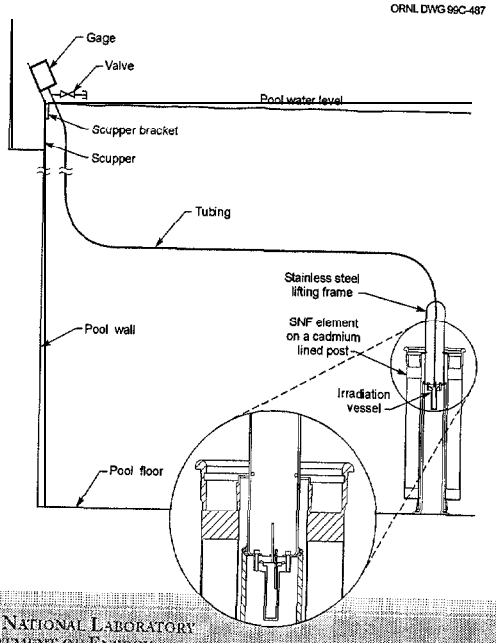


Sketch of small vessel used in HFIR SNF irradiations





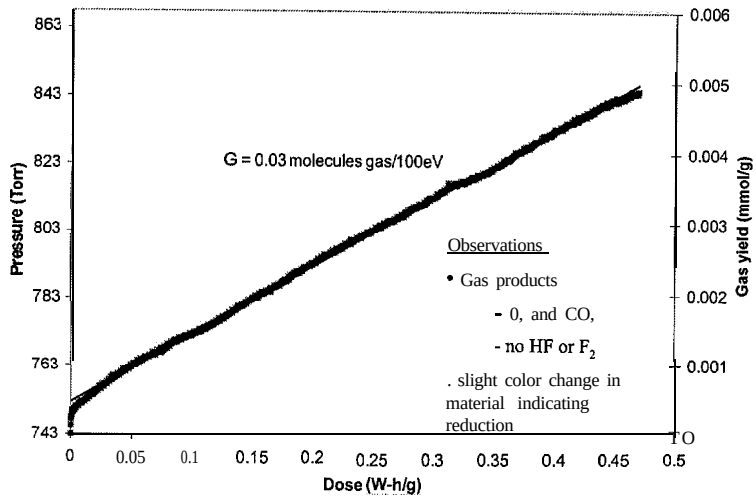
Vessel used in HFIR SNF multiple-sample irradiations.



HFIR SNF irradiation configuration

$UO_2F_2 \cdot 0.4\ H_2O$ ^{60}Co radiolysis (loaded in helium)

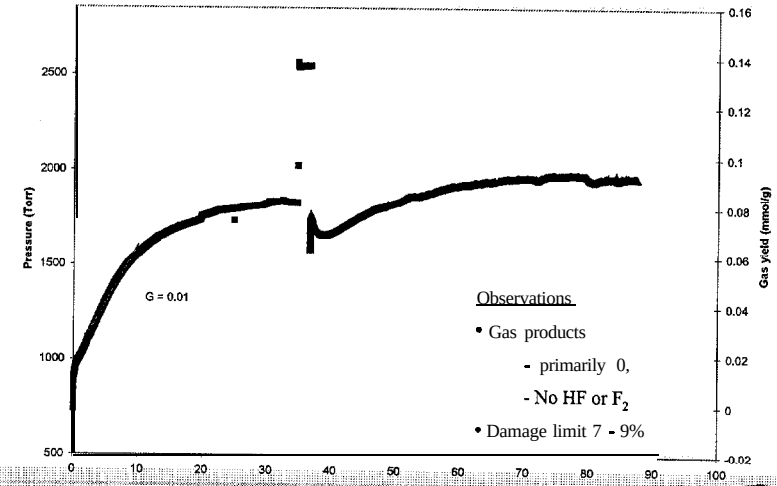
Small pressure increase observed



Observations

- Gas products
  - 0, and CO,
  - no HF or F_2
- . slight color change in material indicating reduction

HFIR SNF element radiolysis of $UO_2F_2 \cdot 0.4\ H_2O$ (loaded in helium)



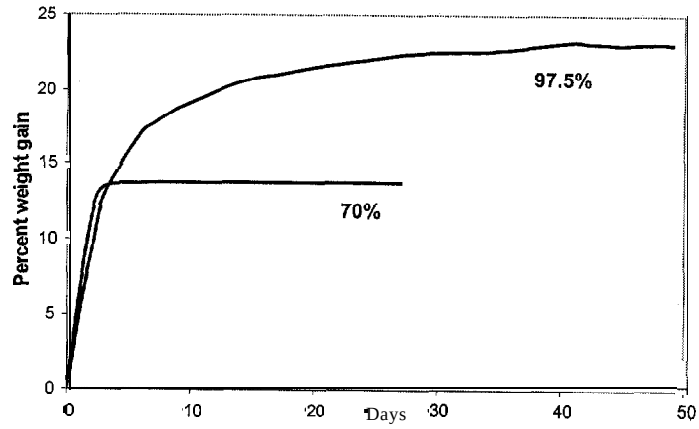
Observations

- Gas products
  - primarily 0,
  - No HF or F_2
- Damage limit 7 - 9%

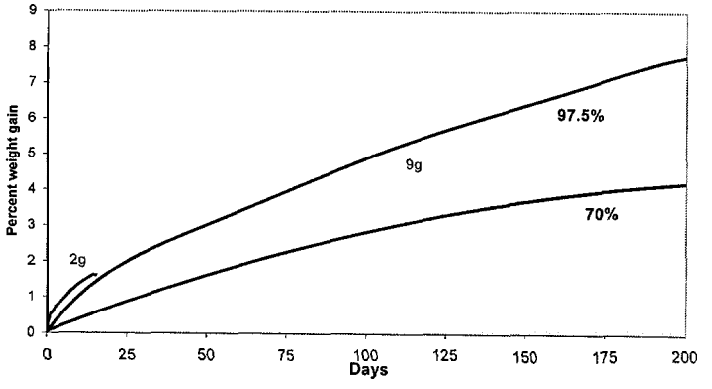
Water sorption experiments

- Surrogate samples of UO,, U_3O_8, and UO, prepared
- Samples placed in a controlled atmosphere (97.5 %, 70 % relative humidity), stirred and weighed daily
- TGA analysis performed on some samples

UO_3 weight gain in 70% and 97.5% relative humidity



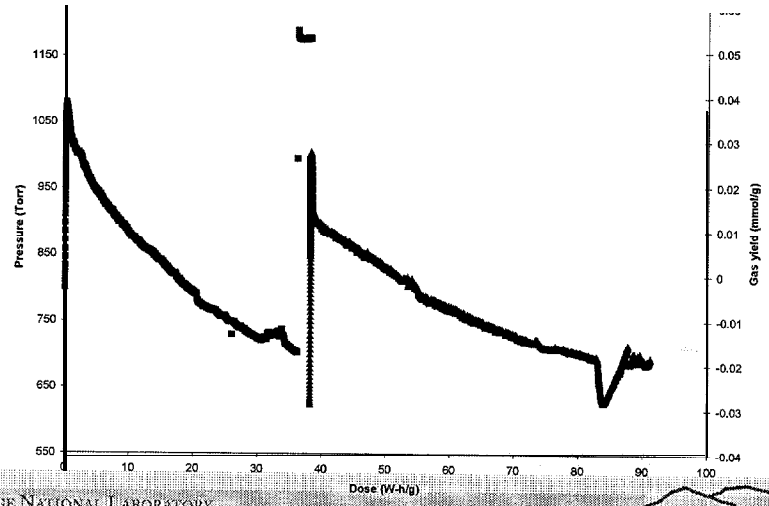
U_3O_8 weight gain in 70% and 97.5% relative humidity



Moisture gain and loss for uranium oxide compounds

Compound	Weight gain (%) in 97.5 % humidity	Weight loss (%)				
		Ovendrying			TGA	
		120°C (16 h)	400°C (24 h)	650°C (24 h)	60°C/min.	120°C/min.
UO_3	33	24.5	32.6	33.8	32.8	27.2
U_3O_8	1.6	0.97	1.43	1.68	1.77	1.64
UO_2	0				0	

HFIR SNF element radiolysis of U_3O_8 containing 1.48 wt% H_2O (loaded in air)



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HFIR SNF element radiolysis of U_3O_8 containing 6 wt% H_2O (loaded in air)

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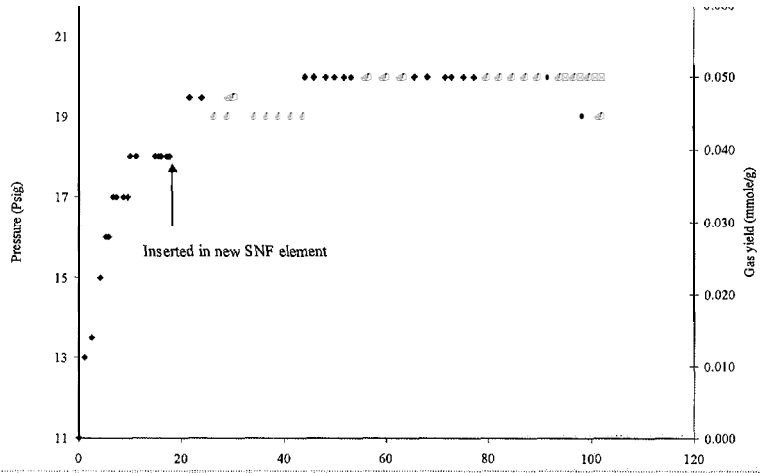
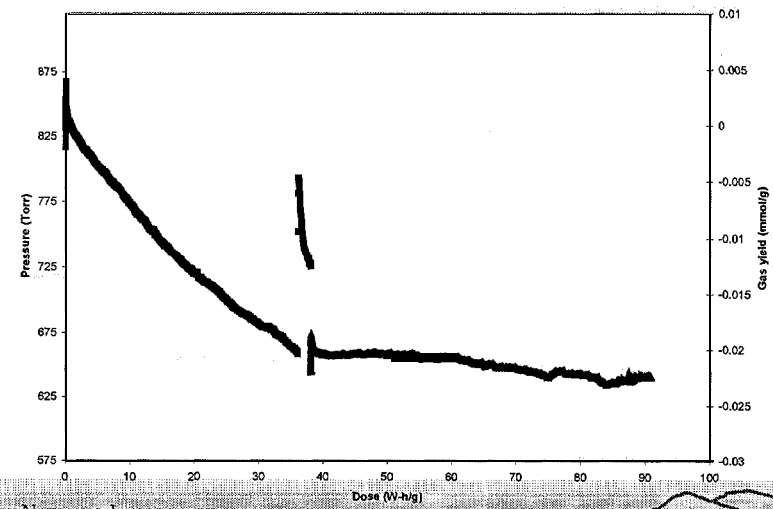
HFIR SNF element radiolysis of $UO_3 \cdot 2H_2O$ (loaded in air)



HFIR SNF element radiolysis of UO_2 dried at 400°C (loaded in air)



Summary of results of uranium oxide gamma radiolysis experiments

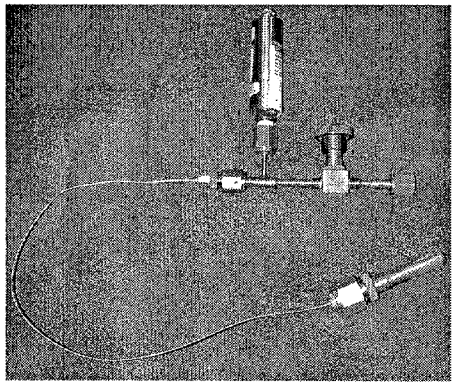
- $UO_3 \cdot xH_2O$
  - -One high-moisture, high dose rate sample had a pressure increase upon irradiation
    - primarily H_2 produced and 0, was depleted
    - pressure reached a plateau
  - -Overall pressure of other samples decreased
    - small amounts of H_2 produced and 0, was depleted in some samples
    - H_2 production appears to be related to the degree of hydration and total dose
  - -Thermal treatment of UO, at 400°C will remove all water; at 650°C will result in its conversion to U_3O_8

Summary of results of uranium oxide gamma radiolysis experiments (cont.)

- U_3O_8
  - – Samples had an overall pressure decrease upon irradiation
  - – 0, was consumed and very small amounts of H_2 were in the gas samples
  - – 0, may have been consumed through several mechanisms
    - Major contributor is likely the oxidation of the uranium oxide--valance analysis showed an increase in U(VI)
    - Minor contributors: NO, and CO, production
  - -neither large pressures nor unacceptable H_2 concentrations produced for the range of moisture contents studied (0 to -9 wt%)--Extraordinary means to remove all water from this material for long-term storage not necessary

Alpha radiolysis experiments initiated during FYO 1

- Surrogate samples of $UO_3 \cdot xH_2O$, U_3O_8, and $UO_2F_2 \cdot xH_2O$ prepared
- Samples doped with ^{244}Cm
- Samples will be monitored for several months
- Results to date similar to those seen with the gamma radiolysis experiments



Documents

- *Radiolytic Effects on Fluoride Impurities in a U_3O_8 Matrix,* ORNL/TM-20001157
- *A Gamma Radiolysis Study of $UO_2F_2 \cdot 0.4H_2O$ Using Spent Nuclear Fuel Elements from the High Flux Isotope Reactor,* ORNL/TM-2001/138 (Draft in review)
- *Water Sorption and Radiolysis Studies for Uranium Oxides,* ORNL/TM-2001/59 (Draft in review)

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