Technical Review of Depleted Uranium Uses Research and Development Program

M. Jonathan Haire, ORNL

Robert R. Price, DOE-NE

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Overview: Depleted Uranium Uses R&D Program

M. Jonathan Haire, Task Leader
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6179

Overview: DU Uses R&D Program

- The U.S. government has more than 700,000 metric tons of surplus depleted uranium hexafluoride (DUF_6), resulting from uranium enrichment operations, stored at sites across the country.
- "Record of Decision (ROD) for Long-Term Management and Uses of Depleted Uranium Hexafluoride," August 2, 1999.
  - promptly convert the DUF_6 inventory to a more chemically stable form
  - initiate DU Uses R&D Program to explore potential beneficial uses of conversion plant products
  - carry out research activities necessary to ensure the direct disposal of this material
- Implement "DUF_6 Materials Use Roadmap"
- DOE has committed to the state of Ohio EPA to have a "good faith" effort to find beneficial uses for uranium enrichment facility tails

Paducah Gaseous Diffusion Plant

Program Organization

Task no.	Task
110	Repository applications (cermet, fill)
120	Heavy concrete (DUCRETE)
210	Dose calculation
220	Reg. facilitation
230	Cyl. reuse
310	Long-term storage
320	DU disposal
410	UO_2 alteration
420	High value fluorine
430	Basic research (DU catalysts, semiconductors)
440	International collaboration
510	Systems analysis
520	Management

Repository Applications For Depleted Uranium (DU)
(Fill, Cermet, and Invert)

Charles W. Forsberg, Task Leader

Oak Ridge National Laboratory

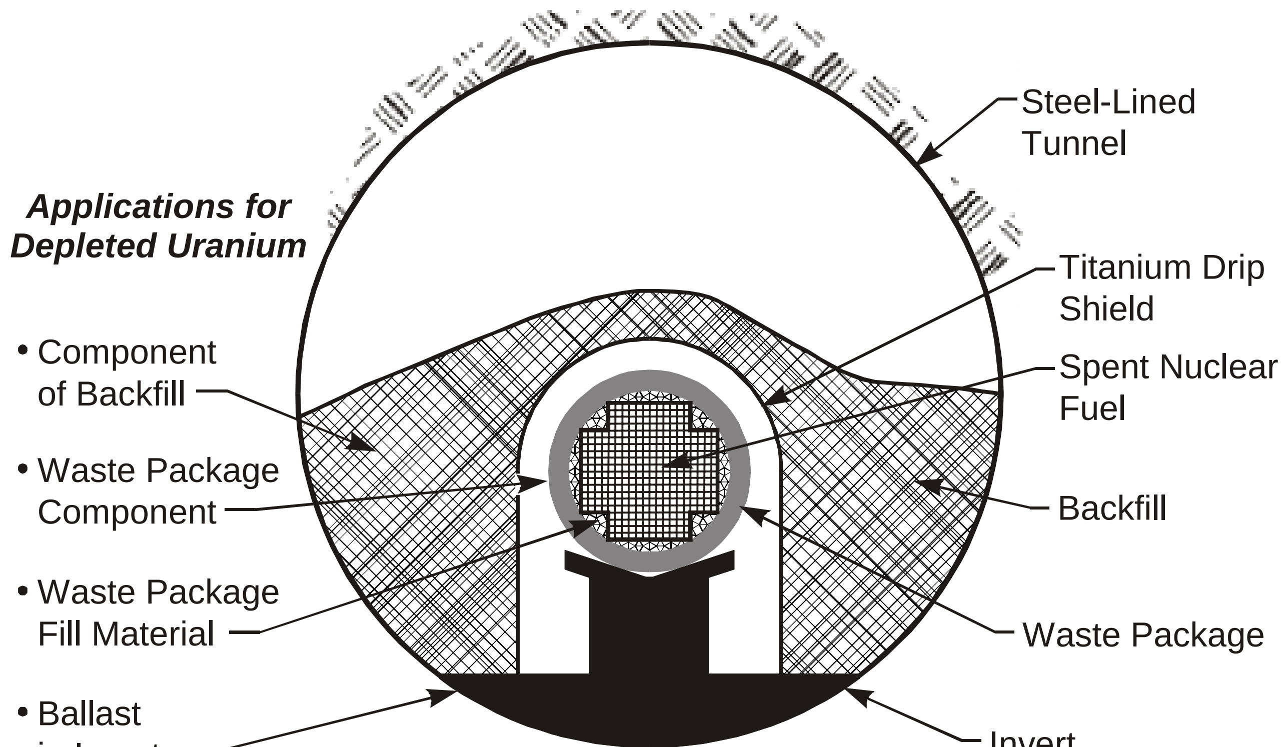
P.O. Box 2008; Oak Ridge, TN 37831-6180

Tel: (865) 574-6783; Email: forsbergcw@ornl.gov

Task Justification

- Potential to beneficially use the entire inventory
  - Fill material (DUO_2)
  - Package material of construction
    - Cermet for Yucca Mountain waste package
    - Cermet/metal for WIPP applications (limited application)
- Potential large repository benefits (Largest for fill, then cermet, then invert)
  - Criticality control
  - Reduced radionuclide release rate from the repository
  - Shielding
- Minimal regulatory and public acceptance issues
  - DU in a nuclear application
  - Meets regulatory requirements (DOE, NRC, EPA, etc.)

Schematic of Potential Depleted Uranium Uses at a High-Level-Waste Repository



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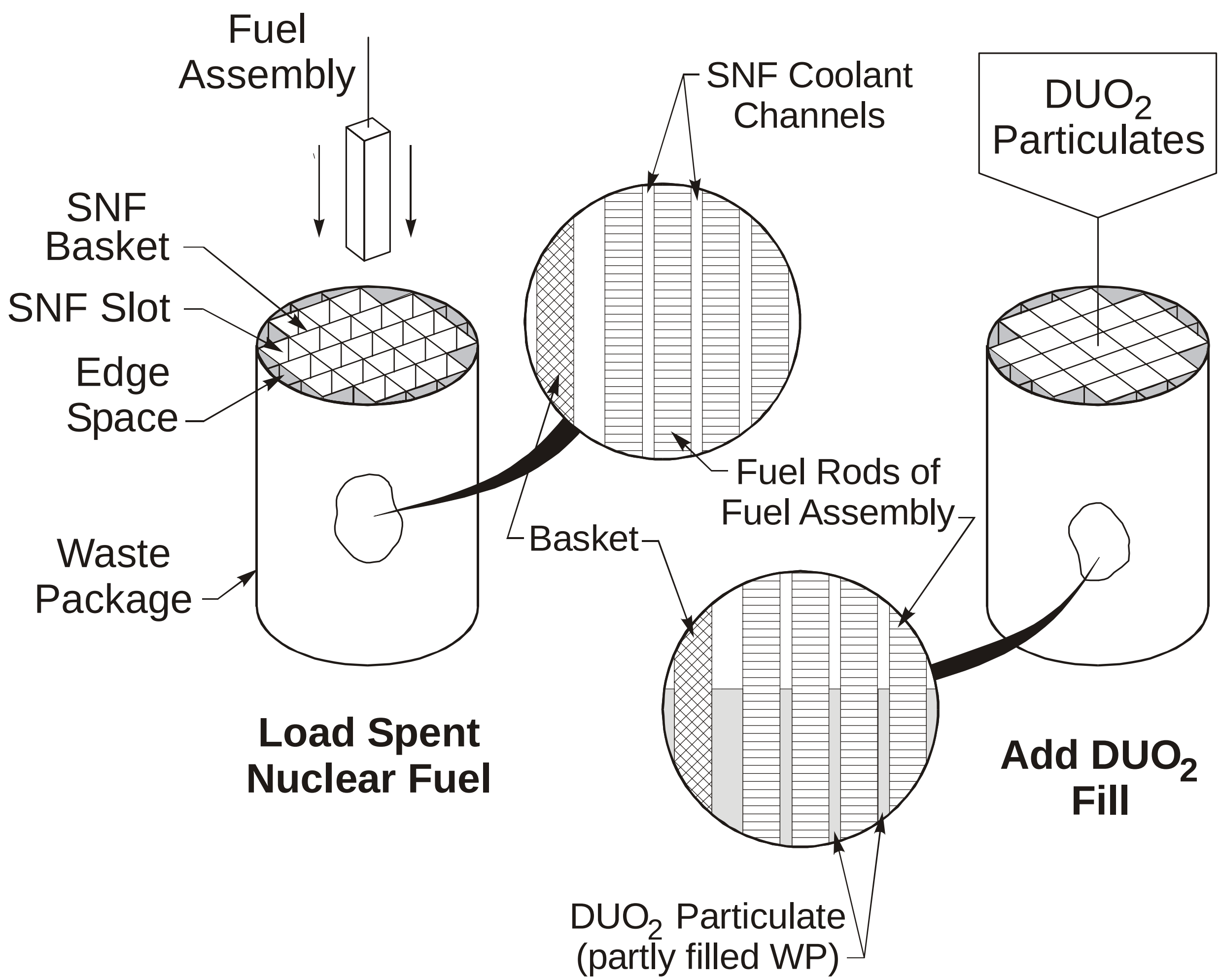
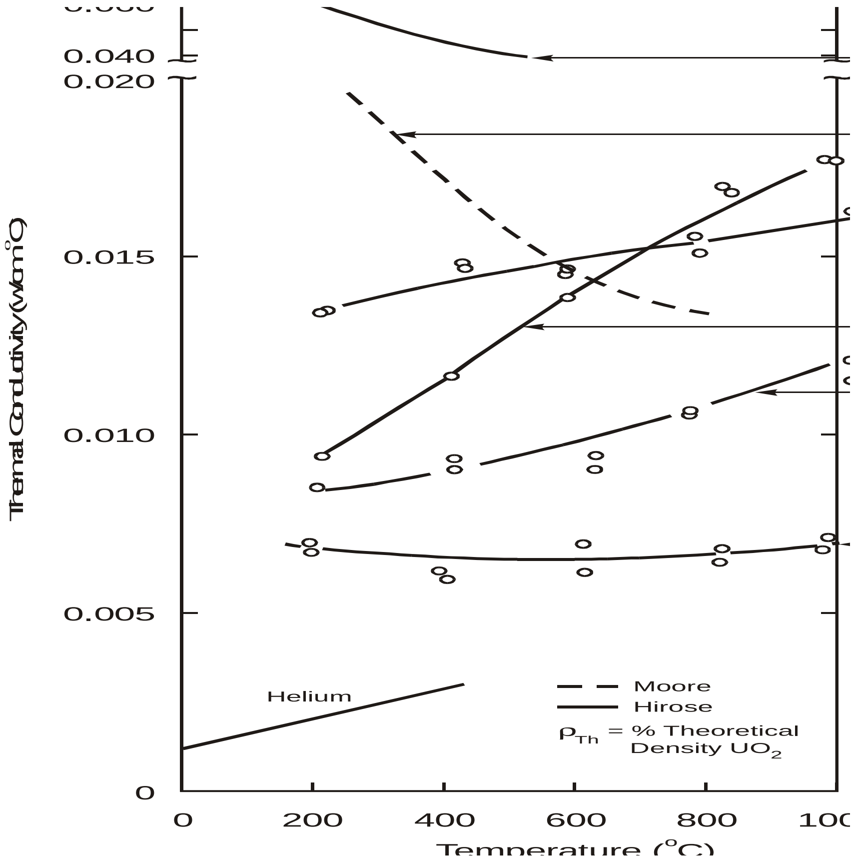
UT-BATTELLE

ORNL DWG 99C-352R

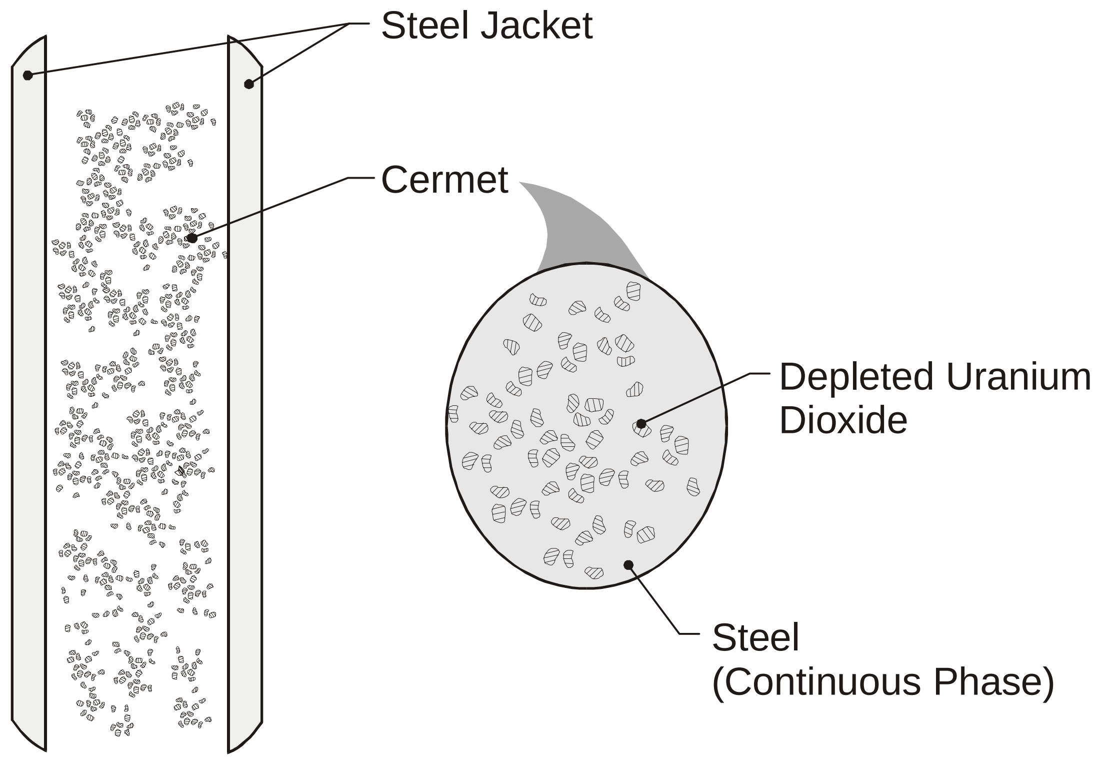
DUO_2 Fill Waste Package Loading Sequence



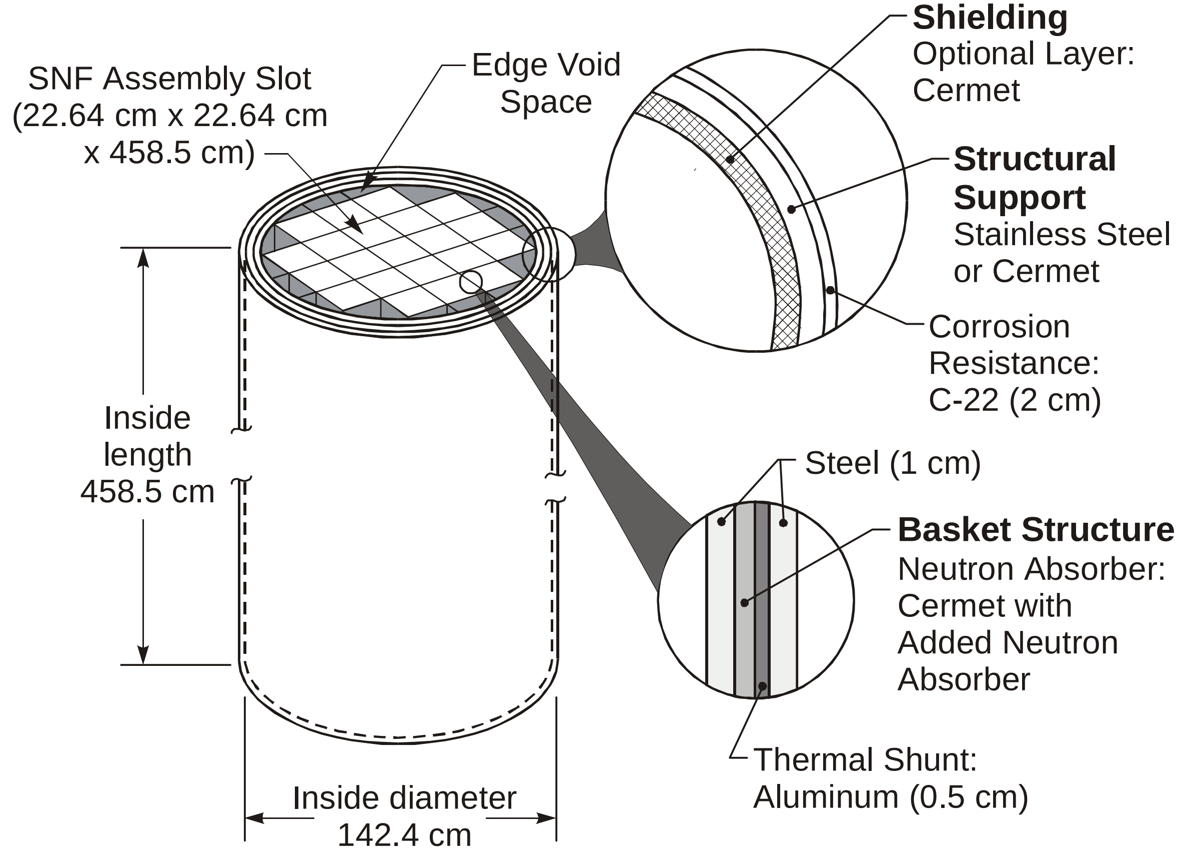


Experimental thermal conductivity for uranium dioxide particulate bed in helium (~1 atm)

A CERMET Is A *CER*amic *MET*allic Composite That Can Replace Steel In Waste Packages



Uses Of DUO_2-Steel Cermets In PWR Spent Nuclear Fuel Waste Packages



Accomplishments

- Fill interface with potential users (papers and contacts)
  - Peer reviewed journal article on fill (Nuclear Technology)
  - Spectrum paper in the YM waste package session
  - YM considering fills for special applications
- Identification and development of the cermet concept
  - Introduced concept (ANS conference and paper)
  - Discussions with multiple programs (DOE/ORO, others)
- Showed that waste package heat transfer requirements (avoid high temperatures) can be met using a DUO_2 fill
  - Identified as go/no-go issue in the DU roadmap
  - Literature search of earlier experimental work identified measured properties of DUO_2 particulate beds
- Experimental plan
  - Base-line description of expected system behavior
  - Identified experimental materials

Planned Accomplishments For FY 2001

- Complete search and evaluation of reported experiments on DUO_2 particulate bed physical properties
  - Available thermal and mechanical property data
  - Avoids the need for many experiment
- Interface with YM and WIPP
  - Build user interface with YM understandings
  - User input required to define important issues to address
- Initiate experimental program
  - Experiments to confirm (or disprove) baseline description of expected behavior of UO_2 particulate bed
    - Massive amount of information on UO_2 behavior
    - Uncertainties are with DUO_2 as a *particulate bed*
  - Examine ion-exchange/adsorption of fission products and actinides on degraded DU oxides (Proposed Russian work)
- Identify other programmatic funds to investigate cermet options

Heavy Concrete for Spent Fuel and Waste Storage Silos

Les R. Dole, Catherine Mattus, and Roger Spence
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6111

Bill Quapp
Teton Technologies
Idaho Falls, Idaho 83401

Task Justification

- Low technical risk, uses large quantities of depleted uranium (DU) in radiologically regulated areas (i.e., has low regulatory risks)

- Objective: bring heavy concrete — i.e. DUCRETE—technology to the point where a demonstrated technical basis for deployment exists

Shielding Capability

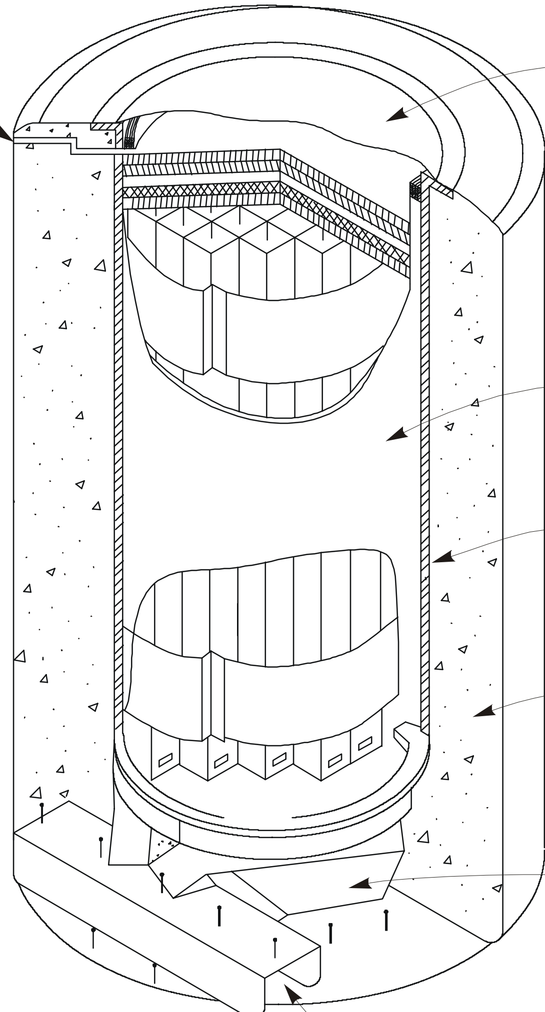
- Heavy concrete is more volume and weight efficient[a], enabling:
  - Thinner walls, smaller diameter (~2.5 ft)[b]
  - ~40 tons lower weight casks than with conventional concrete[b]
- Volume efficiency results in[b]:
  - Factory fabrication
  - In-pool loading
- Capital costs of spent fuel concrete ventilated storage cask with DU are comparable (i.e., approximately equal) to current concrete casks costs[b]
- Net result
  - Estimated to be cost-effective without DU subsidies
  - Reduced dose[b]
  - Can transport to repository for disposal or use

[a]C. Itoh, et al., "Development of Heavy Concrete with Depleted Uranium," *Proc. International Symposium on Safety and Engineering Aspects of Spent Fuel Storage*, sponsored by the International Atomic Energy Agency and OECD, Vienna, Austria, October.
[b]F. P. Powell, "Comparative Economics for DUCRETE Spent Fuel Storage Cask Handling, Transportation, and Capital Requirements," April 1995, INEL-95/0166.

Stainless Steel Clad DUCRETE Drum Overpack

Cross Section of Large DUCRETE Block (16 x 18 x 5 inches)

Ventilated Storage Cask



Accomplishments

- Program Plan written
- Subcontract put in place for Bill Quapp services
- Request to Starmet Inc. to estimate cost, schedule for fabricating DUAGG

Planned Accomplishments for FY 2001

- Testing safety summary approved for laboratory
- Assemble and test equipment and measurement methods
- Fabricate concrete blanks for testing and for comparison standards in experiments
  - SRS RFP for DU storage casks awarded ≈April 2001 (reassess task: e.g., purchase DUAGG, choose commercial vendor with which to collaborate
- Issue contract to fabricate DUAGG
- Fabricate DUCRETE, acquire samples
- Initiate long-term stability tests

DUCRETE™ Test Conditions

- Service exposure conditions with saturated moisture in autoclaves:
  - Normal service bulk at 66°C for 30 to 360 days
  - Normal service inner surface at 138°–142°C for 30 to 360 days
  - Accident at 350°C for 90 minutes
- Measure physical characteristics using standard ASTM methods:
  - Direct:
    - Unconfined compressive strength
    - Flexural strength
    - Thermal conductivity
    - Radiation attenuation
  - Indirect:
    - Divergent ratio of flexural and compressive strength
    - Comparisons with standard aggregates

Facilitate Intact Cylinder Reuse

Dan O'Connor, Task Leader
Engineering Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-8038

Purpose of Task is to Demonstrate Feasibility

- **Demonstrate the institutional feasibility and economic attractiveness of reusing intact DUF_6 cylinders as low-level waste (LLW) disposal packages by cutting an opening in the cylinder, loading it with LLW, welding a cover plate over the opening, and transporting the package to the Nevada Test Site (NTS) for disposal**

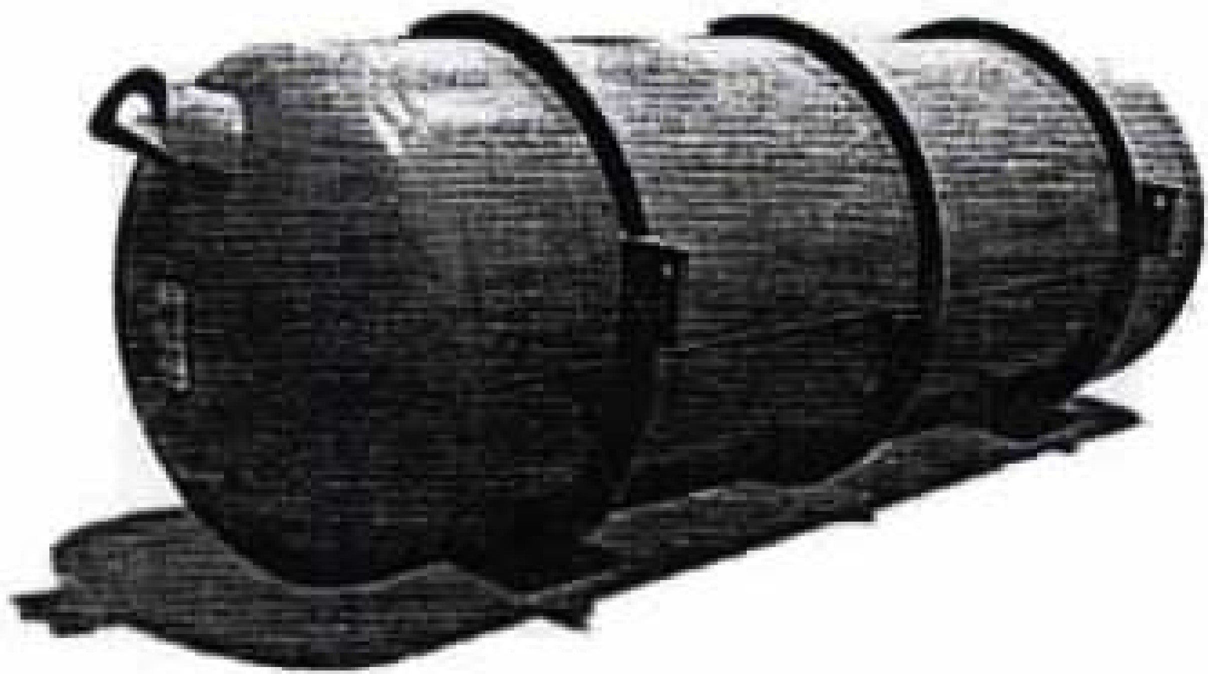
Justification for Task

- *Draft DUF_6 Materials Use Roadmap* recommends using DUF_6 cylinders as LLW packages
  - Moderate net cost savings from avoided purchase of LLW packages plus avoided moderate cylinder disposal cost
- Equivalent cost of 5.6M ft^3 for B25 boxes is $32.1M
- One-Site vs. Two-Site Comparative Evaluation report indicates the cost to cut, crush, transport, and dispose of DUF_6 cylinders is $58.2M
- Combined avoided cost is $90.3M

Task Accomplishments

- **Completed ORNL/CF-00/36, *Assessment of Reusing 14-Ton, Thin-Wall, Depleted UF_6 Cylinders as LLW Disposal Containers***
  - **No structural problems are anticipated**
  - **Bechtel Jacobs procedure FS-B-2403, Rev. 1, *Weld Patch Repair of Large Diameter DOE UF_6 Cylinders*, provides a basis for a reasonable approach to developing a filling and patching procedure**
  - **Cylinders would meet Department of Transportation regulations as strong tight containers for low specific activity (LSA) LLW**
  - **It is reasonable to believe cylinders filled with LSA LLW would be acceptable at NTS**

14-Ton DUF_6 Cylinder



Task Plans for FY 01

- Prepare and execute a plan to resolve issues that arise, which will lead to a clearly defined specification for reuse of cylinders as LLW disposal containers

- Initiate cylinder demonstration for two cylinders, one containing contaminated soil and one containing converted DU

Basic Research
Uranium based catalysts

Sheng Dai (CTD)

S. H. Overbury (CASD)

Erin Meyers, Mahesh Konduru

Uranium Oxide as VOC Catalyst

TABLE 2 Comparison of catalytic performance for the destruction of chloro-organic compounds

Catalyst	Chlorocompound	Concentration (p.p.m.)	Temperature (°C)	Gas flow (h^{-1})	Conversion (%)	Exit concn (p.p.m.)	Ref.
U_3O_8	Chlorobenzene	10,000	350	70,000	99.7	31	This work
U_3O_8	Chlorobutane	10,000	350	70,000	>99.5	<50	This work
$CuCl/KCl/SiO_2$	Methylene chloride	10,000	350	300	98.4	160	2
$0.1\%Pt/Al_2O_3$	Chlorobenzene	398	530	30,000	92.0	32	7
Co-Y	Trichloroethane	1,500	325	2,361	100	–	9
Cr_2O_3	Trichloroethane	10,000	650	3,600	99.7	30	10
TiO_2	CF_2Cl_2	2,000	400	10,500	98.0	40	11
WO_3/Al_2O_3	CF_3CF_2Cl	6,700	600	15,366	60.0	2,680	12

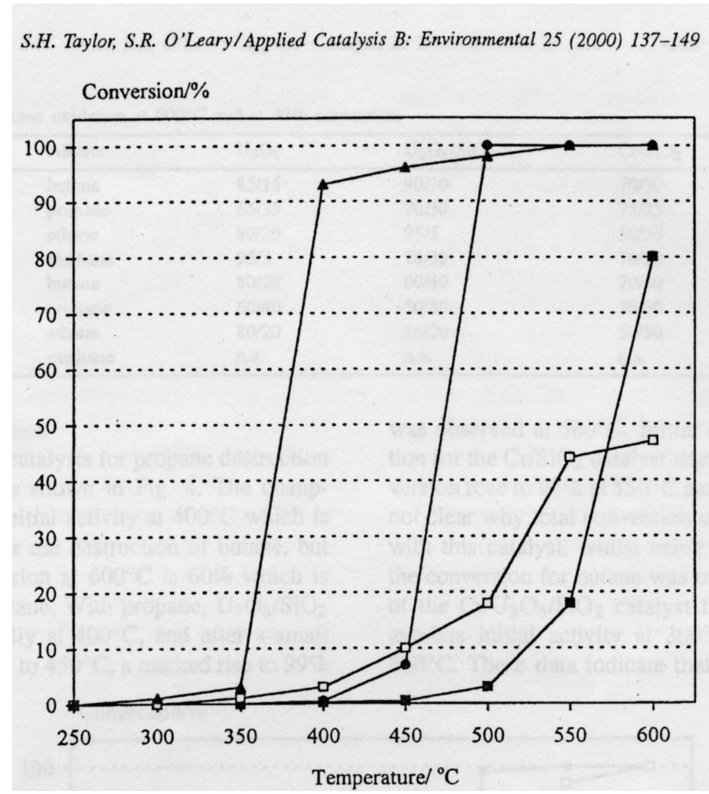
* Defined as ml STP gas per h per ml catalyst.

Hutchings et al. reported that U_3O_8 a is an active catalyst for HVOC destruction

Hutchings, G. J., C. S. Heneghan, et al. (1996). “Uranium-oxide-based catalysts for the destruction of volatile chloro-organic compounds.” Nature **384**(28): 341-343.

Uranium in Catalysts

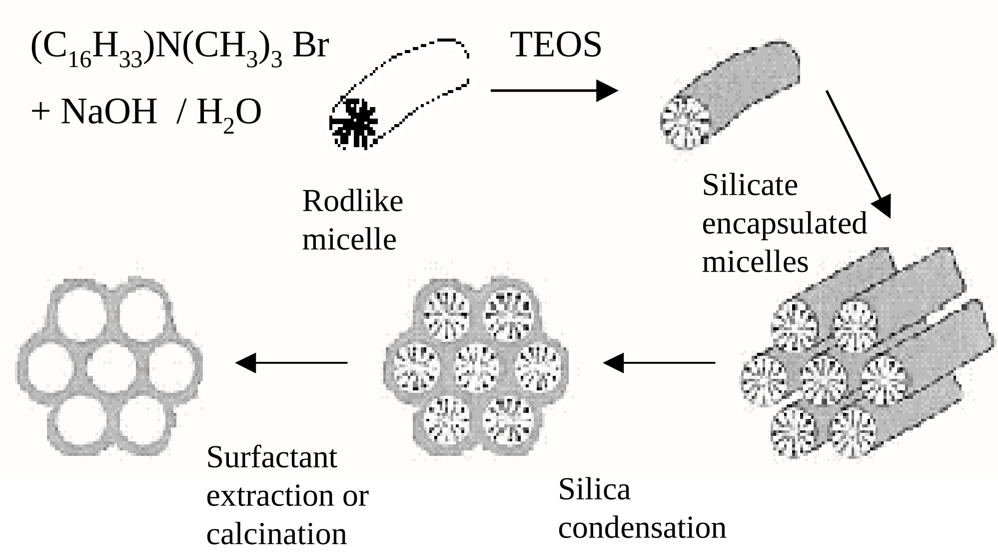
- Hutchings and Taylor reported that U_3O_8 is an active catalyst for VOC destruction
  - Hutchings, G. J., C. S. Heneghan, et al. (1996). "Uranium-oxide-based catalysts for the destruction of volatile chloro-organic compounds." Nature **384**(28): 341-343.
  - Figure shows light-off curve for oxidation of butane
  - high activity for chlorobenzene also
- USb_3O_{10} previously patented as selective oxidation catalyst
  - Grasselli, R. K. and D. D. Suresh (1972). "Aspects of Structure and Activity in U-Sb-Oxide Acrylonitrile Catalysts." J. Catalysis: 273. US Patents 3,198,750 and 3,308,151.
- Uranium containing catalysts also show activity for methane steam reforming, methane partial oxidation and NO reduction



■ U_3O_8; ● U_3O_8/SiO_2; □ Cr/SiO_2; ▲ $Cr/U_3O_8/SiO_2$.

Synthesis of Mesoporous Materials

- Micelles of variable sizes used as template molecules
- TEOS produces Si gel around template molecules. Dope with uranium nitrate.
- alignment (crystallization) of micelles leads to ordered arrays
- surfactant "burned out" or removed by extraction



Synthesis Results

- Various uranium containing, mesoporous catalysts have been synthesized
  - varied U/Si ratio
  - varied surfactant used to assemble mesoporous structure
    - PL is Pluronic P123 (neutral block copolymer)
    - CT is cetryl trimethyl aminio bromide (CTAB)
- resulted in variable surface area and pore volumes

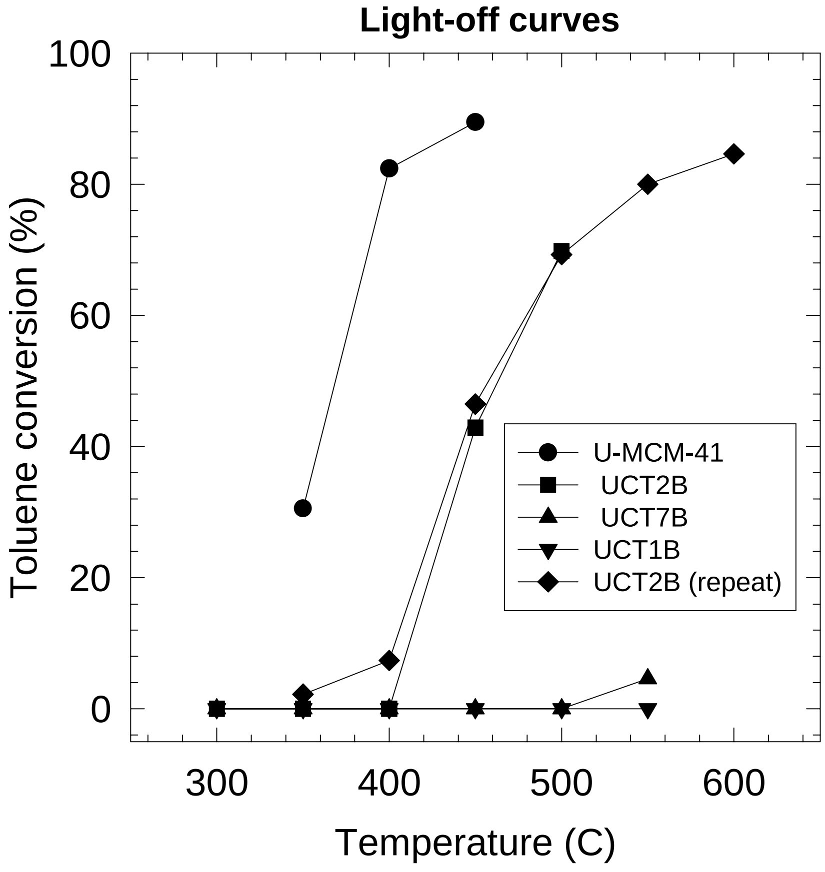
SAMPLE	SURFACE AREA (m^2/g)	TOTAL PORE VOLUME (cc/g)	ADSORPTION PORE DIAMETER (A)	DESORPTION PORE DIAMETER (A)	MOLES OF SILICON	MOLES OF URANIUM
UCT1B	545.65	0.6266	59.3-75.2	38.9-48.4	0.006	0.0002
UCT2B	398.52	0.5692	60.5-72.2	34.8-45.0	0.006	0.0002
UCT6B	500.37	0.5123	55.2-64.1	28.8-40.4	0.003	0.0001
UCT7B	515.46	0.5469	39.3-51.7	30.9-39.4	0.012	0.0002
UCT7A	538.56	0.5545	49.8-62.7	35.2-43.6	0.012	0.0002
UPL1B	445.59	0.4258	36.2-49.8	29.3-39.6	0.006	0.0002
UPL2B	401.23	0.3989	31.5-39.5	28.7-39.1	0.006	0.0002
UPL7B	429.88	0.4651	34.7-51.7	30.9-34.8	0.012	0.0002

Chemicals Used: (prepared by Mark Burleigh)

*0.2 M UO^{+2} in triflic acid (pH approximately 0.2)
*Methanol
*Tetramethylorthosilicate (TMOS)
*surfactant dissolved in 2 M HCl

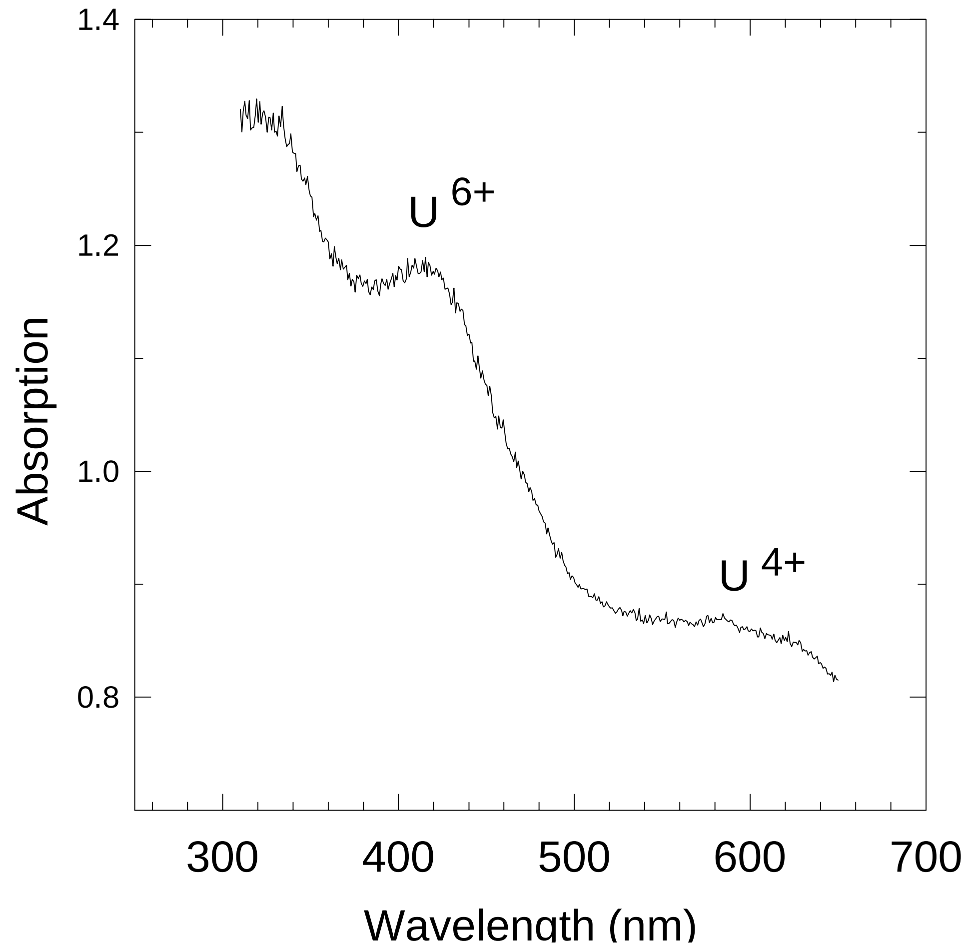
Toluene Decomposition Over Uranium Oxide Catalysts

- Various uranium containing catalysts have been tested for activity for toluene decomposition
- uncalcined catalysts UCT7b and UCT1b are inactive (probably due to lack of active U^{4+})
- good activity is obtained from U-MCM41
  - silicate MCM-41 impregnated with uranyl nitrate and calcined to 800C
- U-CT2b is slightly less active
  - mixed U and Si mesoporous oxide grown assembled with CTAB micelles



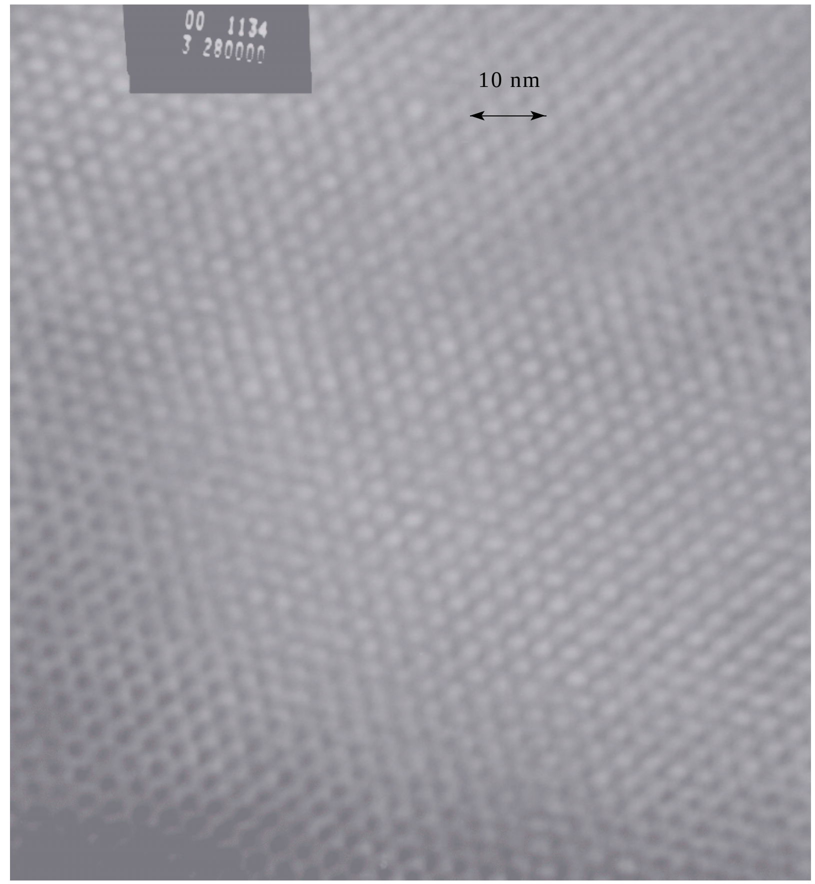
UV-Visible Spectroscopy to Analyze Oxidation State of Uranium Catalysts

- Non-destructive techniques to determine oxidation state of U are needed to test catalysts
  - oxidation state is critical factor related to activity
- UV-visible spectroscopy is sensitive to oxidation state of U
  - U^{4+} compounds (e.g. UO_2)exhibits pronounced feature near 600 nm
  - U^{6+} compounds (e.g. UO_3) exhibit sharp feature near 450 nm
  - however, feature near 600 nm is broadened and weak in mixed oxidation state compounds
- Attenuated reflection FTIR will be tested to test validity as probe of oxidation state.



Characterization of Mesoporous Materials

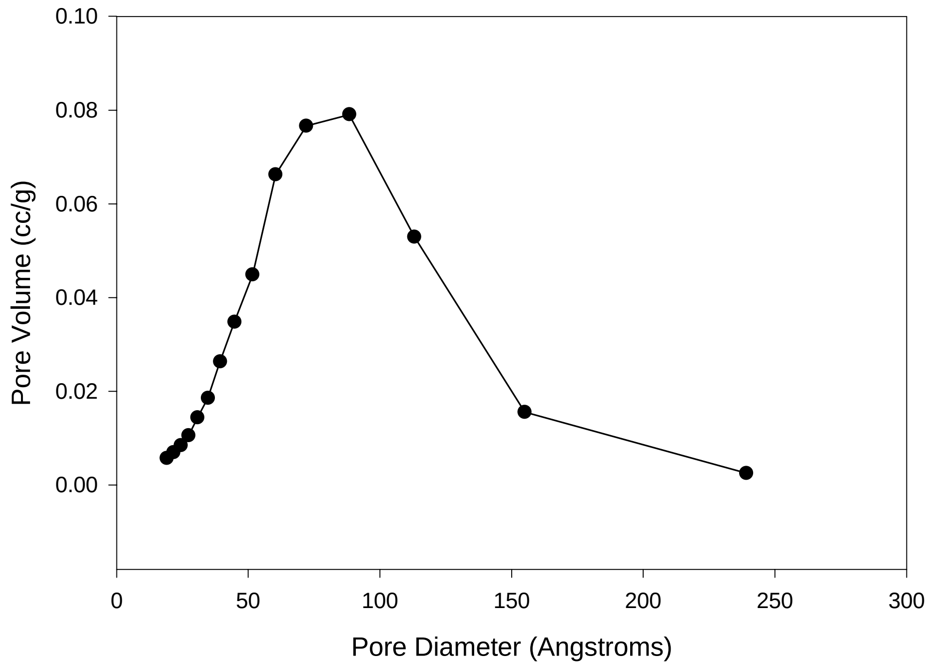
- X-ray diffraction
  - describes ordering of pores
- TEM
  - size and ordering of pores, properties of impregnated material
- BET
  - surface area and pore size distribution
- UV spectrometry
  - oxidation state of uranium
- FTIR spectrometry
  - adsorbate species and mechanisms



Major Accomplishments

- Synthesis
  - catalysts of variable Si-U ratio in gels
  - high surface areas 510 m^2/g
  - neutral surfactant
- catalyst properties
  - test reactor assembled
  - reactor and VOC by-passes
  - GC outfitted for VOC detection
  - MS with sampler for CO_2 analysis
- measured light-off curve on cobalt catalysts

Pore Distribution



Planned Accomplishments

- synthesize uranium oxide based catalysts to achieve desired properties
  - characterization resulting materials by BET, XRD, and possibly TEM
- complete reactor and screen activities of catalysts
- improve on reactor and detection system
  - quantify detection of CO_2
  - exclude unwanted oxygen
  - analyze for less volatile products

Basic Research – Uranium Based Semiconductors

Prof. Tom Meek
University of Tennessee
Knoxville, Tennessee

M. Jonathan Haire
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6179

Task Justification

- Semiconductor devices that are based on uranium oxides appear possible and could offer significant improved performance compared to conventional Si, Ge, and GaAs materials
- If depleted uranium (DU) were used instead of silicon for semiconductive devices, 42,000 t/y of DU would be consumed. Approximately 20,000 t/y of DU is produced each year as tails from uranium enrichment operations
- Objective is to develop order of magnitudes improvements, new markets, and consume entire DU inventory

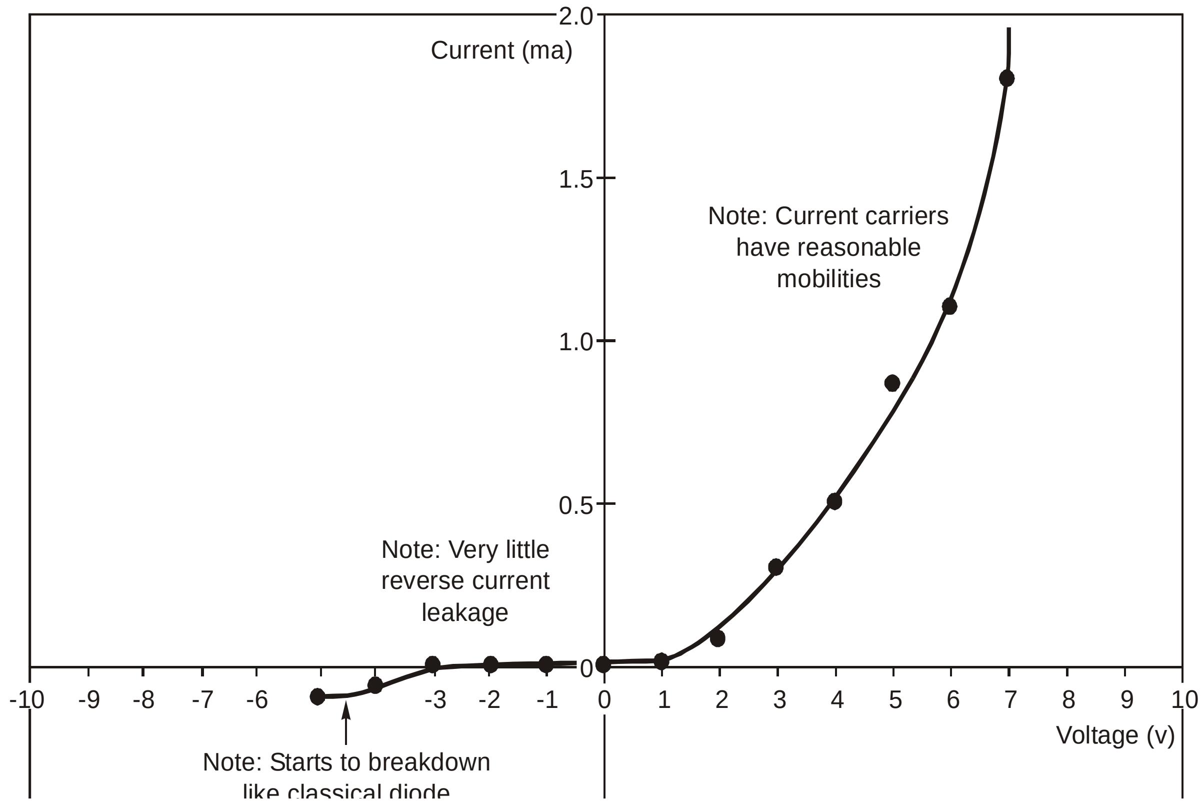
Semiconductive Properties of UO_2

- Intrinsic electrical and electronic properties of UO_2 are equivalent to or much better than Si, Ge, GaAs
  - Electronic band gap for UO_2 lies between Si and GaAs
  - Electronic conductivity of UO_2 is approximately equal to GaAs
  - Dielectric constant of UO_2 is two times greater than that for Si
  - Seebeck coefficient is three times better than that for current best thermoelectric material
  - UO_2 can withstand much higher temperatures (~2,600 K) than Si can (~473 K)
  - Ceramic oxide, UO_2, is more resistant to radiation damage
- Thus, a variety of semiconductive devices are possible: electronic (integrated circuit), solar cell, thermoelectric, etc.

Major Accomplishments

- Completed comprehensive literature search
- Acquired urania samples
  (UO_2 polycrystal, UO_3 natural single crystal)
- Fabricated UO_3 Schottky diode
- Characterized UO_3 Schottky diode
  - dynamic resistance
  - reverse breakdown characteristic
  - forward conducting characteristics

Electronic Characteristics of Natural Urania (UO_3) Schottky Diode



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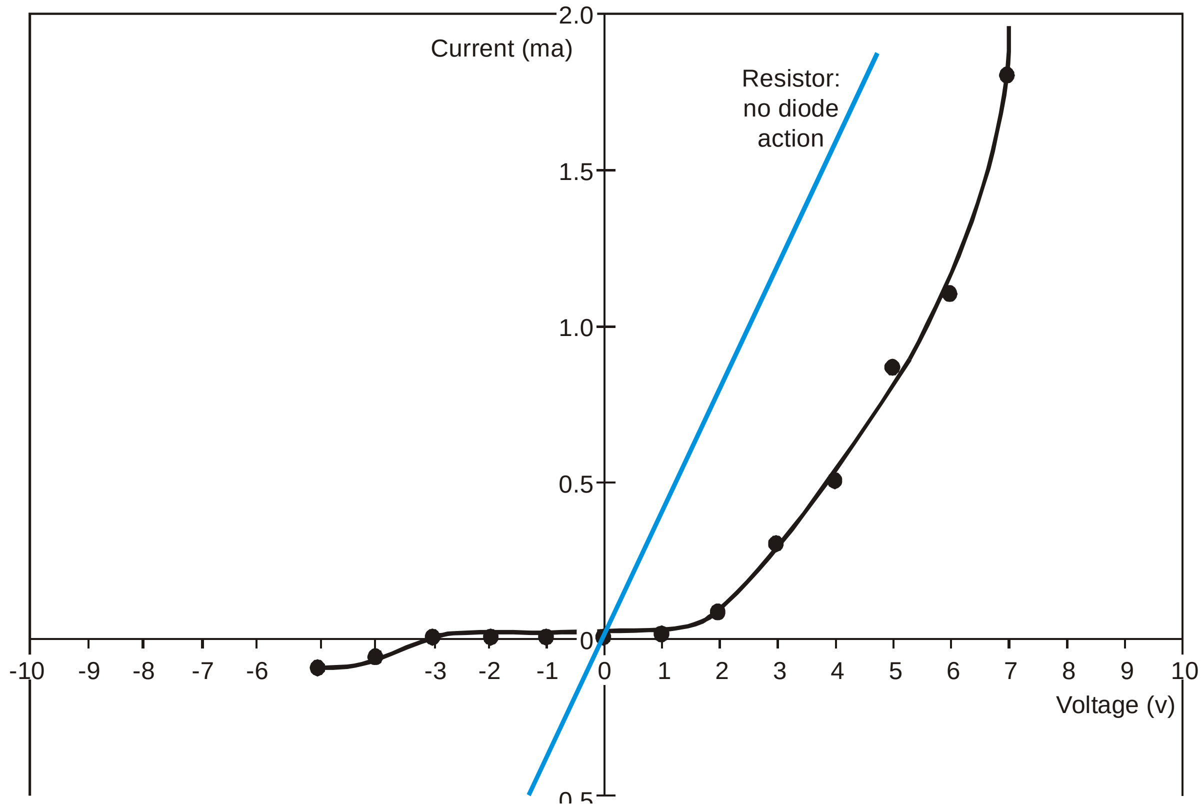

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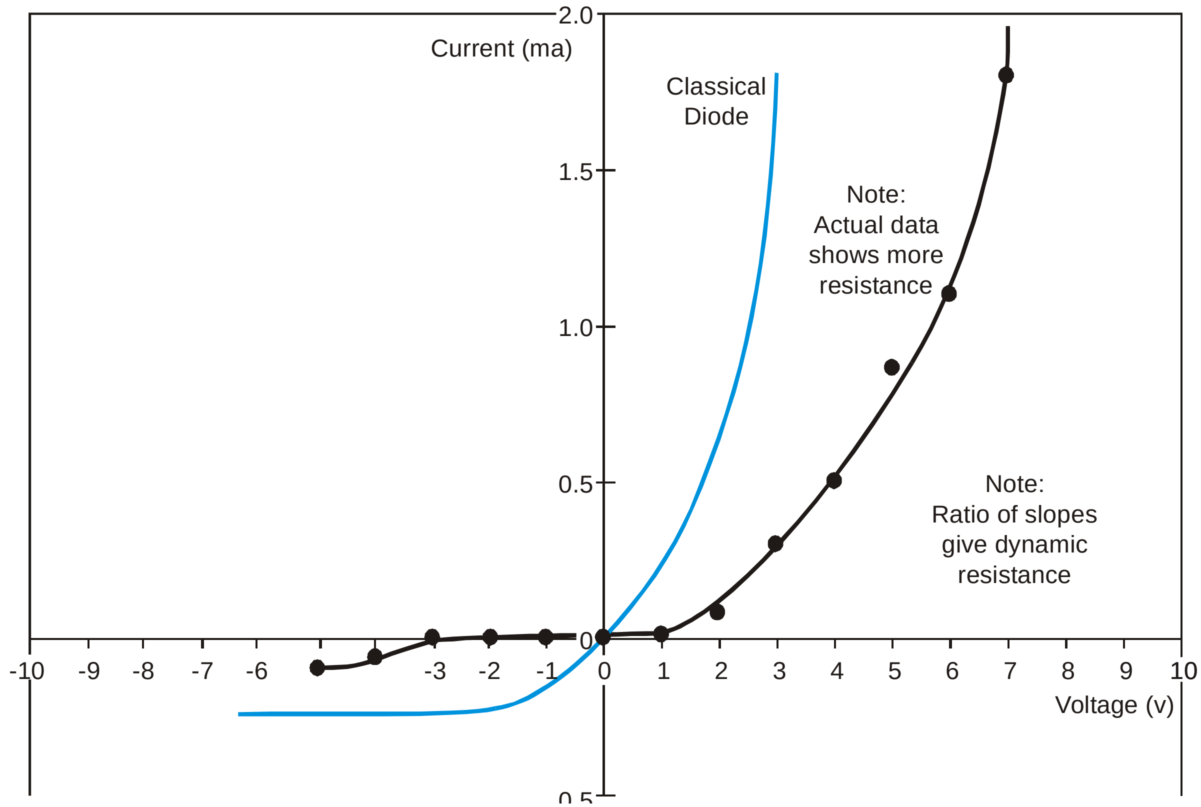

Planned Accomplishments for FY 2001

- Fabricate uranium diodes and evaluate their performance
- Report initial results in a national forum

DU Uses R&D Funding ($K)

Task no.	Task	Spent prior FY+	Committed funding FY 01	FY 01 funding plus supplement	Proposed FY 02
110	Repository applications (cermet, fill)	67	160	230	375
120	Heavy concrete (DUCRETE)	48	160	210	375
210	Dose calculation	0			
220	Reg. support	0		50	50
230	Cyl. reuse	19		50	150
310	Long-term storage	0			
320	DU disposal	0			
410	UO_2 alteration	0	0	30	50
420	High value fluorine	0	30	30	150
430	Basic research (DU catalysts, semiconductors)	87	100	100	250
440	International collaboration (Russia Workshop)	0	170*	170*	50
510	Systems analysis	0		40	50
520	Management	10	107	217	250
	TOTAL	231	727	1,127	1,750

+Authorized funding in FY 00 was $340K for DU R&D plus $225K for roadmap.
*An additional $150K was held back by DOE for Russian Academy of Science work.

Summary of Program Review

- Made good progress with little money
- International collaboration task will take ~1/3 of allotted R&D funds